Controlled Symmetry Breaking in Superconducting UPt_3

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(Received 26 February 1996; revised manuscript received 8 January 1997)

We have developed a biaxial-stress calorimeter for use at milli-Kelvin temperatures to study the nature of the double superconducting transition in single crystal UPt_3. We suppress the basal-plane antiferromagnetism and merge the two transitions through **c**-axis stress, and then break the hexagonal symmetry of the basal plane in a regulated manner through stress along $\hat{\mathbf{a}}$. We recover a double superconducting transition, but with a shift in the relative sizes of the specific heat jumps for the upper and lower transitions, as well as a different measure of the strength of the symmetry-breaking field. [S0031-9007(97)02580-5]

PACS numbers: 74.70.Tx, 74.25.Bt, 74.25.Dw, 74.62.Fj

In the solid state, heavy-fermion materials provide the most compelling evidence for the existence of high-order pairing in the superfluid condensate. These highly correlated Ce- and U-based systems embody additional interesting degrees of freedom in the relative coordinates of the Cooper pairs as compared to conventional, isotropic, *s*-wave superconductors. The extra freedom permits such exotica as multiple superconducting transitions and anisotropic gap functions.

Experimental studies of thermodynamic, magnetic, and transport properties of UPt_3 have established the existence of nodes in the superconducting gap [1]. More recent observations of two closely spaced superconducting transitions in zero field [2], as well as an apparent tetracritical point in the H-T plane [3], have underlined the question of the origin of the splitting. Two classes of models have been proposed to describe the complex phase diagram of UPt_3: one based on distinct order parameters which are (nearly) accidentally degenerate [4], and the other based on the coupling of a superconducting order parameter with internal degrees of freedom to a symmetry-breaking field [5,6].

A natural candidate for the symmetry-breaking field in UPt_3 is the reduced moment antiferromagnetic order which coexists with the superconducting state [7]. However, magnetic x-ray and neutron scattering experiments find that neither the suppression of the antiferromagnetic scattering intensity in the superconductor nor the magnetic correlation lengths depend on whether UPt_3 crystals display one or two superconducting transitions [8]. To further complicate matters, a subtle structural modulation, identified in transmission electron micrographs [9], also may play a symmetry-breaking role if found to extend into the bulk.

It has been found experimentally that pressure suppresses both the weak basal-plane antiferromagnetic order [10] and the zero-field splitting of the superconducting transition [11]. In particular, it is the stress component applied along the **c** axis, perpendicular to the hexagonal basal plane, which serves to merge the two transitions [12]. Hence, it is possible in principle to restore the degeneracy of the superconducting state with **c**-axis stress, and then, while maintaining a suitably large stress along $\hat{\mathbf{c}}$, apply a uniaxial stress in the basal plane to break the hexagonal symmetry in a controlled and identifiable fashion. We report here just such a sequential application of stress fields to UPt_3, measuring the specific heat in a newly developed biaxial stress cell constructed from superconducting materials to reduce background contributions to a negligible level. We find that the merged transition indeed can be split into two with **a**-axis stress, and that both the energy scale and the entropy characteristics of the stress-induced double transition differ significantly from the original, unperturbed response.

Single crystals of UPt_3 were grown by the vertical-float-zone refining method, annealed at 950 °C for 12 h, and then slowly cooled [12]. Typical crystal dimensions were $(1.3 \times 1.1 \times 1.1)\ \mathrm{mm}^3$, with faces spark cut and polished parallel to the **a** and **c** axes. As illustrated in Fig. 1, the main body of the stress cell is a NbTi hollow tapped cylinder. The **c** axis of the UPt_3 crystal is oriented parallel to the long axis of the cylinder and uniaxial stresses up to 3 kbar could be applied using a torque wrench. A NbTi spacer prevented sample rotation during tightening. After the chosen **c**-axis stress is reached, two lever arms are added which apply the adjustable stress in the basal plane using a clothespin-type mechanism. This part of the cell also is formed from NbTi, except for two 0.75 mm diameter Ti-6Al-4V alloy pins about which the arms rotate. Ti-6Al-4V has a higher elastic modulus, yield stress, and ultimate tensile strength than NbTi, but its lower superconducting transition temperature (2 vs 10 K) results in a greater background contribution at $T \sim 0.5$ K and restricts its use to low mass applications. Shearing of the

