Field-Dependent Specific Heat and Multiple Superconducting Phases in UPt_3

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We have measured the specific heat, C, of single-crystal UPt_3 in the superconducting regime as a function of temperature, T, and magnetic field, H, parallel to the c axis. We find that $C(T)$ at fixed $H < H_{c2}$ shows no evidence for different superconducting states. In contrast, our field-sweep data, $C(H)$ at fixed T, have sharp changes in slope at $H \approx H_{c2}/2$. The phase diagram deduced from these features agrees with neutron-scattering and torsional-oscillator results on the same samples. These thermodynamic measurements as a function of magnetic-field constrain theories of exotic superconductivity in UPt_3.

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While many questions about the heavy-fermion system UPt_3 remain unanswered, there is a growing consensus that the superconducting state is non-BCS, both from the standpoint of the source of the attractive interaction and in the nature of the resultant pairing. Early work[1] suggested that magnetic fluctuations rather than phonons supplied the effective attraction. This has been borne out by recent inelastic neutron-scattering experiments[2] which reveal the existence of antiferromagnetic (AFM) fluctuations with energies comparable to the superconducting transition temperature, $T_c \approx 0.5$ K. Furthermore, elastic neutron and muon-spin-resonance data[2-4] have shown that UPt_3 is an antiferromagnet well before it goes superconducting. This is particularly important since a wide variety of measurements (e.g., ultrasound,[5] torsional oscillator,[6] and specific heat[7]) have hinted at a rich phase diagram in the H-T plane for $T < T_c$. These phases are usually understood by postulating that UPt_3 undergoes d-wave pairing, giving a vector rather than a scalar order parameter, which, in turn, can nontrivially couple to the AFM order parameter. Thus, while the details are still uncertain,[8] it is clear that UPt_3 supports a most unusual low-temperature quantum state.

In an effort to better understand this state, we have performed extensive magnetic-field and temperature-dependent specific-heat measurements on a single-crystal sample of UPt_3 with the field parallel to the c axis. While our zero-field temperature-sweep data show only one, fairly broad transition, rather than two as in Ref. 7, our fixed-temperature field sweeps display sharp features located at field values $H_1 \approx H_{c2}/2$. Interpretation of these features as signatures of a thermodynamic phase transition leads to an H-T phase diagram consistent with those obtained by various nonthermodynamic means,[2,5,6,9] but in contrast to fixed-field, variable-temperature calorimetry.[10] The advantages of field sweeps for locating the phase boundary prevail in a variety of measurements and are discussed in greater detail below.

The experiments were performed using standard heat-pulse techniques in a helium dilution refrigerator for $0.1 \le T \le 0.6$ K and $0 \le H \le 30$ kOe. The thermometer was a carbon chip whose magnetoresistance made it necessary to recalibrate it at every magnetic-field point during field sweeps. The heater was made of Au/Cr and was field independent to better than 0.02% up to 30 kOe. Our sample was a 0.15-g single crystal of UPt_3 oriented such that $\mathbf{H} \parallel \mathbf{c}$. Previous characterization[2] using microprobe and mass spectrometry revealed no contamination greater than 10 ppm by weight. It is notable that our sample is a piece of one of the crystals used in the neutron-scattering work of Ref. 9, making direct magnetic and thermodynamic comparisons possible. For example, the data demonstrate that the evolution of the AFM order parameter seen in Ref. 9 can occur in a sample with a single transition in the zero-field specific heat.

We plot in Fig. 1 specific heat as a function of temperature for several fixed fields. That the zero-field data shows one transition can be seen best in a plot of C/T vs T as in the inset of Fig. 1. The data in the normal state give a Sommerfeld constant $\gamma = 0.46 \pm 0.005$ J/mol K^2, consistent with previous measurements.[7] Interestingly, while our broad transition may indicate an imperfect sample, our residual linear specific heat $\gamma_0 = C/T|_{T=0}$ at zero field (listed in Table I and considered a measure of sample quality) is smaller than that of the samples in Ref. 7, even though the latter samples have narrower transitions. The increase in γ_0 as H is increased is presumably due to the presence of vortex-core quasiparticles at zero temperature. Values of the entropy for several field values are also tabulated. They are calculated using a $C \sim T^2$ extrapolation at low temperatures,

