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# Emerging evidence for FFLO states in layered organic superconductors

(**Review Article**)

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In this short review, we report on the recently found growing experimental evidence for the existence of Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) states in quasi-two-dimensional organic superconductors. At high magnetic fields aligned parallel to the conducting organic layers, we observe an upturn of the upper critical field beyond the Pauli limit, as evidenced by specific-heat and torque-magnetization measurements. Inside the superconducting state a second thermodynamic transition emerges. These features appear only in a very narrow angular region close to parallel-field orientation.

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74.25.Dw Superconductivity phase diagrams;
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Contents



## Introduction

When applying a magnetic field parallel to the superconducting planes of a material consisting of alternating superconducting and normal-conducting layers, the usually dominating orbital Cooper-pair breaking is greatly reduced. In that case, the orbital critical field, $\mu_0 H_{\rm orb}$, may easily exceed the Pauli paramagnetic limit, $\mu_0 H_P = \Delta_0/(\sqrt{2}\mu_B)$, with $\mu_B$ the Bohr magneton and $\Delta_0$ the superconducting energy gap at $T = 0$ [1,2]. This limit occurs in spin-singlet superconductors when the Zeeman energy becomes larger than the superconducting condensation energy. In such a case [3] and if the superconductor is in the clean limit with a mean free path much larger than the coherence length, an unconventional, spatially modulated, superconducting state may appear at high magnetic fields and low temperatures. This was predicted independently in 1964 by Fulde and Ferrell [4] as well as Larkin and Ovchinnikov [5]. Such superconductivity, therefore, is now called FFLO or LOFF state.

At high magnetic fields, the Zeeman-split Fermi surfaces for up- and down-spin electrons do not allow for the usual BCS-like pairing with zero total momentum. In the FFLO state, however, Cooper pairing may appear with a finite center-of-mass momentum of the order $|q| = 2\mu_B H/(\hbar v_F)$, where $v_F$ is the Fermi velocity (Fig. 1) [6,7]. This, in turn, results in an oscillating part of the superconducting order parameter also in real space. By that, the superconductor "sacrifices" part of its volume to the normal state allowing to extend superconductivity to even higher magnetic fields.

The materials of choice for searching for FFLO states are the layered, quasi-two-dimensional (2D) molecular superconductors based, e.g., on the organic molecules BEDT-TTF (bisethylenedithio-tetrathiafulvalene) or BETS (bisethylene-dithio-tetraselenafulvalene). These well-studied materials

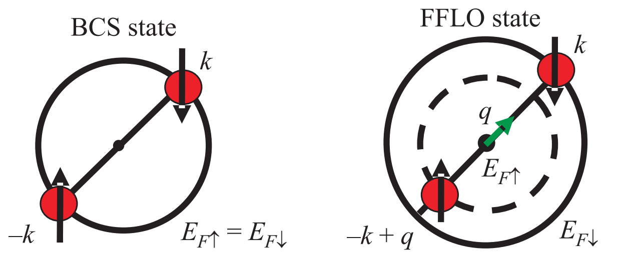


*Fig. 1.* (Color online) Schematic presentation of (left) the usual BCS pairing state with zero resulting momentum and spin and (right) the FFLO pairing state with a finite center-of-mass momentum, *q*. The circles represent the Fermi surfaces for spin-up and spin-down bands.

[8–12] are strong type-II spin-singlet superconductors of high purity with long mean free pathes. During the last years, there indeed have been a number of reports giving growing evidence for the existence of an FFLO state in 2D organic superconductors [13–20].

Besides the 2D organic materials, heavy-fermion superconductors have been suggested to show FFLO states as well. These claims, however, later had to be revised or are inconclusive (see [7] for an overview). For the heavy-fermion compound $CeCoIn_5$, clear thermodynamic evidence for a field-induced phase inside the superconducting state was found [21,22]. This phase, however, does not show the features expected from the FFLO prediction, but rather an antiferromagnetically ordered state [23,24]. Further to that, recent thermodynamic experiments showed an entropy decrease when going from the homogenous superconducting into the unknown phase in $CeCoIn_5$ which disagrees with the formation of an FFLO state, but fits to the emergence of antiferromagnetic order [25].