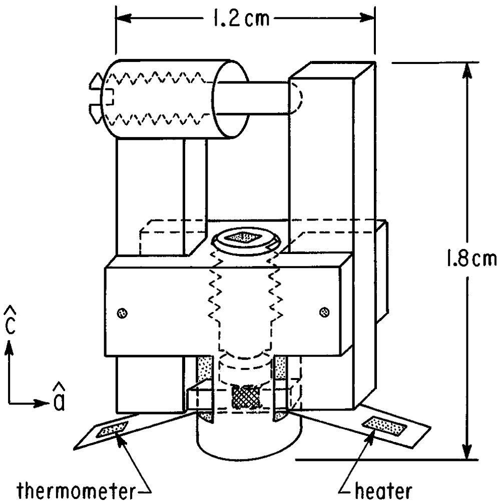

FIG. 1. Schematic of the superconducting, biaxial-stress calorimeter. The $\sim$1 mm^3 UPt_3 crystal (cross hatched) sits on a Cu foil with the thermometer and heater. After fixing the stress along $\hat{\mathbf{c}}$ by torquing the vertical screw, the two lever arms are added to apply stress along $\hat{\mathbf{a}}$ with the horizontal screw.

pin limited the stress along $\hat{\mathbf{a}}$ to 2.5 kbar. The overall size of the cell, $(1.8 \times 1.2 \times 0.2)$ cm^3, was constrained by the dimensions of the top-loading chamber of the dilution refrigerator.

The stress was calibrated for both directions using the cell as a Brinell hardness indenter [13], with a small Al block and a WC ball bearing taking the place of the UPt_3 crystal for this procedure. Absolute values of uniaxial stress should be accurate within 10%. All values of stress were determined at room temperature, but the differential thermal contraction between NbTi and UPt_3 is small. We estimate a negligible ($<$0.05 kbar) offset at mK temperatures along $\hat{\mathbf{c}}$ and an upper bound to the offset along $\hat{\mathbf{a}}$ of 0.2 kbar.

The specific heat was determined by measuring the exponential decay of the temperature after application of a known heat pulse. The AuCr heater and the Speer carbon chip thermometer were mounted on the outside edges of a thin copper foil whose center was compressed between the sample and the bottom of the tapped cylinder. The poor thermal conductivity of the superconducting stress cell permitted it to serve as its own heat leak. The addendum from the stress cell is always less than 20% of the peak value at all temperatures of interest.

We plot in Fig. 2 the variation of the two superconducting transitions with **c**-axis stress, $S_{\hat{c}}$, without any stress applied in the basal plane. The upper transition moves to lower T with increasing $S_{\hat{c}}$, while the lower transition moves to higher T, until they merge at approximately $S^*_{\hat{c}} = 1.5$ kbar and $T_c = 487$ mK. The single superconducting transition then moves to lower temperature for $S_{\hat{c}} > 1.5$ kbar, at a rate of 6.8 ± 0.5 mK/kbar, assuming a linear variation between 1.5 and 3 kbar.

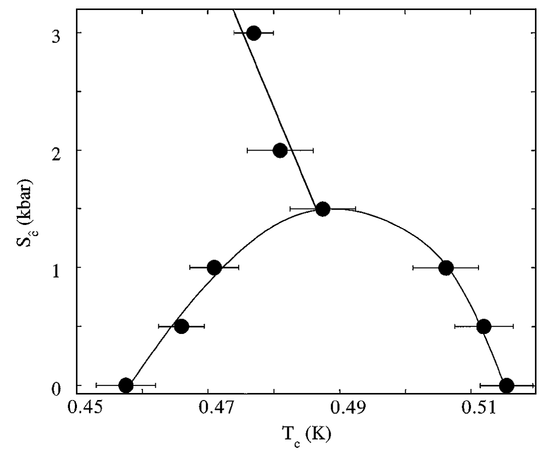

FIG. 2. The upper and lower superconducting transitions merge under **c**-axis stress at $S^*_{\hat{c}} \approx 1.5$ kbar. The resulting single transition moves to lower temperature at a rate of 6.8 ± 0.5 mK/kbar (best-fit line for $1.5 < S_{\hat{c}} < 3$ kbar).

