Possible Formation of a Nonuniform Superconducting State in the Heavy-Fermion Compound UPd_2Al_3

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Thermal expansion of magnetostriction measurements on single crystalline UPd_2Al_3, a very clean, strongly Pauli-limited, heavy-fermion superconductor ($T_c \simeq 1.82$ K), have been utilized to establish a first-order transition at $T \leq \tilde{T} \simeq 1.5$ K and $B < B_{c2}(T)$. This is ascribed to the hitherto unobserved formation of a nonuniform superconducting state, as predicted theoretically in 1963.

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In 1963, Fulde and Ferrell [1], and independently Larkin and Ovchinnikov [2], have predicted the existence of a nonuniform superconducting state (hereafter referred to as the FFLO state) in the presence of a magnetic field acting on the electron spins. In the FFLO state the superconducting order parameter is spatially modulated with a wave vector q of order ξ_0^{-1}, the inverse of the superconducting coherence length at $T=0$. The FFLO state occurs only at temperatures smaller than $\tilde{T} \simeq 0.55T_c$ (T_c being the superconducting transition temperature). The phase transition between this nonuniform and the ordinary uniform superconducting state is of first order. The exact position of the corresponding phase boundary in the magnetic field (B) versus temperature (T) diagram is not yet known, but the estimate [1,2] reveals a rather narrow existence range of the FFLO state. Up to now, there have been no experimental observations proving the existence of this modulated state. This can be understood, because usually the magnetic properties of a superconductor are governed by the orbital rather than the paramagnetic effect of the magnetic field. In addition, impurity scattering further narrows the existence range of the FFLO state [3].

In an extension of the original work [1,2], both paramagnetic and orbital effects have been considered in Ref. [4]. As a result, the FFLO state exists if the parameter $\beta=\sqrt{2}B_{c2}^0/B_p$, which characterizes the strength of the paramagnetic relative to the orbital effect, is larger than 1.8. Here, $B_{c2}^0=0.70T_c(-dB_{c2}/dT)_{T_c}$ is the orbital critical field as $T\rightarrow 0$, and $B_p=\Delta_0/\sqrt{2}\mu_B \simeq 1.8$(T/K) $\times T_c$[in K] is the Clogston paramagnetic limit (Δ_0 being the energy gap at $T=0$ K). Because of their large B_{c2}^0 values, some of the Chevrel phases like $PbMo_6S_8$ [5] might be considered good candidates to exhibit the FFLO state, the formation of which is, however, prevented by their extremely small electronic mean free paths ($l \ll \xi_0$). Therefore, in order to observe the FFLO state one has to find a "clean superconductor" ($l \gg \xi_0$) with a small Clogston limit (large β value). But even in this fortunate case, the FFLO state will be confined to a very narrow range in the B-T plane, i.e., at $T < \tilde{T} \simeq 0.55T_c$ and in the vicinity of the upper-critical-field curve, $B_{c2}(T)$.

While for the classical superconductors large initial slopes $(-dB_{c2}/dT)_{T_c}$ and, thus, large β values usually correspond to short mean free paths l, heavy-fermion superconductors inherently show giant $B_{c2}(T)$ slopes, owing to a very small Fermi velocity of their ("heavy") quasiparticles [6]. For example, polycrystalline samples of the new heavy-fermion superconductor UPd_2Al_3 exhibit $T_c=2$ K and $(-dB_{c2}/dT)_{T_c}=4.3$ T/K [7], ensuring a large β value, $\beta=2.4$, which is prerequisite for the FFLO state to form. In addition, this superconductor was found to be in the "clean limit," i.e., to show $l \simeq 700$ Å, which greatly exceeds the superconducting coherence length $\xi_0 \simeq 85$ Å [7]. In this Letter we present results of thermal expansion, magnetostriction, and specific-heat experiments on a UPd_2Al_3 single crystal which prove the existence of a first-order phase transition distinctly below T_c and not far below $B_{c2}(T)$, as predicted in the presence of the FFLO state.

