FFLO State in Heavy Fermion Superconductors

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Abstract: The Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state can arise in superconductors in large magnetic field, characterized by cooper pairs with non-zero total momentum and a spatially non-uniform order parameter. For the FFLO state to appear, Pauli pair breaking is required to be the mechanism to suppress superconductivity, which is not the case for conventional superconductors whose orbital pair breaking is stronger. On the other hand, in heavy-fermion superconductor, the f-electrons of the rare earth or actinide atoms hybridize with the normal conduction electrons leading to quasiparticles with enhanced masses, which suppress orbital pair breaking. Recent studies on the heavy fermion superconductors have shown evidence of the FFLO states. In this paper, we will present the theoretical backgrounds and experimental progress of the FFLO state in heavy fermion superconductors. In particular, we will address the recently discovered quasi-two-dimensional superconductor CeCoIn5, which is a strong candidate for the formation of the FFLO state.

Introduction

The Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state was first proposed by two groups of scientist, one by Perter Fulde and Richard Ferrel [1], and the other by Anatoly Larkin and Yuri Ovchinnikov [2] in the 1960s, to describe a new state for certain superconducting materials in the magnetic field.

For a conventional superconductor described by the BCS theory, if its ground state, consisting of Cooper pair with center-of-mass momentum$q = 0$, is subjected to magnetic field, the spin structure will stay the same until the Zeeman effect is strong enough to break Cooper pair, thus destroying the superconductivity. However, for certain normal metallic materials placed in the same magnetic field, the Zeeman effect may lead the Fermi surfaces of spin-up and spin-down electrons to different energy levels, thus might lead to superconducting state with Cooper pairs formed with center-of-mass momentum of finite$\boldsymbol{q} \neq 0$, which is shown in Figure 1. Additionally, the non-vanishing momentum $\boldsymbol{q}$ of the cooper pairs leads to a spatially moderated parameter with periodicity based on a function of $\boldsymbol{q}$. This state for certain superconductivity regime is called the FFLO state.

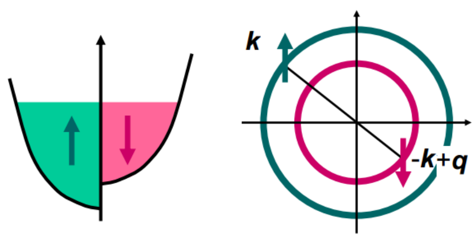


Figure 1: Splitting of Fermi surfaces for spin-up and spin-down electrons in magnetic field, and formation of Cooper pairs with momentum $(\mathbf{k}\uparrow, -\mathbf{k}+\mathbf{q}\downarrow)$

Therefore, for the FFLO state to appear, the orbital breaking of the Cooper pairs in the magnet field has to be weaker, while the Pauli pair breaking is required to suppress superconductivity, so that the superconductivity survives up to the Pauli limits. However, this is not the case for BCS, or the conventional superconductors, whose orbital breaking effects are stronger. Several candidate compounds for the FFLO phase have been proposed, such as the heavy fermion superconductors, layered organic superconductors, cuprate superconductors, and some Chevrel phase materials $(like\ PbMo_6S_8)$ [3].

In this paper, we will focus on the research of the FFLO phase in the heavy fermion superconductors. Heavy fermion materials are compounds named for the enormous effective mass of their charge carriers, containing rare earth or actinide elements. The f-electrons of these atoms hybridize with the normal conduction electrons, leading to quasi-particles with an enhanced mass. And specific heat experiments of the heavy-fermion materials have shown that the superconductivity is caused by the cooper-pairs of the quasi-particles [4]. The enhanced mass of the charge carries of the heavy-fermion superconductors will lead to the low Fermi velocity of the quasi-particles, and in turn, enhance the Maki parameter (see Section: FFLO State). For this reason the heavy-fermion superconductors have raised considerable attention in the search of the FFLO state.

In the following, we will review the theoretical description of the FFLO state and experimental progresses on searching of the FFLO phase in heavy-fermion superconductors, especially experiments on the newly discovered layered compound, $CeCoIn_5$, which showed some strong evidence of the FFLO state.

