Possible Fulde-Ferrell-Larkin-Ovchinnikov Superconducting State in CeCoIn$_5$

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We report specific heat measurements of the heavy fermion superconductor CeCoIn$_5$ in the vicinity of the superconducting critical field H_{c2}, with magnetic fields in the [110], [100], and [001] directions, and at temperatures down to 50 mK. The superconducting phase transition changes from second to first order for fields above 10 T for $H \parallel$ [110] and $H \parallel$ [100]. In the same range of magnetic fields, we observe a second specific heat anomaly within the superconducting state. We interpret this anomaly as a signature of a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) inhomogeneous superconducting state. We obtain similar results for $H \parallel$ [001], with the FFLO state occupying a smaller part of the phase diagram.

In the early 1960s, following the success of the BCS theory of superconductivity, Fulde and Ferrell [1] and Larkin and Ovchinnikov [2] developed theories of inhomogeneous superconducting states. At the core of FFLO theory lie competing interactions of a very basic nature. One is the interaction of the spin of the electron with magnetic fields and the other is the energy of the superconducting coupling of electrons into Cooper pairs, or the condensation energy. In the normal state, the electrons are free to lower their total energy by preferentially aligning their spins along the magnetic field, leading to a temperature-independent Pauli susceptibility. For spin-singlet superconductors (both *s* wave and *d* wave), the condensate contains an equal number of spin-up and spin-down electrons. Therefore, Pauli paramagnetism will always favor the normal state over the spin-singlet superconducting state, and will reduce the superconducting critical field H_{c2} which suppresses superconductivity. This effect is called Pauli limiting, with the characteristic Pauli field H_P determining the upper bound of H_{c2} [3]. Another effect of magnetic fields that leads to the suppression of superconductivity is orbital limiting, or suppression of superconductivity when the kinetic energy of the supercurrent around the normal cores of the superconducting vortices in type II superconductors becomes greater than the superconducting condensation energy. The orbital limiting field H_{c2}^0 defines H_{c2} in the absence of Pauli limiting. The relative strength of Pauli and orbital limiting, the so-called Maki parameter $\alpha = H_{c2}^0/H_P$, determines the behavior of the system in high magnetic fields. The prediction of FFLO theory is that for a clean type II superconductor with sufficiently large α (for $\alpha > 1.8$ in the calculations of Ref. [4]), a new inhomogeneous superconducting FFLO state will appear between the normal and the mixed, or vortex, state below the critical temperature T_0 [4]. Within the particular realization of Larkin and Ovchinnikov [2], this state is characterized by the appearance of a periodic array of planes of normal electrons that can take advantage of the Pauli susceptibility.

A number of conventional superconductors were proposed as candidates for observation of the FFLO state, or the first order superconducting transition expected under similar conditions [5], due to their high orbital critical field H_{c2}^0 and, therefore, relatively strong Pauli limiting effect, in the early and mid-1960s. Experimental searches, however, yielded null results [6–9]. The failure to observe the first order superconducting transition was attributed to a high spin-orbit scattering rate in these compounds [10]. In the past decade, the FFLO state was suggested to exist in heavy fermion UPd$_2$Al$_3$ [11] and CeRu$_2$ [12], based on thermal expansion and magnetization data, respectively. Subsequent research identified the magnetization feature in CeRu$_2$ as due to flux motion [13], and the region of the suggested FFLO state in UPd$_2$Al$_3$ was shown to be inconsistent with theoretical models [14]. Most notably, multiple phase transitions that can be associated with the FFLO state have not been observed with a single measurement technique. It is precisely such data that we present in this Letter, where two specific heat anomalies are observed in CeCoIn$_5$, one at the normal-to-superconducting phase boundary, and the second anomaly deep in the superconducting state, which we identify with the phase transition into the FFLO state.