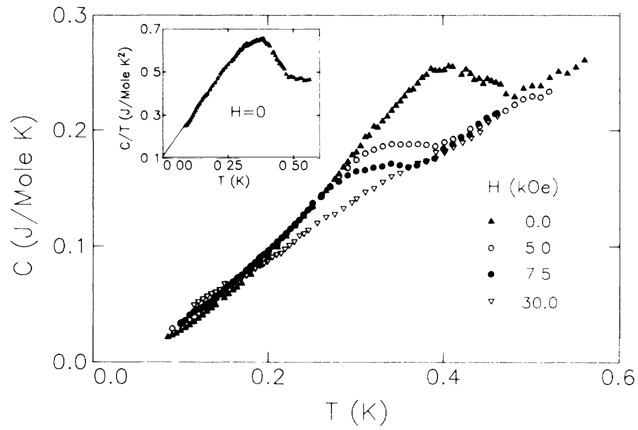

FIG. 1. Specific heat, C, of UPt_3 as a function of temperature, T, for various fixed magnetic fields, **H**||**c**. Inset: C/T for $H=0$ with a T^2 extrapolation to $T=0$. No features indicative of a phase-boundary crossing are visible for the temperature sweeps in the superconducting regime ($H<30$ kOe).

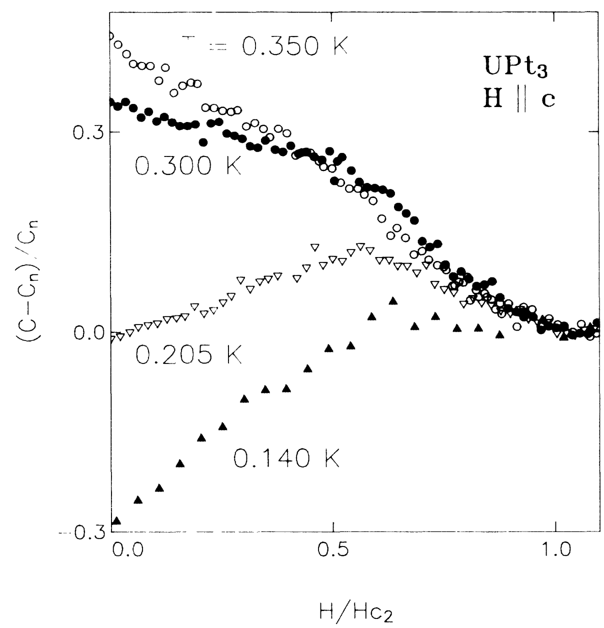

FIG. 2. Specific heat of UPt_3 as a function of magnetic field at fixed temperatures. The specific heat and magnetic field have been normalized by the normal-state specific heat, C_n, and the upper critical field, H_{c2}, respectively. Distinct features in the form of slope changes and maxima occur at field values $H \approx H_{c2}/2$ at all T.

and compared with the expected normal-state entropy $\gamma T_c(H)$. We find the zero-field entropy to be well conserved. (The normal-state entropy, S_n, is within 6% of the superconducting value, S_{sc}.) With increasing field, however, the agreement is less satisfactory, with the superconducting entropy falling substantially below its normal-state counterpart. This may reflect a field-dependent variation in the power law describing the low-temperature specific heat. It is difficult to quantify this effect, however, due to the limited temperature range over which it is possible to take data.

Phase diagrams for superconducting UPt_3 derived from ultrasonic attenuation and other data indicate that our specific-heat temperature sweeps for $H<30$ kOe cross a phase boundary at roughly $H=H_{c2}/2$. However, we observe no features indicative of such a crossing in the data of Fig. 1. We therefore took data cutting the H-T plane orthogonal to the temperature sweeps by sweeping field at fixed T. A similar approach is necessary in, for example, ultrasonic-attenuation measurements, the reason probably being that the phase boundary is more nearly parallel to the T axis in the temperature range of interest (see, for example, Ref. 5 and our Fig. 4). Thus, the transition may be undetectable in a temperature sweep, but it would remain sharp and accurately defined in a field sweep.

TABLE I. Summary of sample parameters derived from specific-heat measurements $C(T)$ in different magnetic fields.