FFLO State

The FFLO sate is originated from the paramagnetism of conduction electrons [1, 2]. In magnetic field, the Zeeman effect will split parts of the Fermi surface between the spin-up and spin-down electrons, which might produce a new superconducting pair with momentum $(\mathbf{k}\uparrow, -\mathbf{k}+\mathbf{q}\downarrow)$, in which $\mathbf{q}$ is finite for the FFLO state. However, it contradicts to the BCS theory, in which, the superconducting pairs have to be $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$, Figure 2 illustrates these pairing states.

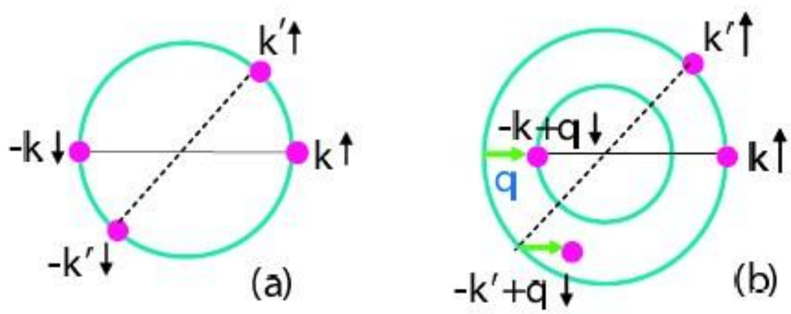


Figure 2. Schematic figure of pairing states. (a) BCS pairing state. (b) FFLO pairing state. The inner and outer circles represent the Fermi surface of the spin down and up bands, respectively. The electron with $-\mathbf{k}'+\mathbf{q}\downarrow$ is not on the inner Fermi Surface. [5]

Due to the finite center-of-mass momentum, $\mathbf{q}$, the superconducting parameter

$$\Delta(\mathbf{r}) \propto \langle \varphi_{\downarrow}^{+}(\mathbf{r})\varphi_{\uparrow}^{+}(\mathbf{r})\rangle \qquad (1)$$

has an oscillating component $e^{\mathbf{iq\cdot r}}$, which is the source of the spatial symmetry breaking and the inhomogeneous superconducting state. [6]

At the core of the FFLO state, there lie two fundamental mechanisms, one is the interaction of the spin of elections with the magnetic field; the other is the condensation energy, which is the energy of the superconducting coupling electrons into Cooper pairs. In the normal state, by aligning to the direction of magnetic field, the electrons are free to minimizing their energy, leading to a temperature-independent Pauli susceptibility [7]. While in the superconducting singlet state, there are equal number of the spin-up and spin-down electrons. Then, in order to polarize the paired electrons, the cooper pairs have to be broken. This destruction of superconducting pairs occurs when the Pauli energy

$$E_P = \frac{1}{2}\chi_n H^2 \qquad (2)$$

become greater than superconducting condensate energy

$$E_c = \frac{1}{2} N(0)\Delta^2 \qquad (3).$$

Here, $\chi_n = \frac{1}{2}(g\mu_B)^2 N(0)$, is the spin susceptibility in the normal state, where g is the spectroscopic factor of an electron [6]. Therefore, the Pauli mechanism favors the normal state over the superconducting singlet state, thus lowering the critical field H_{c2}, which suppresses the superconductivity. This mechanism is called Pauli limiting, and the upper limit of critical filed is defined by H_{c2}^P, from Eqn. (2) and (3),

$$H_{c2}^P = \frac{\sqrt{2}\Delta}{g\mu_B} \qquad (4)$$

Another effect of the magnetic field that will lead to the suppression of the superconductivity is called orbital limiting [5]. In Type-II superconductors, the kinetic energy of the supercurrent around the core of the superconducting vortices will reduce the condensate energy, and the critical field for superconductivity susceptibility due to the effect of the orbital movement of the supercurrent (excluding the Pauli effect) is defined as H_{c2}^{orb}, which is given as

$$H_{c2}^{orb} = \frac{\Phi_0}{2\pi\xi^2} \qquad (5)$$

Where, $\Phi_0 = \frac{hc}{2|e|}$, is the flux quantum [5].

