Specific Heat of UPt_3: Evidence for Unconventional Superconductivity

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The specific heats of two samples of UPt_3 have been measured in the vicinity of the transition to the superconducting state. In both cases the specific-heat anomalies are sharper than any previously observed, and *two* maxima are clearly resolved. The results are interpreted as evidence of a splitting of the transition and unconventional pairing. A model that is consistent with the known sample dependence of the superconducting-state specific heat is used to derive "intrinsic" values of the related parameters.

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From the initial discoveries of superconductivity in $CeCu_2Si_2$,[1] UBe_{13},[2] and UPt_3,[3] it has been clear that these heavy-fermion superconductors (HFS) are unusual, and it was soon recognized[4] that the coupling mechanism and the nature of the superconducting state might be unconventional. A number of differences between the properties of the superconducting state in HFS and in conventional BCS superconductors have been observed, for example, in the temperature dependences of both transport and thermodynamic properties. However, the interpretation of these results has been clouded by questions associated with sample quality, and particularly by the inhomogeneity implied by the broad superconducting transitions generally observed. In the case of UPt_3, the temperature dependences of the upper critical field[5] and the rf susceptibility,[6] as well as the field dependence of the ultrasonic attenuation,[7] suggest the existence of two distinct superconducting states that occur at different fields. It has since been pointed out that this is to be expected for *d*-wave pairing, and that even in zero field there should be two transitions occurring at different temperatures.[8] It seems possible that these transitions would appear as two separate anomalies in the specific heat, C, as is observed in the case of liquid ^3He. The discontinuity in C at the critical temperature T_c, $\Delta C(T_c)$, can also be expected to give information about the nature of the pairing in the superconducting state (see Ref. 9 and others cited there). However, most measurements on UPt_3 have been made on samples that showed broad transitions with no sign of structure in C.[3,10–12] The exceptions are measurements on a series of three samples that were prepared at Grenoble: Measurements there,[13–15] and also at Berkeley on one of the samples,[16] have shown "shoulders" on the high-temperature sides of the anomalies at T_c. The recurrence of that feature from sample to sample was highly suggestive, but, in view of the known dependence of T_c on sample quality,[3,5] the results were interpreted cautiously, and until now it has not been claimed that this structure was an intrinsic property of UPt_3.

Specific-heat measurements on two new samples of UPt_3, each of which shows two distinct maxima near T_c that correspond to two transitions separated by approximately 60 mK, are presented in this Letter. The new samples were prepared in different laboratories by different techniques, and in both cases their properties reflect substantial improvements in sample preparation. In particular, the specific-heat anomalies are sharper than any observed previously, and this explains the appearance of the double transition which was incompletely resolved in earlier measurements.[13–16] Since the 60-mK separation and the relative sizes of the two maxima are consistent with the shoulders observed previously, the calorimetric evidence (from measurements in two different laboratories on samples from three different sources) now strongly suggests that a double transition to the superconducting state in the zero magnetic field *is* an intrinsic property of UPt_3, and constitutes persuasive new evidence that the superconductivity of UPt_3 is unconventional and involves pairing that is not pure *s* wave.

Sample 1 was a polycrystalline cylinder (5 mm diameter by 28 mm length). It was prepared in ultrahigh-vacuum conditions by a zoning technique based on rf heating and a water-cooled copper crucible. This same method was used successfully in the production of single crystals for de Haas–van Alphen measurements.[17] As a result of the precautions taken, the concentration of chemical impurities is expected to be very low and the homogeneity high. However, this does not necessarily imply a low level of dislocations or disorder, and such de-

TABLE I. Parameters derived from the specific heats of different UPt_3 samples, listed in order of decreasing values of $\gamma(0)$. Symbols are defined in the text. Units are in K, mJ, and mol.

T_c	γ	$\gamma(0)$	B	f_s	$\frac{BT_c}{\gamma}$	$\frac{BT_c}{f_s\gamma}$	$\frac{\Delta C(T_c)}{\gamma T_c}$	$\frac{\Delta C(T_c)}{f_s\gamma T_c}$	Reference
0.37	426	265	875	0.38	0.76	2.00	0.38	1.00	12 (Ref. 19 sample)
0.40	422	260	960	0.38	0.91	2.39	0.57	1.50	11
0.40	430	165	1340	0.62	1.25	2.02	0.65	1.05	This work (sample 2)
0.47	434	140	1300	0.68	1.41	2.08	0.78	1.15	This work (sample 1)
0.54	426	110	1250	0.74	1.58	2.14	0.86	1.16	13
0.50	461	80	1560	0.83	1.69	2.04	0.87	1.05	15
0.59	450	56	1430	0.88	1.87	2.13	1.00	1.14	14

fects may play an important role.[3,5] Sample 2 was a cylinder (6.5 mm diameter by 2.5 mm length) cut from the sample that was used in the muon-spin-relaxation (μSR) measurements of Cooke *et al.*,[18] which had in turn been cut from a large arc-melted polycrystalline ingot that had been annealed at 950 °C for 90 h.