The prime result of the biaxial stress experiment is demonstrated in Fig. 3. We first fix $S_{\hat{c}} = 2.0$ kbar, a sufficient stress to be sure that we have merged the original two superconducting transitions. The specific heat C divided by temperature as a function of T for this reference point is represented in Fig. 3 by open diamonds connected by the solid line. We then apply a series of stresses in the basal plane along the **a** axis, $S_{\hat{a}}$. Representative specific heat curves for $S_{\hat{a}} = 1.0$, 2.0, and 2.5 kbar clearly depict the reemergence of two superconducting transitions, split above and below the reference T_c. We have checked that the splitting repeats under broken hexagonal symmetry for $S_{\hat{c}} = 2.5$ kbar, but

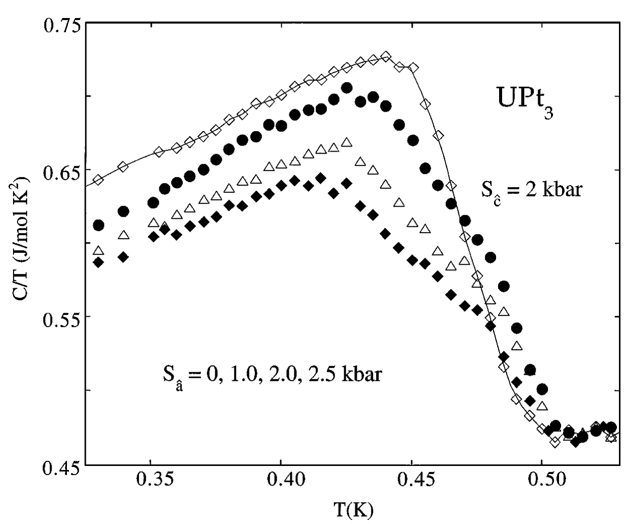

FIG. 3. Specific heat C divided by temperature T vs T at a series of **a**-axis stresses, $S_{\hat{a}}$, with fixed $S_{\hat{c}} > S^*_{\hat{c}}$. The single, merged transition (open diamonds with line guide) splits into two with broken hexagonal symmetry. Basal plane stresses of 1.0, 2.0, and 2.5 kbar correspond to filled circles, open triangles, and filled diamonds, respectively.

it is difficult to perform quantitative analyses because the overall amplitude of C decreases rapidly with both increasing $S_{\hat{\mathbf{a}}}$ and $S_{\hat{\mathbf{c}}}$.

We plot in Fig. 4 the full $S_{\hat{\mathbf{a}}}$-T phase diagram in the presence of $S_{\hat{\mathbf{c}}} = 2.0$ kbar $> S^*_{\hat{\mathbf{c}}}$. The upper and lower superconducting transitions are defined by the two sharp features in the derivative of C/T vs T (Fig. 5). These values of T_{c1} and T_{c2} agree within error bars with the transition temperatures obtained from fits of the data to two entropy-conserving, broadened transitions. Moreover, we have checked explicitly that the data are fit better by two broadened transitions than by one transition subject to a smoothly varying uniaxial stress distribution.

Compressing the UPt_3 crystal along $\hat{\mathbf{a}}$ concomitantly expands the crystal along the orthogonal axes. This results in an effective increase in the stress along $\hat{\mathbf{c}}$. We make a first-order correction for this effect by using the previously determined (Fig. 2) dependence of the merged transition temperature on $S_{\hat{\mathbf{c}}}$ alone. Specifically, we define a $T'_c = T_c + (S_{\hat{\mathbf{a}}})\,(6.8\ \mathrm{mK/kbar})\,(0.48)$ for both branches of the phase diagram, where $S_{\hat{\mathbf{a}}}$ is in kbar, 6.8 mK/kbar is the best-fit slope for $S_{\hat{\mathbf{c}}} > S^*_{\hat{\mathbf{c}}}$, and the appropriate Poisson's ratio (ν_{13}) of 0.48 follows from the measured elastic constants of UPt_3 [14]. The dashed lines in Fig. 4 reflect this correction to the raw data. The adjustment is small, but it does remove the apparent nonmonotonicity of the upper branch of the phase diagram. We underscore the point that the effect of a positive Poisson's ratio, independent of the nature of any correction to T_c, is to increase the **c**-axis stress, maintaining the suppression of the antiferromagnetism and keeping $S_{\hat{\mathbf{a}}}$ as the sole symmetry-breaking field.