The relative strength of the Pauli and orbital limiting is called Maki parameter,

$$\alpha = \sqrt{2}\frac{H_{c2}^{orb}}{H_{c2}^P} \qquad (6)$$

Which is the ratio of the H_{c2}^{orb} and H_{c2}^P at zero temperature [8]. It has been proved that the orbital breaking effect is detrimental to the formation of the FFLO state [10]. The FFLO state can only exit at a low temperature if α is greater than 1.8 [7]. For the conventional superconductors, $\alpha \sim \frac{\Delta}{\epsilon_F}$, where ϵ_F is the Fermi energy, the Maki parameter is usually less than a unity. However, for the heavy fermion materials, because of their enormous effective mass of charge carriers, the Fermi energy ϵ_F is often negligible, thus making the Heavy fermion superconductor one of the most promising candidates for the FFLO state. The Maki parameter of some heavy fermion superconductors are listed in Table 1.

	Tc/K	α
UPd_2Al_3	2.0	2.4
$CeCoIn_5 \parallel$	2.3	5.0
$CeCoIn_5 \perp$		4.6
$CeIn_3 \parallel$	0.2	3.6
$CeIn_3 \perp$		4.5

Table 1. Maki Parameter and Tc for some heavy fermion superconductors. The data for Tc is from [4]. α of UPd_2Al_3 and $CeCoIn_5$ is from [5], α of $CeIn_3$ is from [9].

Another key factor of the FFLO state is its periodic order parameter. In the presence of a magnetic field of $\boldsymbol{H} = (0,0,H)$, the order parameter is decided by the cyclone motion of the cooper pairs perpendicular to the direction of the magnetic field $\boldsymbol{H}$**.** The order parameter is forced by the orbital effect to be the eigenvalues of the operator $\boldsymbol{\mathcal{H}}^2$, where $\boldsymbol{\mathcal{H}}$is defined as

$$\boldsymbol{\mathcal{H}} = -i\hbar\boldsymbol{\nabla} - \frac{2e}{c}\boldsymbol{A} \qquad (7)$$

Here, $\boldsymbol{A} = (0, Hx, 0\ )$.

And the eigenvalues of $\boldsymbol{\mathcal{H}}^2$ have been solved solved as [5]

$$\frac{2\hbar^2}{\xi_H^2}\left(n + \frac{1}{2}\right) + \hbar^2 q^2 \qquad (8)$$

Where, $\xi_H = \sqrt{\Phi_0/_{2\pi H}}$, n is the Landau level index. The second term represents the kinetic energy of the Cooper pairs, which contradicts with the BCS theory, as this term vanishes at the BCS limit when $q = 0$. Therefore, the order parameter given by Eqn. (1) can be modified as

$$\Delta(\mathrm{r}) \propto e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\phi_n^{(k)} \qquad (9)$$

Where, $\phi_n^{(k)}$is the Abrikosov function with Landau level index n,

$$\phi_n^{(k)}(\boldsymbol{\rho}) = (-1)^n e^{iky} H_n\left[\sqrt{2}\frac{x - x_k}{\xi_H}\right] \qquad (10)$$

Where, $\boldsymbol{\rho} = (x, y)$, $x_k = k\xi_H$, H_n is the Hermite polynomial.[5].

To sum up, the FFLO is a theoretical prediction for an exotic superconducting state at low temperature in finite magnetic field with:

- ✓ Finite momentum of Cooper pairs
- ✓ Spatial modulation of order parameter

Heavy-Fermions Based Experiment on FFLO State

In spite of the clear theoretical prediction of the FFLO state, no obvious progress on the experiment has been reported until recently, because of the stringent criteria on the superconducting materials. Summary of the requirement for the formation of the FFLO states [5]:

- "Strongly Type–II superconductors with very large Ginzburg–Landau parameter $\kappa \equiv \lambda/\xi \gg 1$ and large Maki parameterα, such that the upper critical field can easily approach the Pauli paramagnetic limit."
- "Very clean, $\xi \ll \ell$, since the FFLO state is readily destroyed by impurities."
- "Anisotropies of the Fermi–surface and the gap function can stabilize the FFLO state."