Heavy-fermion superconductor CeCoIn$_5$ satisfies all requirements of theory for the formation of the FFLO state. It is very clean, with an electronic mean-free path on the order of microns in the superconducting state, which significantly exceeds the superconducting correlation length [15]. Its Maki parameter $\alpha \approx 3.5$ is twice the minimum required for the formation of the FFLO state, due in part to high H_{c2}^0 characteristic of the heavy fermion superconductors [16]. It was recently discovered that the superconducting phase transition changes from second to first order at $T_0 \approx 0.3T_c$ for field $H \parallel$ [001], which was taken as an indication that Pauli limiting drives the

physics of CeCoIn$_5$ at low temperature and high magnetic field [5,16,17]. The critical point T_0 was found to be in very good agreement with the one predicted by FFLO theory for a compound with $\alpha = 3.5$ [4]. Magnetization measurements of Tayama *et al.* [18] showed that the superconducting transition in CeCoIn$_5$ becomes first order at a critical temperature $T_0 = 0.7$ K for both $H \parallel$ [001] and $H \parallel$ [100]. Magnetization measurements of Murphy *et al.* [19] with $H \parallel$ [110] indicated the presence of a second temperature-independent, $H \approx 8$ T, anomaly below 1.4 K, and the authors suggested that these results were consistent with the FFLO state.

Materials with quasi-two-dimensional Fermi surfaces, which are likely to exhibit Fermi surface nesting, are expected to have more stable FFLO phases when the magnetic field lies within the 2D-like planes [20]. De Haas–van Alphen studies of CeCoIn$_5$ revealed that a part of its Fermi surface is an undulating cylinder with the axis along the (001) direction, characteristic of the quasi-two-dimensional systems with planes perpendicular to [001] [21]. These theoretical [20] and experimental observations motivated us to perform specific heat investigation of CeCoIn$_5$ with magnetic field $H \perp$ [001].

Specific heat data were collected by employing two techniques: the standard quasiadiabatic method and the temperature decay method, where a complete specific heat data set for a given field was obtained by differentiating a single temperature versus time curve, generated as the sample was coming into equilibrium with the bath starting from high temperature (above 1 K). This technique was employed previously to resolve a sharp specific heat anomaly associated with the first order superconducting phase transition in CeCoIn$_5$ for $H \parallel$ [001] [16], and was demonstrated to give high resolution data consistent with the quasiadiabatic method.

Figure 1 shows specific heat data of CeCoIn$_5$ collected with the quasiadiabatic method, as Sommerfeld coefficient $\gamma = C/T$ after subtraction of the Schottky anomaly tail at low temperature, due to In and Co nuclear levels [15], for magnetic field $H \parallel$ [110] [panel 1(a)], and specific heat for $H \parallel$ [100] [panel 1(b)], as a function of temperature. The superconducting anomaly at lower fields $H \lesssim 10$ T is mean-field-like, with a step in the specific heat at T_c, similar to the case of $H \parallel$ [001] when the field is far from H_{c2} [16]. In this range, increasing the magnetic field simply reduces the magnitude of anomaly, without changing the character of the transition. As the field is increased further, the trend changes dramatically: The magnitude of the anomaly in the specific heat starts to increase, and the anomaly itself sharpens up and acquires symmetric character, characteristic of first order phase transitions. The specific heat data indicate that the change from second to first order occurs at a critical magnetic field $H_0 \approx 10$ T and a critical temperature $T_0 \approx 1$ K. As the superconducting transition temperature is suppressed by the magnetic field below ≈ 500 mK, the transition becomes hysteretic [the data for 11.2 and 11.4 T
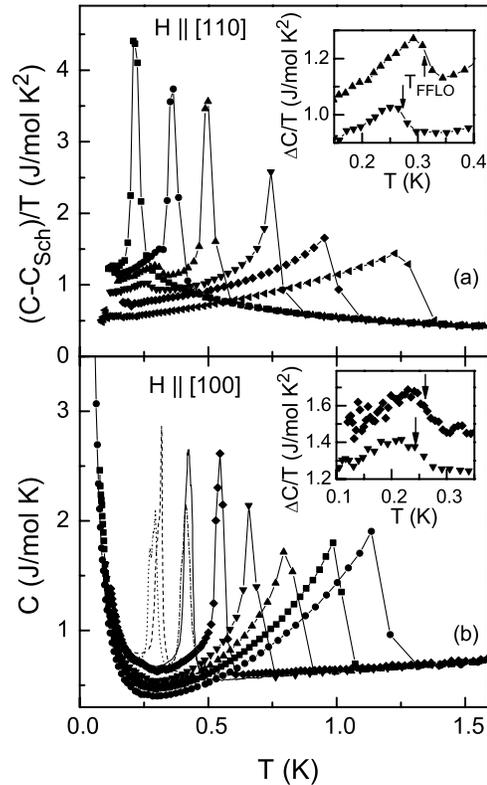