Although for properly annealed, pristine UPt_3 there is a double superconducting transition and for biaxially stressed UPt_3 there is a double superconducting transition, the parameters which describe the splitting are conspicuously different in the two cases. In the context of the Ginzburg-Landau theory developed for two-dimensional representations of the superconducting order parameter coupled to a symmetry-breaking field [6], the transition temperatures are given by $T_{c1} = T_{c0} + \tau$ and $T_{c2} = T_{c0} - (\beta_1/\beta_2)\tau$. Here, T_{c0} is the transition temperature in the absence of a symmetry-breaking field, β_1 and β_2 are the Ginzburg-Landau coefficients of the quartic terms, and τ is a measure of the symmetry-breaking energy scale. The ratio β_2/β_1 can be determined from fits to ideal specific-heat jumps at the two transitions which conserve entropy: $(\Delta C_2/\Delta C_1) = (1 + \beta_2/\beta_1)\,(T_{c2}/T_{c1})$, where both ΔC_1 and ΔC_2 are referenced to the normal-state specific heat.

We compare the specific heat jumps in C/T for $S_{\hat{\mathbf{c}}} = 0.5$ kbar, $S_{\hat{\mathbf{a}}} = 0$ and $S_{\hat{\mathbf{c}}} = 2.0$ kbar, $S_{\hat{\mathbf{a}}} = 1.0$ kbar. These data sets bracket $S^*_{\hat{\mathbf{c}}}$ and have been chosen for the comparable splittings between the upper, T_{c1}, and lower, T_{c2}, superconducting transitions [$(T_{c1}$-$T_{c2}) = 46$ and 38 mK, respectively]. Fitting each data set to two ideal superconducting transitions determines the ratio β_2/β_1. Values of β_2/β_1 from 0.2 to 0.5 have been reported for UPt_3 at ambient pressure [11,12], with 0.5 being the BCS weak-coupling limit. We find $\beta_2/\beta_1 = 0.25 \pm 0.05$ for the double superconducting transition with $S_{\hat{\mathbf{c}}} < S^*_{\hat{\mathbf{c}}}$, but $\beta_2/\beta_1 = 0.95 \pm 0.1$ for **a**-axis symmetry-breaking with $S_{\hat{\mathbf{c}}} > S^*_{\hat{\mathbf{c}}}$. This corresponds to a major shift in the relative weights of the specific heat jumps (and integrated entropies) for the upper and lower transitions.

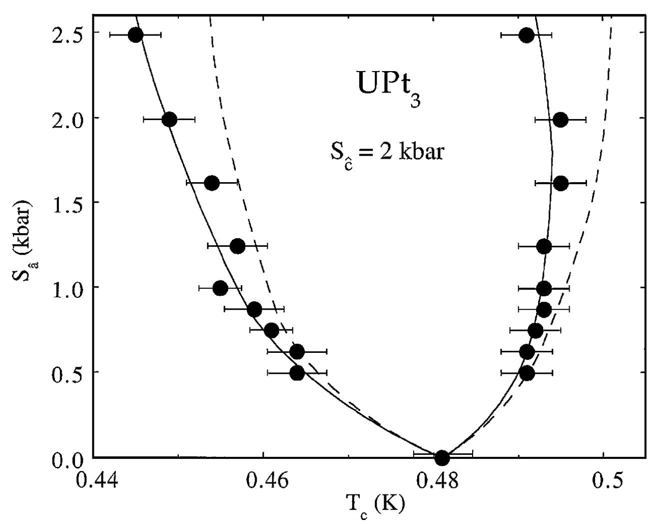

FIG. 4. Phase diagram for both branches of the double superconducting transition with basal-plane uniaxial stress, $S_{\hat{\mathbf{a}}}$, as the symmetry-breaking field. Filled circles are the raw data, solid lines are guides to the eye, and dashed lines reflect a correction to the raw data taking into account the change in **c**-axis stress with increasing **a**-axis stress via Poisson's ratio.