Generally speaking, there are several ways to study the FFLO states, such as measurement of the penetration depth, thermal conductance, magnetization and magnetostriction, nuclear magnetic resonance (NMR), and ultrasound velocity. In the past, some experiments based on these methods have shown some features of certain heavy-fermion materials ($e.g. UPd_2Al_3, UBe_{13}$) that might be descripted by the FFLO theory. However, none of these results are well-standing until the discovery of a new kind of the Ce based superconductor, $CeCoIn_5$ [5].

The extraordinary characteristics of $CeCoIn_5$ make the material stands out from other heavy Fermion superconductors, and make the material regarded as one of the most promising candidates for the FFLO state. The $CeCoIn_5$ crystal is "very clean, having an electronic mean free path on the order of microns in the superconducting state, which significantly exceeds the superconducting correlation length" [5]. The T_c of $CeCoIn_5$ is 2.3K, the highest among the currently-found $Ce\ and\ U$ based heavy-fermion superconductors, and holds the highest value of Maki parameter α, which is around 5 [7], the α values for different lattice direction is listed in Table 1. $CeCoIn_5$ exhibits a 2-D layered structure of alternating $Ce\mathrm{In}_3$, which is a superconductor under pressure, and CoIn_2, which is less conducting [11]. The crystal structure of CeCoIn_5 is shown in Figure 3. The 2-D nature of $CeCoIn_5$ is believed to be essential for the formation of the FFLO state, because "both the strong reduction of the orbital pair-breaking and the nesting properties of the quasi-2D Fermi surface are expected to stabilize the FFLO state" [15].

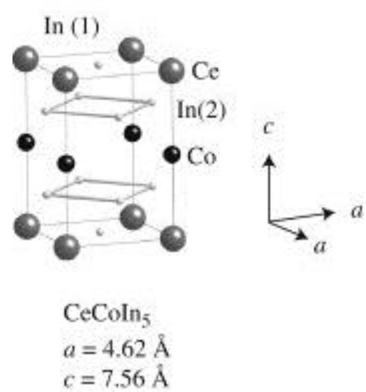


Figure 3: Crystal structure of $CeCoIn_5$ [11]

The penetration depth measurement is one of the effective methods to study the FFLO state, According to the results of a tunnel diode oscillator (TDO) experiment done by Agosta *et al*, clear evidence of the FFLO state has been found, which agrees with the results of other experiments [12]. Agosta *et al* claimed that the TDO method has the advantage of eliminating problems of resistance and additional stress, as it does not require physical contact of the sample. The principle for the TDO is that the frequency shift is proportional to the London penetration depth for superconductors or the skin depth for metallic state. Their results of tunnel diode oscillations in $CeCoIn_5$ (H is perpendicular to the ab-plane of the crystal) are shown in Figure 4. The most prominent feature of the results of is the spike near 5T, above which, the TDO is measuring the skin depth of the metallic state. The data gives some clue for the existence of the

FFLO state. However, the critical field measurement via the method, which is also mentioned by the authors, shows no evidence of the Pauli limiting, which is crucial to the FFLO sate.

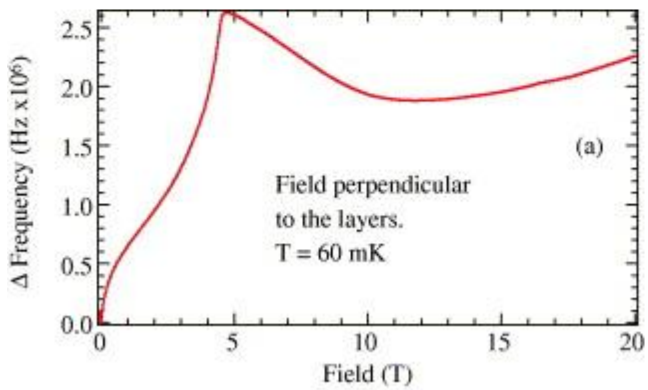


Figure 4: The TDO signal showing the superconducting transition in $CeCoIn_5$ [12]