The investigated UPd_2Al_3 single crystal was grown in a tri-arc furnace and annealed for about 120 h at 900 °C to ensure a high crystalline perfection. For measuring relative length changes of the sample, Δl, we used a parallel-plate capacitive dilatometer in a ^{3}He-^{4}He dilution refrigerator; longitudinal magnetic fields ($B \parallel l$) up to 4 T could be applied with the aid of a superconducting solenoid [8].

Figure 1 shows the linear thermal expansion as α/T vs T taken at zero magnetic field both parallel and perpendicular to the hexagonal c axis. Large mean-field-type peaks of opposite sign are found at the Néel temperature. The main feature at the superconducting transition temperature T_c is a change in slope of $\alpha(T)/T$. Only for $\alpha(T)/T$ parallel to [110], a small negative jump occurs at T_c, whereas no discontinuity can be resolved along the c axis; cf. insets of Fig. 1. These small thermal-expansion anomalies, contrasting a gigantic specific-heat jump [7,9] at the superconducting phase transition are unique for UPd_2Al_3, while much more pronounced effects are ob-

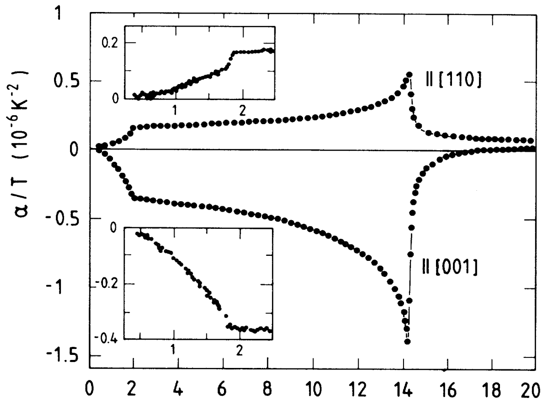

FIG. 1. Thermal expansion as α/T vs T for UPd_2Al_3 single crystal along [110] and [001]. Insets show blowups near $T_c = 1.82$ K.

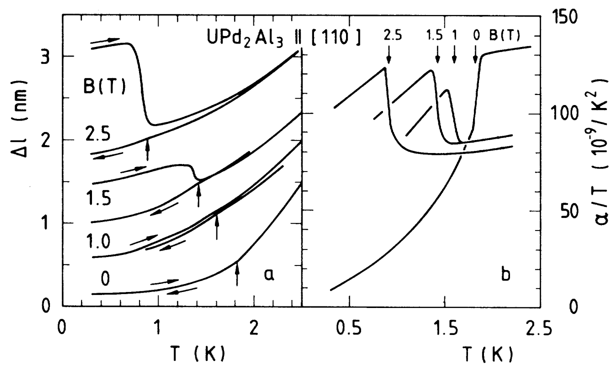

FIG. 2. (a) Length change Δl vs T of UPd_2Al_3 single crystal ($l \| B \| [110]$) at four different fields. Data in applied fields were taken upon warming to 4.2 K after zero-field cooling and upon subsequent cooling in the same field. Arrows indicate T_c values as deduced from α/T vs T; cf. (b). (b) Coefficient of thermal expansion as α_{110}/T vs T, derived from the field-cooled data of (a) [17].