FIG. 1. Specific heat of CeCoIn$_5$ with $H \perp$ [001]. (a) $H \parallel$ [110] data for fields of 9, 10, 10.6, 11, 11.2, and 11.4 T from right to left, collected with the heat pulse method. Inset: Low temperature region for 10.6 and 11 T (same symbols) emphasizing the T_{FFLO} anomaly. Arrows indicate phase transition temperatures from equal area construction. (b) $H \parallel$ [100] solid symbols: heat pulse data for fields of 9.5, 10, 10.5, 10.8, and 11 T from right to left. Solid (dash-dotted) curve is for 11.2 T data collected with the decay method with temperature swept up (down). The dashed (dotted) curve is for 11.4 T with temperature swept up (down). Inset: T_{FFLO} anomalies for 10.8 and 11 T.

in Fig. 1(b)], proving unambiguously that the superconducting transition in CeCoIn$_5$ at high fields close to the critical field H_{c2} is indeed first order. At a temperature of about 300 mK, the specific heat data display an additional anomaly within the superconducting state for $H \gtrsim 10$ T, which we call a T_{FFLO} anomaly. The low-temperature region, in the vicinity of the T_{FFLO} anomaly, is shown in the insets of Figs. 1(a) and 1(b), where T_{FFLO} for different fields are indicated by the arrows. The T_{FFLO} anomaly can be described as a step followed by a gradual decrease of the specific heat with decreasing temperature, a behavior characteristic of the second order phase transition. The T_{FFLO} anomaly is observed only in the superconducting state, and disappears when the superconducting phase transition is suppressed by a magnetic field below T_{FFLO}, as illustrated by the data for $H = 11.4$ T in Fig. 1(a), or when $H \leq 10$ T.

The specific heat data collected with the decay method for $H \parallel$ [110] are displayed in Fig. 2(a) as a surface
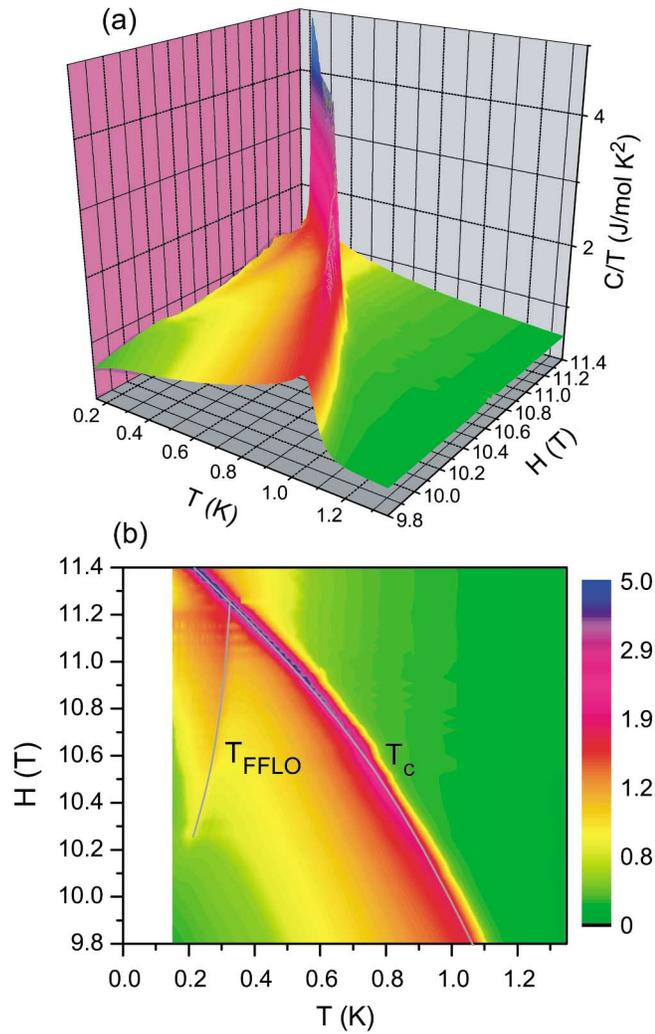
FIG. 2 (color). (a) Electronic specific heat of CeCoIn$_5$ divided by temperature with $H \parallel [110]$ collected with the temperature decay method, as a function of field and temperature. (b) Contour plot of the data in (a) in the H-T plane. Grey lines indicate the superconducting phase transition T_c and the FFLO-mixed state T_{FFLO} anomaly. The color scale is the same in (a) and (b).