The magnetization and magnetic relaxation is another effective method in search of the FFLO state, and has been performed by different groups. One of the most recent experiments utilizing this method on $\mathrm{CeCoIn_5}$ was done by L. Mendonc, et al, which shows crossing over anomalies at the vicinity of H_{c2} and additional features associated with relaxation effect of the vortices lattice below the FFLO state [13]. The experiment is carried out by means of a force magnetometer operating in a plastic dilution refrigerator in a 18T magnetic field. Data are collected with magnetic field both parallel and perpendicular to the ab-plane, which are shown in Figure 5. From field-derivative of the magnetization dM/dH ((c), (d) in Figure 5) the anomalies are clear seen. However, the peak effect of the magnetization is not found right at $H_{c2}^{\parallel}$, but found well below $H_{c2}^{\parallel}$.

Spatially-resolved Nuclear magnetic resonance (NMR) is another method to probe internal structure in highly correlated superconductors. Anomalous NMR spectra of $\mathrm{CeCoIn_5}$, which provides a microscopic evidence of for the occurrence of spatially-modulated superconducting order parameter expected in the FFLO state, was reported by Kumagai, *et al* from Japan [14, 15]. As Kumagai, *et al* claimed, NMR can monitor the local information of low energy quasiparticle excitations and antiferromagnetic fluctuation sensitively. NMR has special advantage to measure and the spatially non-uniform superconducting state of FFLO. In the experiment of Kumagai, *et al*, they apply the magnetic field both perpendicular and parallel to the ab-plane, and carry out the phase-coherent pulsed NMR measurement for three atomic sites ($\mathrm{Co, In(1), and\ In(2)}$). The results for $^{115}\mathrm{In(2)-NMR}$ spectra for $H \perp ab-plane$ under various temperatures are shown in Figure 6. Similar experimental results have been achieved for different atomic sites. From the spectra, we can see, upon entering the superconducting state, the NMR intensity is strongly reduced, and the NMR spectra are shifted to the lower frequency side with decreasing temperature. Kumagai, *et al* state the phenomenon is typical in all superconductors, as it is a reflection of the decreasing of spin-susceptibility in the magnetic field. The evidence of the FFLO state is shown in the anomalies for spectra under magnetic field above 4.7T. Double peak structure can be found in (b), just across the SC transition, and persist down with decreasing temperature, while no other signals and broadening of the spectra have been detected . The authors argue that while the lower frequency part in the (b) arises from the SC region, the other corresponds to the signal from the normal region. Thus a disproportionate AF order is ruled out, and they conclude that the inhomogeneous SC phase with a nodal plane structure as expected in the FFLO state exist in the narrow range of the H-T diagram corner.