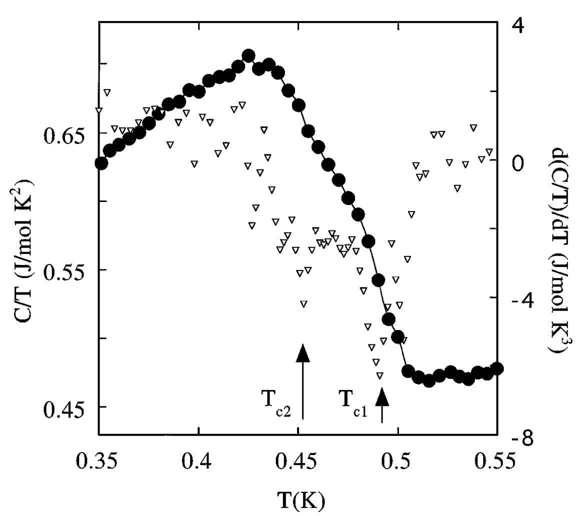

FIG. 5. Specific heat C divided by temperature T and its derivative vs T for $S_{\hat{\mathbf{c}}} = 2$ kbar and $S_{\hat{\mathbf{a}}} = 1$ kbar. The sharp features in the derivative define the upper and lower superconducting transitions T_{c1} and T_{c2} (arrows). The solid line is a cubic spline fit to the C/T data.

Using $\beta_2/\beta_1 = 0.95$, we find the measure of the strength of the symmetry-breaking field, τ, to range from 15 mK at $S_{\hat{\mathbf{a}}} = 1.0$ kbar to 22 mK at $S_{\hat{\mathbf{a}}} = 2.5$ kbar for hexagonal symmetry broken by basal-plane stress. In the unperturbed double transition, where the basal-plane antiferromagnetism remains the most likely symmetry-breaking field, τ is 60% the value at comparable splitting ($\tau = 9$ mK at $S_{\hat{\mathbf{c}}} = 0.5$ kbar), reaching a maximum of 13 mK at $S_{\hat{\mathbf{c}}} = 0$. Finally, we extract $T_{c0} = 480 \pm 5$ mK, in accord with the measured transition temperature for $S_{\hat{\mathbf{c}}} = 2.0$ kbar and $S_{\hat{\mathbf{a}}} = 0$. In addition to agreeing with experiment, the calculation of T_{c0} provides a good check on the validity of the Poisson's ratio correction to the phase diagram of Fig. 4 (dashed line); the quoted value of T_{c0} is independent of $S_{\hat{\mathbf{a}}}$ only after the correction has been made.

In conclusion, we exploit the fact that the double superconducting transition in crystalline UPt_3 responds anisotropically to uniaxial stress to address the question of the origin of the splitting. Uniaxial stress applied along $\hat{\mathbf{c}}$ restores the degeneracy of the two superconducting transitions; by contrast, stress applied solely in the basal plane has no major influence on the splitting and is not believed to destroy the antiferromagnetic order [12]. In this situation, it is not possible to determine whether the **c**-axis stress removes a near accidental degeneracy of different order parameters or whether it affects a single two-dimensional order parameter coupled to a symmetry-breaking field of magnetic or structural character. In the experiments reported here, we extend the use of stress calorimetry to a biaxial configuration, thereby creating a situation where the physical genesis of the double superconducting transition is clear. We use sufficient **c**-axis stress to merge the two transitions and, while maintaining the $\hat{\mathbf{c}}$ component of the stress field, introduce a uniaxial component along $\hat{\mathbf{a}}$. The **a**-axis stress now provides a symmetry-breaking field of unambiguous origin, destroying the hexagonal crystal symmetry (D_{6h}) of the basal plane. An explanation in terms of (nearly) accidentally degenerate order parameters cannot apply. We find that one superconducting transition splits into two, making the biaxial stress configuration qualitatively similar to the pristine case. Quantitatively, however, there are significant differences in the Ginzburg-Landau parameters: for equivalent values of $(T_{c1} - T_{c2})$, β_2/β_1 increases by a factor of 4 and τ by a factor of 2.

We are grateful to D. G. Hinks for providing the crystals of UPt_3 and to H. Krebs for his skillful machining, and we thank B. Ellman for enlightening discussions. The work at the University of Chicago was supported by NSF DMR95-07873. The work at Northwestern University was supported by NSF DMR90-23629.

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