The specific heats of the two samples were measured from approximately 0.2 to 30 K. The data for the normal- and superconducting-state specific heats, C_n and C_s, respectively, are described first to introduce values of parameters that are relevant to the subsequent discussion of the anomalies at T_c. The normal-state specific heat can be approximately represented[3,10,19] over a wide range of temperature (up to about 20 K) by

$$C_n = \gamma T + \delta T^3 \ln T + \epsilon T^3 . \tag{1}$$

However, it has been noted[19] that the values of the parameters in Eq. (1) derived from 20-K fits would be influenced by the omission from Eq. (1) of higher-order terms in both the lattice and electronic contributions, except in the improbable case that those terms were either negligible or canceled. For the measurements reported here, and also for measurements[19] on another sample on the same temperature scale, 20-K fits with Eq. (1) do represent C_n to within several percent, but the deviations are greater than the expected experimental error. For all three of these samples, it is necessary to limit the fits to the data below 5 K to reduce the deviations to the expected level. The values of γ derived from the 5-K fits are given in Table I.

The data below 1 K are shown in Fig. 1 as C/T vs T. The data for C_s fall close to the solid straight lines, so that, at least in the temperature interval from 0.25 K to near T_c,

$$C_s = \gamma(0) T + BT^2 , \tag{2}$$

with the values of $\gamma(0)$ and B given in Table I. A temperature dependence of this form has been observed in other measurements[11,13,14] on UPt_3 in this temperature interval, but, as shown in Table I, the values of $\gamma(0)$ and B vary widely from sample to sample. It was first noticed by Franse *et al.*,[11] and subsequently by others,[13,14] that extrapolations of Eqs. (1) and (2) to 0 K lead to an entropy discrepancy at T_c—the entropy derived for the superconducting state is greater than that for the normal state—and this is the case for the measurements reported here. In the absence of any clear evidence as to the origin of the discrepancy, it has in some cases been resolved[11] by preserving the form of Eq. (2) in the region below 0.25 K but with values of $\gamma(0)$ and B changed to achieve an entropy balance at T_c while maintaining continuity of C_s at the lowest-temperature experimental data. Although there is some indication of such a downward curvature of C_s in the measurements reported here (especially for sample 2 for which the data extend to a lower temperature) and in other work,[13,14,20] the avail-

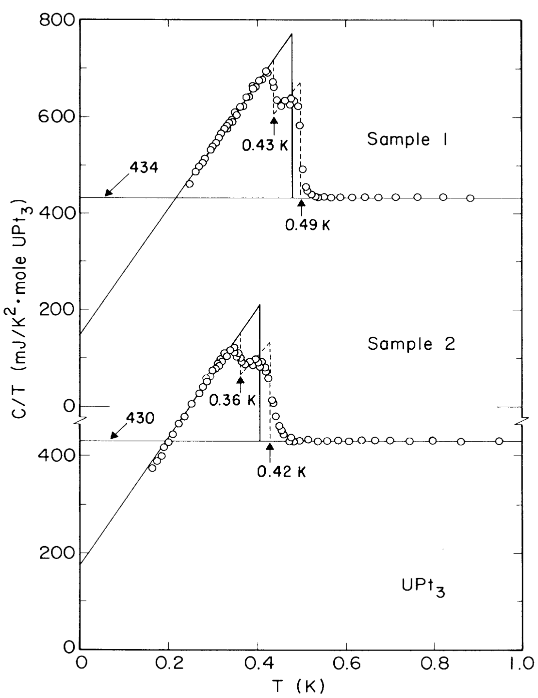

FIG. 1. The specific heat of UPt_3 in the vicinity of the superconducting transition for samples 1 and 2. The dashed lines represent two ideally sharp transitions at T_a and T_b; the solid lines represent an ideally sharp single transition, with the same total entropy, at T_c.

able experimental data leave considerable uncertainty about the very-low-temperature region. The entropy discrepancy could also be resolved by an increase in C_n/T in the low-temperature region, or by a combination of an increase in C_n/T and a decrease in C_s/T. For UBe_{13} the value of C_n/T does increase[21,22] significantly in the region below 1 K, but, since the characteristic temperature that determines the normal-state properties appears to be appreciably higher for UPt_3 than for UBe_{13}, such an increase in C_n/T for UPt_3 seems less probable.