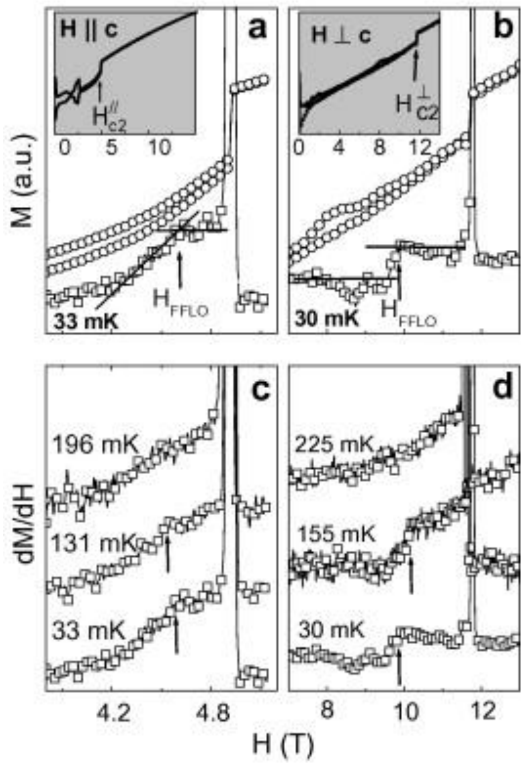


Figure 5: Magnetic behavior of a $CeCoIn_5$ single crystal. Panels (a) and (b): Details of magnetization curves in the vicinity of the upper critical field H_{c2}. Circles and squares denote $M(H)$ and the corresponding derivative dM/dH, respectively. The complete isothermal magnetization hysteresis loops $M(H)$ are shown in the insets. Panels (c) and (d): derivative curves dM/dH at select temperatures for experiments with $H \parallel c$ and $H \perp c$, respectively. The arrows indicate the anomaly at H_{FFLO} in the derivative curves. [13]

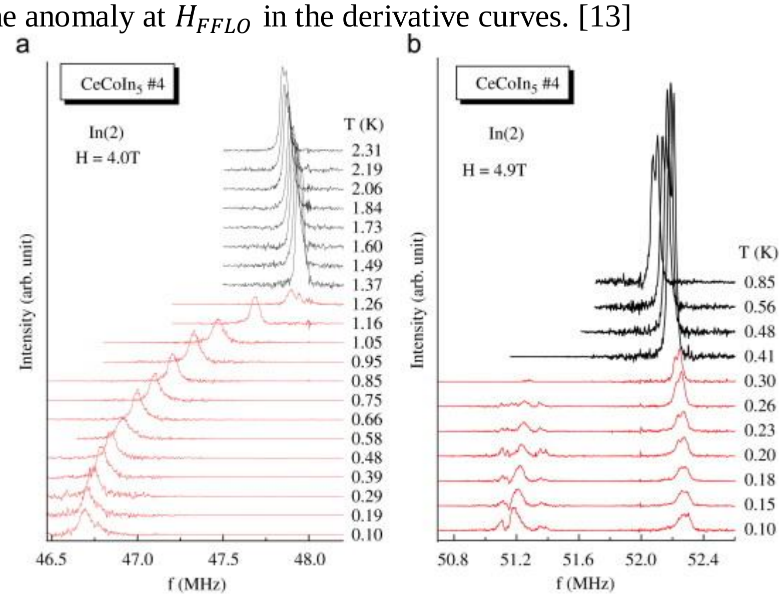


Figure 6: $^{115}\mathrm{In}(2)-$NMR spectra of $\mathrm{CeCoIn_5}$ for various temperatures from a normal state (black lines) to a superconducting state (red lines) at (a) $\mathrm{H}=4.0\mathrm{T}$ (left panel), (b) 4.9T (right panel). [15]

Kumagai, *et al* also reported the results of Knight shift of ^{56}Co, via the NMR method. The results are shown in Figure 7. For high field above 4.6T, jump of the Knight shift appears discontinuously at $T_c(H)$, which clearly reveals the first order transition from the normal to the superconducting state. Kumagai, *et al* state the value-splitting and jump at $T_c(H)$, gives microscopic observation of the superconductivity order parameter, which shows the discontinuous change of the local spin susceptibility at $T_c(H)$.