contour plot in the H-T plane. We can see a clear evolution of the character of the specific heat anomaly with increasing magnetic field from a mean-field-like step to a very sharp peak at a higher magnetic field, as well as the development of the second low-temperature T_{FFLO} anomaly (a red ridge) in the low-temperature/high-field corner of the H-T plane. By plotting the data as a color contour plot in Fig. 2(b), we can immediately obtain the low-temperature/high field part of the phase diagram of CeCoIn$_5$ with $H \parallel [110]$, where both superconducting-normal phase boundary T_c and the T_{FFLO} anomalies are indicated by gray curves.

The complete H-T phase diagram of CeCoIn$_5$ based on our specific heat measurements is displayed in Fig. 3 for three orientations of the magnetic field, $H \parallel [110]$, $H \parallel [100]$ [closed and open symbols in panel 3(a), respec-

tively], and $H \parallel [001]$ [panel 3(b)]. The second-to-first order change is indicated by $T_0 = 1.1 \pm 0.1$ K for $H \parallel [110]$, which is about 10% higher than T_0 for $H \parallel [100]$. The T_0 is obtained from the evolution of the specific heat anomaly and the magnetocaloric data (not shown), with analysis similar to the one performed for $H \parallel [001]$ with $T_0 \approx 0.7$ K [16]. There is anisotropy for the field in the a-b plane of CeCoIn$_5$ [17,19]. This anisotropy is manifested in $\approx 1.1\%$ higher critical field in the [100] direction which develops above $H = 10$ T, the region of the first order superconducting transition. Inset (c) of Fig. 3(a) shows the evolution of the entropy with magnetic field $H \parallel [100]$ spanning the region of fields from well into the first order (11.4 T) to well into the second order (8.6 T) regions of the superconducting phase transition. The entropy is clearly conserved (all curves collapse on a single curve at $T \approx 1.5$ K), proving that in both regimes the specific heat anomalies are due to the same electrons (and no other degrees of freedom) participating in
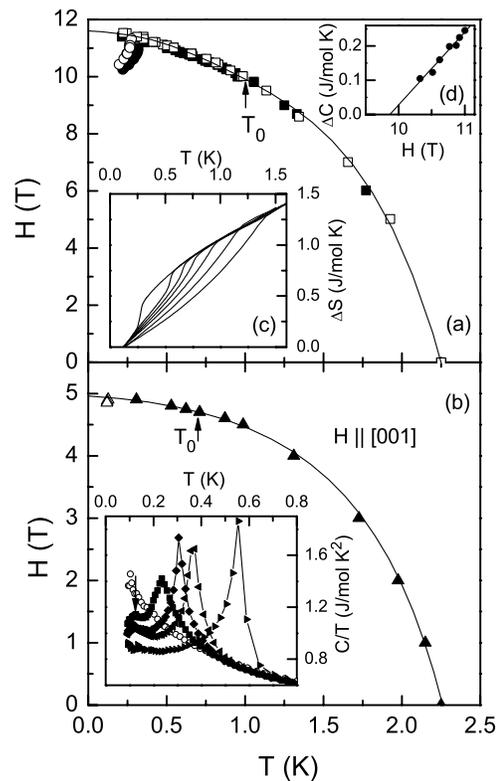