The most interesting feature of the new results—the occurrence of separate and distinct discontinuities in C corresponding to two superconducting transitions—is evident in Fig. 1. The two transitions are particularly conspicuous for sample 1, but they are also clear for sample 2, for which the transitions are slightly broader. Idealized sharp discontinuities for the two separate transitions at T_a and T_b are represented by the dashed lines. For comparison with other measurements, and particularly with estimates of $\Delta C(T_c)/\gamma T_c$ for other samples, solid lines that represent entropy-conserving constructions corresponding to single transitions at T_c are also shown. The values of T_c and $\Delta C(T_c)/\gamma T_c$ are included in Table I; the values of T_a and T_b are indicated in Fig. 1. The similarity of the structure in the anomalies for samples 1 and 2, in both the relative magnitudes of the two steps in C and their separation in temperature, the consistency with the shoulders observed for other samples as mentioned earlier,[13–16] and the sharpness of the two components of the anomaly all argue against the possibility that the structure reflects inhomogeneity in the samples. The constancy of $T_a - T_b$, at 60 mK, in spite of an overall shift of the anomaly by 70 mK, also suggests that the two components of the anomaly have a similar origin, and both the observed dependence of T_c on residual resistivity,[5] mechanical stress,[3] and nonmagnetic impurities[23] and the theoretical expectation[24] that non-s-wave superconductivity would be particularly sensitive to such parameters suggest that the origins of both components of the anomaly are related to the transition to the superconducting state.

In his analysis of d-wave superconductivity, Joynt[8] has shown that for the case of tetragonal symmetry, there exists a phase that would exhibit a double transition in zero field, and he suggested that for UPt_3 the hexagonal symmetry might be reduced to orthorhombic as a result of antiferromagnetic ordering at 5 K. Since there remains some uncertainty as to the intrinsic nature of the minute antiferromagnetic moment observed in μSR measurements[18] and in some[25] (but not all[26]) samples investigated by neutron scattering, further investigations are required to verify the proposed identification of the states associated with the double transition. Although no quantitative predictions were made, the results reported here are qualitatively consistent with Joynt's model.[8]

The temperature dependence of C_s is also of interest in connection with the nature of the superconductivity. The noteworthy features of C_s are the strong sample dependence of the parameters $\gamma(0)$, B, $\Delta C(T_c)/\gamma T_c$, and T_c; the obvious correlations among them (see Table I); and the temperature dependence itself (the sum of terms in T and T^2). The magnitude of $\gamma(0)$, which is in the heavy-fermion regime, demonstrates that only "dirty" UPt_3 can be its cause, because other phases are not heavy. The likely explanation for nonzero, variable values of $\gamma(0)$ is a sample-dependent gapless superconductivity associated with pair breaking.[27,28] In particular, for a polar-state superconductor, an infinitesimal concentration of impurities gives a finite $\gamma(0)$.[28] As a further comparison with this model, the uncertainty about the behavior of C_s below 0.25 K is ignored, and the fraction f_s of the electronic states that contribute to the development of an energy gap is estimated from $\gamma(0)$: $f_s \equiv [\gamma - \gamma(0)]/\gamma$. Relevant data for a number of samples are collected in Table I. The values of BT_c/γ, which has been suggested to be a universal constant in certain cases,[9] and $\Delta C(T_c)/\gamma T_c$ vary considerably—by factors of as much as 2.5. However, the spread in the values is reduced substantially when they are normalized by $1/f_s$: With the exception of those reported in Ref. 11, they are then constant to within $\pm 10\%$, about what might be expected for experimental error in determining B and, particularly, $\Delta C(T_c)$. This result is itself interesting as support for the assumed interpretation of $\gamma(0)$, although it certainly does not rule out contributions to $\gamma(0)$ by other mechanisms[22,29] that might be masked by these larger contributions in samples of poor quality. Beyond that, however, the values of $\Delta C(T_c)/f_s \gamma T_c$, which are presumably characteristic of the "fully superconducting" state, are very close to the value 1.00 calculated for d-wave pairing in a hexagonal superconductor by Monien *et al.*[9] The same authors predict $C_s/\gamma T_c = 1.22(T/T_c)^2$, corresponding to $BT_c/f_s\gamma = 1.22$. The experimental values, however, are close to 2, which is the value calculated for polar p-wave states.

In summary, the splitting of the superconducting transition, an extremely unusual phenomenon, provides persuasive additional evidence that the superconductivity of UPt_3 involves non-s-wave pairing. [It is obviously reminiscent of the second anomaly[30] in (U, Th)Be_{13} which has also been suggested as an indication of unconventional superconductivity. In that case, however, the second (lower temperature) anomaly is associated[31] with weak magnetic ordering and differs qualitatively in shape from the first.] The temperature dependence of C_s and both the strong sample dependence of the superconducting-state parameters and the relations among them are also consistent with expectations for a polar-state superconductor: As the impurity scattering goes down, $\gamma(0)$ decreases, T_c increases, the transition becomes sharper, and $\Delta C(T_c)/T_c$ increases. Thus the properties of the superconducting phase in UPt_3 agree qualitatively with those of a polar *d*-wave state. Although it is too early to reach a conclusion as to the exact nature of the states involved, it is increasingly clear that UPt_3 is an unconventional superconductor.

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