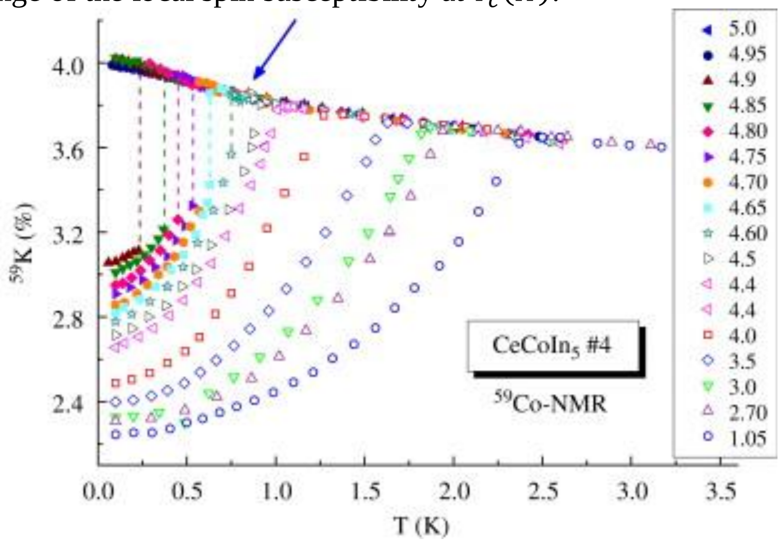
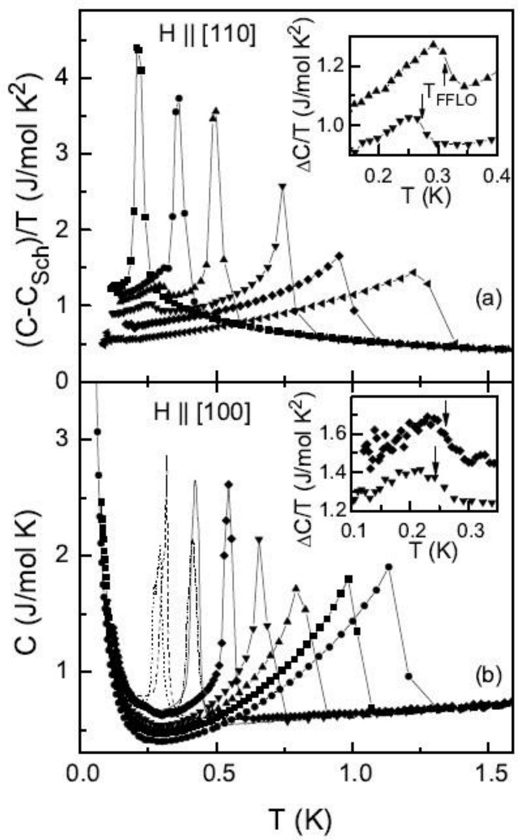


Figure 7: T-dependence of $^{56}\mathrm{Co}-$Knight Shift of $\mathrm{CeCoIn_5}$ [15]

The specific heat measurement is another unique probe for the FFLO state in heavy fermion superconductors because of its remarked sensitivity of the delocalized quasiparticles, since localized quasiparticles do not carry heat, which is similar as thermal conductivity measurement in basic principle. In the experiments carried out by scientists at the Los Alamos National laboratory [7], specific heat of the $\mathrm{CeCoIn_5}$ has been measured in the vicinity of the superconducting critical field H_{c2}, with magnetic field in the [110], [100], and [001] direction, and at temperature down to 50 mK. The Specific data were collected by two different methods, the standard quasi-adiabatic method and the temperature decay method. For H || [110], [100] (H is parallel to the ab-plane), superconducting phase transition from second order to first order above 10T, and anomaly within the superconducting state have been observed, the results are shown in Figure 8. The authors also give the H-T plane diagram for data collected with the decay method for H ∥ [110], which is shown in Figure 9. From Figure 9, we can see clearly evolution of the anomaly of specific heat with the increasing magnetic field from a mean-field-like step to a sharp peak as well as the second order transition anomalies which corresponding to the FFLO state (the red ridge in (a), and the grey line in (b)). The authors claim that their data are in accord with the recent Monte Carlo simulations of the phase diagram of the $d_{x^2-y^2}$superconductors in the magnetic field and conclude that second-order anomaly they found is indeed the boundary for FFLO state transition.