FIG. 3. (a) H-T phase diagram of CeCoIn$_5$ with both $H \parallel [110]$ (filled symbols) and $H \parallel [100]$ (open symbols). ($\bigcirc$) and ($\bullet$) indicate the T_{FFLO} anomaly for $H \parallel [100]$ and $H \parallel [110]$, respectively. Inset (c) shows entropy gain from $T = 0.13$ K for fields of 11.4, 11, 10.8, 10.6, 10.22, 9.5, and 8.6 T from left to right. Inset (d) shows specific heat jump at the T_{FFLO} anomaly obtained from equal area construction. (b) H-T phase diagram for $H \parallel [001]$. ($\triangle$) indicate the T_{FFLO} anomaly. Inset: Sommerfeld coefficient; ($\bigcirc$) 5 T, solid symbols: 4.9, 4.875, 4.85, and 4.8 T from left to right. Arrow indicates T_{FFLO} anomaly at 4.9 T. Solid lines in (a) and (b) are guides to the eye for superconducting phase boundaries.

superconducting phase transitions. Inset (d) of Fig. 3(a) shows the magnitude of the step of the T_{FFLO} anomaly, obtained via the equal entropy construction, as a function of magnetic field $H \parallel [110]$. The data are rather linear in field, indicating the tendency of the anomaly to disappear for fields less than ≈ 9.9 T. The T_{FFLO} anomaly, indicated by solid circles for $H \parallel [110]$, also appears to extrapolate towards fields close to 10 T on the H axis. The inset of Fig. 3(b) shows low-temperature electronic specific heat (Schottky contribution was subtracted) for magnetic fields close to $H_{c2} = 4.95$ T with $H \parallel [001]$. The low-temperature anomaly T_{FFLO} can also be resolved at 4.9, 4.875, and 4.85 T. This anomaly was not observed for $H \leq 4.8$ T. $T_{FFLO} = 130$ mK is about half of the value for $H \parallel [100]$. This indicates that the FFLO state is more stable when the magnetic field is in the a-b plane of this quasi-2D compound, as expected. The tiny high-field/low-temperature corner of the H-T phase diagram occupied by the FFLO phase for $H \parallel [001]$ is indicated by open triangles in Fig. 3(b). The emerging picture therefore is that of a single T_{FFLO} phase boundary carving out a high-field/low-temperature part of the superconducting state of CeCoIn$_5$. Recent work by Radovan et al. [22] presents a similar phase diagram for the field $H \perp [001]$. However, as the field is tilted out of the a-b plane, the FFLO phase is reported to disappear [22], supporting the 2D nature of the FFLO phenomenon in CeCoIn$_5$, in contrast to the 3D picture emerging from the present work.

A number of theoretical approaches were taken to explore the FFLO state, which resulted in a variety of possible phase diagrams [23–26]. Our data are consistent with some of these expectations. The first order superconducting phase transition for $T_c < T_0$ was predicted by Maki [5] for a type II superconductor with strong Pauli limiting. Under these conditions, the FFLO state was calculated to occur below the same temperature T_0 for pure superconductors [4]. Introduction of impurities modifies this picture: The first order normal-to-superconducting phase transition is expected to be rather insensitive to the impurity scattering, while the FFLO state is suppressed to lower temperatures both for the s-wave [27] and d-wave [26] pairing. CeCoIn$_5$ has been shown to be a d-wave superconductor in a clean limit [15,17], with impurity scattering most likely close to the unitary limit, based on low-temperature thermal conductivity measurements. In such a case, a Larkin-Ovchinnikov state is most likely stabilized in the low-temperature/high-field corner of the superconducting state of the H-T phase diagram [26], in accord with our data. Recent Monte Carlo calculations of the phase diagram of the $d_{x^2-y^2}$ superconductor in magnetic field [28] indicate that the superconducting fluctuations modify the first order phase transition below T_0 into the nearly discontinuous crossover (broadened first order phase transi-

tion), observed experimentally in CeCoIn$_5$. These theoretical considerations lead us to conclude that the T_{FFLO} anomaly is indeed the vortex state-FFLO state phase boundary.

In summary, we have observed the low-temperature specific heat anomaly within the superconducting state of CeCoIn$_5$ in a region of the phase diagram where the normal-to-superconducting phase transition is first order, as also demonstrated by the specific heat measurements. On the basis of the experimental data and theoretical expectations, we identify the low-temperature anomaly as due to the formation of the spatially inhomogeneous superconducting FFLO state, predicted first theoretically about 40 years ago.

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