H (kOe)	T_c (K)	γ_0 (J/mol K^2)	$S_{sc}=\int_0^{T_c}(C/T)dT$ (J/mol K)	$S_n=\gamma T_c$ (J/mol K)
0.0	0.485	0.11	0.214	0.226
2.5	0.444	0.14	0.188	0.202
5.0	0.410	0.19	0.174	0.190
6.25	0.400	0.17	0.163	0.182
7.5	0.381	0.22	0.158	0.176

This expectation is borne out by the field-sweep data of Fig. 2 in which the normalized specific heat $[C(H)-C_n]/C_n$ is plotted as a function of H/H_{c2}, where C_n is the normal-state specific heat at $T_c(H)$ and H_{c2} is the calorimetric upper critical field, defined as the field at which $C(H)$ becomes constant. Note that, since $C_n=\gamma T$ for all H, the ordinate is essentially $C/T = dS/dT$. The data display several regimes of behavior. At $T \lesssim T_c$, C drops monotonically to C_n, displaying an abrupt change or "kink" in the slope at $H \approx H_{c2}/2$. At lower T (e.g., our 0.205-K data), $C(H)$ has a sharp maximum at $H_{c2}/2$. Finally, at still lower T, C rises and then suddenly flattens off, again at a field value roughly half that of the critical field.

In interpreting these data, it is important to realize that an ideal conventional superconductor can show somewhat similar qualitative behavior. For example, at temperatures for which the normal-state specific heat is below the zero-field value, C will rise with field as vortices supply quasiparticles, then abruptly fall to C_n at $H=H_{c2}$. Then, if the transition is for any reason smeared out, the peak in C is rounded off and the drop to C_n becomes more gradual. Several factors make it likely, however, that the features observed in our field sweeps are not due to conventional processes. For example, the changes in slope and the maxima in our $C(H)$

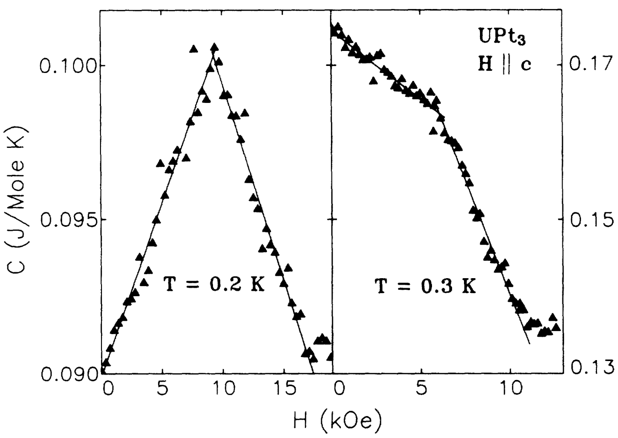

FIG. 3. Field-sweep specific heats $C(H)$ at $T=0.205$ and 0.300 K, plotted without normalization. The change in slope at H_1 is remarkably sharp in contrast to the broadened transition in $C(T)$ (Fig. 1). Solid lines are linear fits to $C(H)$ above and below H_1.

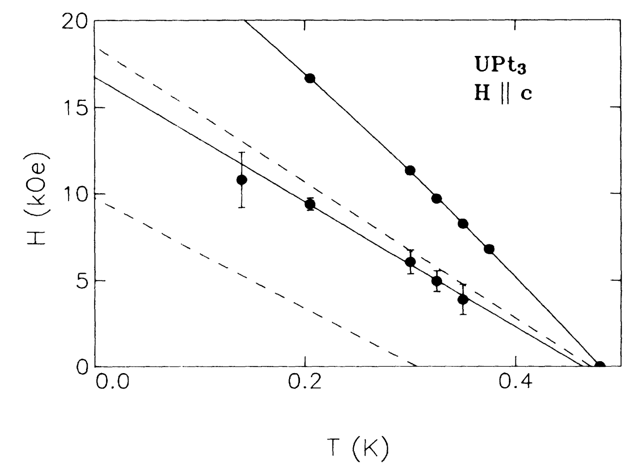

FIG. 4. Phase diagram in the H-T plane. The circles are calorimetric H_{c2}'s and phase-boundary field values as determined from $C(H)$. The dashed lines delineate the phase boundary between superconducting states as determined from neutron-scattering studies done on the same sample (Ref. 9). Solid lines are guides to the eye.

are located relatively near $H=H_{c2}/2$ for all temperatures, in comparison with those in conventional systems which move quickly and smoothly to higher fractions of H_{c2} at lower T. The most convincing evidence that the features in the field sweeps are nontrivial, though, is the acuity of the features themselves. It is very difficult to reconcile the sharpness of the slope changes and maxima with any process that substantially smears out the transition at H_{c2}. Such a reconciliation is necessary, however, if a conventional explanation is to account both for the sharpness (arguing for sudden transitions) and for the fact that the features occur so far from H_{c2}, an observation that argues for a strongly smeared transition. Thus, we believe that the features in the specific-heat field sweeps are signatures of the intrinsic superconducting behavior of UPt_3.