served for other heavy-fermion superconductors [10]. This reflects a rather weak pressure dependence of T_c in UPd_2Al_3 (which changes sign already in a moderate magnetic field as shown below) and is related to an unusually small effective "Grüneisen parameter," $\Gamma_{eff} = c_B V_{mol} \times \beta(T)/C(T) = -3.5$, with the bulk modulus $c_B = 2$ Mbar derived from ultrasound experiments [11,12], the molar volume V_{mol}, the volume expansion $\beta(T) = 2\alpha_{\|[001]}(T) + \alpha_{\|[001]}(T)$, and the specific heat $C(T)$. The small Γ_{eff} seems to be due to a near canceling, below $T = T_N$, of the effects originating in the formation of the heavy-fermion state and the antiferromagnetic ordering, respectively [8]. Such a competition is supported by a large jump of Γ_{eff} at T_N to a value of $+5.5$ in the paramagnetic regime [8]. Heavy-fermion effects are found to dominate the low-temperature dilatation data. For both directions measured, we find $\alpha_i \sim T^{2.9}$ to hold in the superconducting regime—in good agreement with the $T^{2.9}$ power law found in the specific-heat results for $T < 0.8$ K [13]. Very similar asymptotic low-T dependences of the specific heat have been observed earlier for the heavy-fermion superconductors $CeCu_2Si_2$ [14] and UBe_{13} [15].

The effect of a longitudinal magnetic field on the temperature dependence of the length change, measured along [110], is shown in Fig. 2(a). Data were taken upon warming up to $T = 4.2$ K after zero-field cooling (ZFC) and upon subsequent field cooling (FC), respectively. The coefficient of thermal expansion as derived from the FC data is plotted in Fig. 2(b) as α_{110}/T vs T. Applying a moderate magnetic field of 1 T, we observe a change of sign in the jump $\Delta\alpha_{110}$ at T_c, the height of which increases slightly with field. This change of sign in $\Delta\alpha_{110}$ as well as the apparent reduction in the normal state $\alpha_{110}(T)$ might be related to a "canting transition" within the antiferromagnetically ordered state near $B = 0.5$ T, which was found to exist both above and below T_c [16]. This rather broad magnetic transition [12] may also be responsible for the weak anomalies in the $\Delta l(T)$ data below T_c at $B = 1$ T. The occurrence of a jump in $\alpha_{110}(T)$ at T_c indicates that the normal-to-superconducting transition is of second order.

While for magnetic fields $B \le 1$ T, both ZFC and FC measurements yield rather similar $\Delta l(T)$ data, the higher-field data reveal a very pronounced anomaly [cf. Fig. 2(a)]: Upon warming after ZFC a rapid drop in $\Delta l(T)$ sets in at $T_l(B) < T_c(B)$ and terminates just at the superconducting transition temperature [as derived from the data in Fig. 2(b)]. This jump in $\Delta l(T)$ is scarcely seen at $B = 3.0$ T, while it is not there at all in larger fields. (The hysteresis above T_c in the high-field curve corresponds to the hysteresis in the normal-state magnetostriction, and is probably of magnetic origin; see Ref. [18]). The difference in sample length after ZFC and on FC, which increases with field, indicates a nonequilibrium state. From the data in Fig. 2(a) we infer a strong increase in the pinning force on going from $B \le 1$ T to $B > 1$ T. In addition, relaxation into (near) equilibrium upon warming occurs very rapidly, pointing to a first-order transition, at $T_l(B)$, i.e., a temperature somewhat below $T_c(B)$. Figure 3(a) proves that this is not confined to measurements along the hexagonal plane: For zero field and different fields $B \| [001]$, $T_c(B)$ is here defined by the midpoints of the broadened second-order-type phase-transition anomalies in the specific heat [9], when plotted as C/T vs T (idealized jumps are constructed in the usual way by conserving the total entropy). The length measurement (on warming after ZFC) shows for $B = 2$ T a rapid increase, again at a temperature $T_l(B)$ below $T_c(B)$. A small effect can already be seen for $B = 1$ T. We note that no latent heat is resolved in our specific-heat experiment at $T_l(B)$. On the other hand, $\Delta\alpha_{001}/T$ vs T determined upon FC at $B = 1.5$ T shows a change in slope at $T_c(B)$ smoothly interpolating the