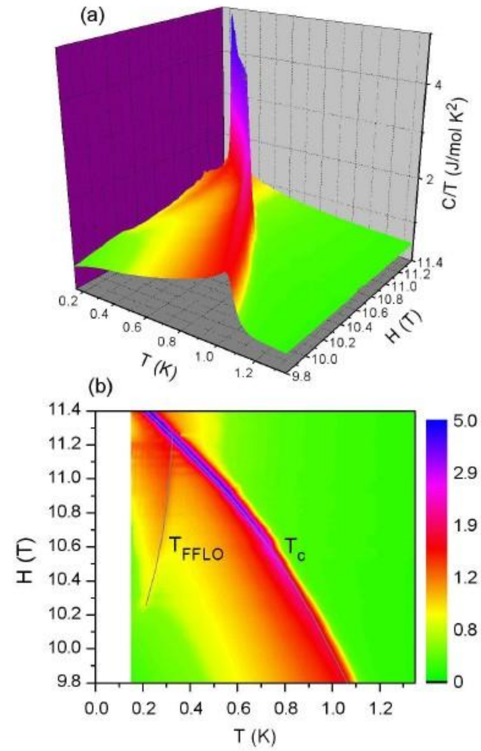


Figure 8 (left): Specific heat of $CeCoIn_5$ with H ⊥ [001] (a) H ∥ [110] data for fields of 9T, 10T, 10.6T, 11T, 11.2T and 11.4T from right to left, collected with heat pulse method. Inset: Low temperature region for 10.6T and 11T. (b) H ∥ [100] Solid symbols: heat pulse data for fields of 9.5T, 10T, 10.5T, 10.8T, and 11T from right to left. Solid (dash-dotted) curve for 11.2T data collected with decay method with temperature swept up (down). Dashed (dotted) curved is for 11.4T with temperature swept up (down). Inset: for 10.8T and 11T [7].

Figure 9 (right): (a) Electronic specific heat of $CeCoIn_5$ divided by temperature with H ∥ [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 [7].

Other methods, such as the measurement of ultrasound velocity also gives some evidence for the FFLO state in $CeCoIn_5$. $CeCoIn_5$ appears to be the unique system, which meet all the requirement for the formation of the FFLO state, and provide an effective platform to carry out the experiment. By applying magnetic field to both parallel and perpendicular directions, consistent results have been reported for different methods, and the H-T diagrams have been fully determined, which is shown in Figure 10. However, some of the microscopic results are controversial and some of the results are different from the original prediction of the FFLO state to some extent [5].

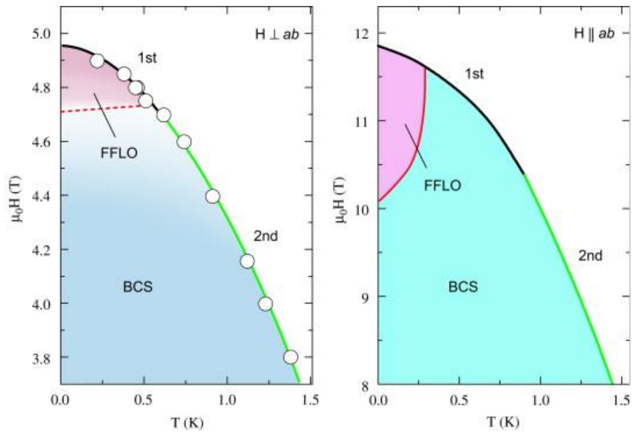


Figure 10: H–T phase diagrams at low temperatures and high fields for $H \perp ab$ (left) and for $H \parallel ab$ (right) [15]

Summary

After the discovery of the new heavy-fermion superconductor, $\mathrm{CeCoIn_5}$, series of the exciting steps in searching of the FFLO superconducting state have been achieved. However, it is still too early to declare the existence of the FFLO state, since certain questions and controversial results need to be answered.

For further researches on the FFLO state, experimental methods like the scanning tunneling microscopy (STM), which can give information of spatial distribution of the quasiparticle distribution, and neutron scattering, which can give information of the polarized spin excitation are necessary. We can also make Josephson junctions between $\mathrm{CeCoIn_5}$ and other BCS superconductors or normal metallic materials. Other experiments like the point contact spectroscopy, or planar tunneling spectroscopy to map the electric structure in low temperature under magnetic field can also be promising.

Besides $\mathrm{CeCoIn_5}$, some other heavy-fermion superconducting materials have been created, such as $\mathrm{Cs_xYb_{1-x}In_5}$, which showed anomalous Upper Critical Field [16], might be another probe for the FFLO state.

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