The aforementioned sharpness of $C(H)$ at $H=H_{c2}$ is more readily visible in Fig. 3, where we plot $C(H)$ at $T=0.205$ and 0.300 K on separate scales without normalization. The linear fits are of the form

$$C(H)=\begin{cases} C_1+m_1H, & H<H_1, \\ C_2+m_2H, & H>H_1, \end{cases} \tag{1}$$

where H_1, the location of the slope change, was varied along with C_1, C_2, m_1, and m_2 so as to minimize the total χ^2. The resulting values of H_1 are plotted in the phase diagram, Fig. 4, along with the calorimetric values of H_{c2} and the neutron results obtained on this sample from Ref. 9 (region bracketed by the dashed lines). Error bars signify deviations of H_1 sufficient to increase χ^2 by 10%. Our results are seen to be consistent with the neutron measurements, reinforcing the contention that the features in $C(H)$ are associated with changes in the order parameters present in UPt_3 below T_c. The phase boundary derived from $C(H)$ agrees within error bars with that determined from torsional-oscillator data[6] for $T>0.3$ K, and lies approximately 20% higher at lower T. We note that the thermodynamic upper critical field also agrees with the torsional-oscillator H_{c2} at high T, and is about 10% greater in the low-temperature regime. Scans of $C(T)$ at fixed H perpendicular to c by Hasselbach *et al.*[11] also indicate the possibility of multiple superconducting phases with the field in the basal plane.

Just as the neutron data probe the role of magnetism in the phase diagram, our results clarify the thermodynamic properties of the phases. Substantial work in recent years has concentrated on calculating a free energy for UPt_3 starting from Landau-Ginzberg-type expansions. Two important examples are the work of Blount, Varma, and Aeppli[8] and that of the groups listed in Ref. 12. In the former, the antiferromagnetic order parameter is resolved into transverse and longitudinal components whose coupling with the superconducting order parameter plays a central role in the energetics. Within this framework, the "phase boundary" of Fig. 4 is not a true thermodynamic phase transition with $\mathbf{H}\|\mathbf{c}$; rather, it is a change in the magnitude of the transverse component of the staggered magnetization. In contrast, the calculations by the groups of Ref. 12 predict a true transition at H_1, even in the absence of magnetic order. The role of the AFM order parameter is then to lower the crystal symmetry in zero field from hexagonal to orthorhombic and therefore to create two transitions.

The sharpness of the features in $C(H)$ presented here seem surprising in the context of a smooth crossover between different states and, at a minimum, must strongly constrain the parameters which enter the Blount, Varma, and Aeppli[8] free energy describing the coupling between the magnetic and superconducting order parameters. If, instead, the observed boundary marks a transition between distinct thermodynamic phases, then the question arises as to the order of the transition. The supposition is made by Joynt and co-workers[12] that the transition in nonzero field is most likely first order. We observed no evidence for hysteresis within 300 Oe in the peak position H_1 of $C(H)$ at $T=0.205$ K when the field was swept sequentially through H_1 in both directions. However, this does not exclude the possibility of a first-order transition since hysteresis depends as well on the degree of nucleation and domain formation in the sample.

Our data also indicate an essentially linear dependence of C on H at all T and for both $H \leq H_1$ and $H \geq H_1$ (but with separate slopes). Although it is difficult to evaluate physical quantities away from H_{c2} and the smearing of the transition in $C(T)$ makes the problem that much more complicated, the robust nature of this result should also provide insight into the form of the excitation spectrum in both regions of the H-T phase diagram.

In conclusion, we have measured the field-dependent specific heat $C(H)$ of UPt_3 with $\mathbf{H} \parallel c$ at a variety of temperatures below the zero-field superconducting transition temperature. Although the sample shows smooth behavior in $C(T)$ at fixed H, we find distinct features in $C(H)$ at fixed T. These thermodynamic features occur at roughly the same field values where neutron-scattering studies reveal a qualitative change in the field evolution of the AFM order parameter.

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