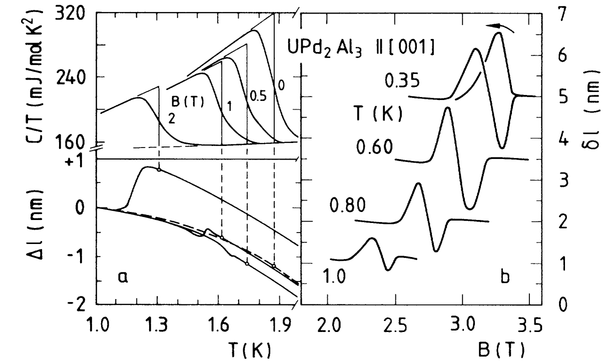

FIG. 3. (a) Specific heat as C/T vs T (top) and length change as Δl vs T (bottom) for UPd_2Al_3 single crystal at $B=0$ and three different B fields, with $l \parallel B \parallel [001]$. Length data points were taken upon warming after zero-field cooling. Broadened specific-heat transitions are replaced by idealized jumps as indicated by thin solid lines; cf. text. (b) Background-corrected magnetostriction, δl vs B, of UPd_2Al_3 single crystal ($l \parallel B \parallel [001]$) at four different temperatures. Data were taken upon increasing B field. In one case ($T=0.35$ K), additional data taken upon decreasing field are shown.

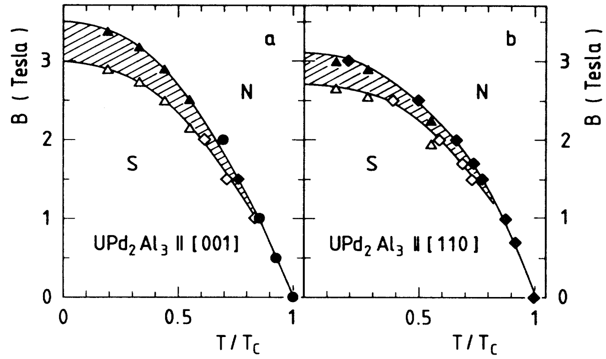

FIG. 4. B vs T/T_c phase diagram of heavy-fermion superconductor UPd_2Al_3 for $B \parallel [001]$ (a) and $B \parallel [110]$ (b). Symbols mark positions of $C(T)/T$ (○, Ref. [9]) and $\alpha(T)/T$ (♦) jumps, measured upon field cooling, irreversible changes of $\Delta l(T)$ (◇) upon warming after zero-field cooling, and off-set (▲) and on-set (△) fields of $\delta l(B)$ anomalies. Hatched region between lines of first- and second-order phase transitions marks existence region of nonuniform superconducting state.

calorimetrically derived values.

A unique anomaly of hysteretic nature below the upper critical field $B_{c2}(T)$ is seen in our magnetostriction results for both orientations of the field. Figure 3(b) displays $\delta l(B) = \Delta l(B) - \Delta l_b(B)$ for $B \parallel [001]$. Here $\Delta l(B)$ is the field-induced length change as measured under isothermal conditions. $\Delta l_b(B)$ is an almost temperature-independent background. The amplitude of the $\delta l(B)$ feature, being of similar size as the change in $\Delta l(T)$ [Fig. 2(a)], is found to increase with decreasing temperature.

Figures 4(a) and 4(b) comprise, in the B-T plane for $B \parallel [001]$ and $B \parallel [110]$, respectively, all phase-transition anomalies discussed before. The upper-critical-field curves, $B_{c2}(T)$, are determined by jumps in $\alpha(T)/T$ and, for $B \parallel [001]$, in $C(T)/T$. It is remarkable to find that the "off-set fields" of the magnetostriction anomalies fall nicely on these $B_{c2}(T)$ curves. In contrast to Sato *et al.* [19], who studied a UPd_2Al_3 single crystal with somewhat lower T_c (and B_{c2}) via magnetoresistivity, we observe an anisotropy of $B_{c2}(T)$ which increases upon cooling and reaches about 12% as $T \to 0$. This is probably caused by the exchange field of the antiferromagnet [20]. At a finite magnetic field, i.e., $1\text{ T} < \tilde{B}(\parallel[110]) < 1.5$ T and $\tilde{B}(\parallel[001]) \simeq 1$ T, respectively, a line of first-order phase transition as defined by the onsets of either $\Delta l(T)$ jumps [Figs. 2(a) and 3(a)] or $\delta l(B)$ [Fig. 3(b)] anomalies, separates from the upper-critical-field curve. As $T \to 0$, this first-order transition occurs at 85% of the respective $B_{c2}(0)$ value. Since the existence of the first-order transition is confined to temperatures below $\tilde{T} \simeq 1.5$ K $\simeq 0.8T_c$, we can safely discard melting of the flux-line lattice as the origin of the observed anomalies, for, in this case, they should also be visible in the vicinity of T_c [21,22].

We think that the first-order transition we have discovered below $\tilde{T} < T_c$ demonstrates the existence of the FFLO state in the heavy-fermion superconductor UPd_2Al_3 at sufficiently high external fields, $B < B_{c2}$. Since the amplitude of the superconducting order parameter should remain practically unchanged at this transition [2], we do not expect a significant latent heat. This explains why the transition into the FFLO state is not resolved in the calorimetric measurements. In contrast to the theoretical models [1–4], in which magnetic order is not considered, UPd_2Al_3 is an antiferromagnet for $T \le T_N = 14$ K, and antiferromagnetism was found to coexist with superconductivity below $T_c = 2$ K [23]. This may explain the observed anisotropy in the existence range of the FFLO state [cf. Figs. 4(a) and 4(b)]. More importantly, the exchange field in the antiferromagnetically ordered state is likely to depress the superconducting transition temperature from its bare value T_c^{bare} to the experimental value $T_c \simeq 2\text{ K} < T_c^{\text{bare}}$ [20]. Consequently $\tilde{T} \simeq 0.8T_c$, the temperature below which the FFLO state forms in UPd_2Al_3, might nevertheless be close to the theoretical value $\tilde{T} \simeq 0.55T_c^{\text{bare}}$. A larger value of T_c^{bare} is also supported by the fact that, following Gruenberg and Günther [4], from the *experimental* values [7] of T_c and $(-dB_{c2}/dT)_{T_c}$ yielding $\beta \simeq 2.4$, $\beta_{c2}(\text{as } T \to 0) \simeq 2.9$ T is estimated, instead of 3.5 T as measured. A more realistic treatment has, therefore, to take into account the effect of antiferromagnetic order on the FFLO state.

Also, the response of the sample length to the formation of this new state has to be explored in more detail. We propose that the spatial modulation of the superconducting order parameter is creating a regular array of genuine pinning centers, with a periodicity somewhat larger than $2\xi_0$. This means that at a field somewhat below B_{c2}, the lattice spacings of both the vortices and those pinning centers must coincide. At slightly lower/higher fields, a force acts on the vortices which may be reflected by the unique $\delta l(B)$ anomalies shown in Fig. 3(b) [24]. The creation of such additional pinning centers in the bulk of the superconductor at $T_l(B)$ also offers an explanation for the pronounced relaxation of the length upon warming in a fixed field after zero-field cooling [cf. Figs. 2(a) and 3(a)]. The surprising difference between low-field ($B < 1$ T) and high-field behavior when subsequently monitoring ZFC and FC $\Delta l(T)$ dependences [Fig. 2(a)] remains to be unraveled by future work.

To conclude, a first-order phase transition, which occurs within the superconducting state distinctly below T_c and somewhat below the upper-critical-field curve, has been discovered for the first time in any superconductor. This observation is considered as strong evidence that the nonuniform FFLO state, which had been unsuccessfully searched for in the past, exists in fact in UPd_2Al_3. Our discovery was possible because this heavy-fermion superconductor is strongly Pauli limited and represents the extreme clean limit of a type-II superconductor. Thus, UPd_2Al_3 meets in an ideal way the strict requirements put on the existence of this nonuniform superconducting state.

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