Here, we present recent specific-heat and torque-magnetization data obtained for two 2D organic BEDT-TTF-based superconductors with transition temperatures, $T_c$, differing by more than a factor of 2 [16–19]. For both materials, we find clear Pauli limitations of the upper critical fields for magnetic fields aligned within the planes. Towards lower temperatures, upturns of the critical fields beyond the Pauli limits appear. The overall shape of the upper critical field lines agrees well with theoretical predictions for a 2D FFLO superconductor. This upturn of the upper critical field is limited to a very narrow angular range of a mere of about ±0.5 deg around in-plane field alignment. All this is strong evidence for the existence of FFLO states in these organic superconductors. For smaller out-of-plane alignment, a second phase transition within the superconducting state emerges, the origin of which is unclear so far.

## Experimental

The investigated single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ were prepared by standard electrochemical processes described elsewhere [26,27]. The specific heat was measured by use of a continuous relaxation technique as described in more detail in the Appendix of Ref. 28. Thereby, the sample together with the platform and Apiezon N grease to fix the sample is heated up by a considerable amount above the base temperature (up to 100%). During the relaxation back to base temperature a large number of data points is taken. As a speciality for β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$, the calorimeter was mounted on a piezoelectric drive inside a $^3$He cryostat equipped with a 20-T magnet. The drive allowed for a precise rotation of the sample with resolution of better than 0.02 deg. The magnetic torque was measured by a capacitive cantilever. More experimental details can be found in Refs. 16, 18, 19.

## Results and discussion

For κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, the upper critical field for in-plane field alignment is somewhat above 20 T which calls for experiments in high-field laboratories. The results shown in Fig. 2 have been obtained at the Grenoble High Magnetic Field Laboratory (LNCMI-Grenoble) [16]. In this experiment, only the complete cryostat could be tilted slightly to orient the sample. Although the crystal was aligned as best as possible, in retrospective a small misalignment on a sub-degree level cannot be excluded (see discussion below).

In Fig. 2, the difference between the specific heat measured in the labeled in-plane magnetic fields and the normal-state specific heat measured for a field of 14 T applied perpendicular to the layers is shown. By that, the specific-heat anomalies at $T_c$ become clearly visible. At 8 T, $T_c$ is reduced from 9.1 K at zero field by a mere of 0.4 K (using the maxima of the λ-like anomalies, Fig. 2). From that, the initial critical-field slope can be estimated to $H'_{c2} = -\mu_0 dH_{c2}/dT = 20$ T/K. This, of course, is a rather conservative estimate since the slope at lower fields most probably is even higher. Anyway, estimating the orbital

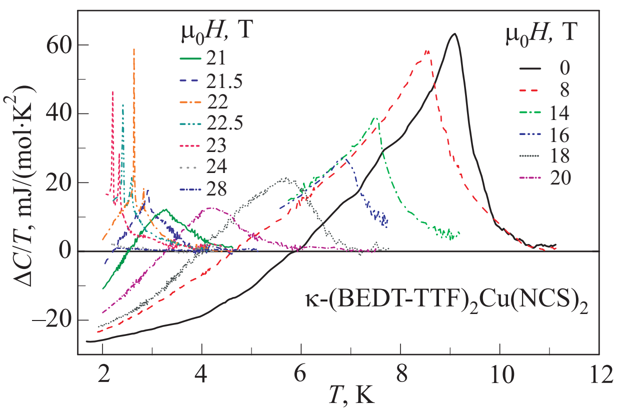


*Fig. 2.* (Color online) Temperature dependence of the specific-heat difference between the superconducting and normal state, $\Delta C/T$, of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in magnetic fields applied parallel to the superconducting layers.

critical field by $H_{orb} = 0.7H'_{c2}T_c$ [29], the extraordinary large value of about 130 T is obtained.

Towards higher magnetic fields, $T_c$ shifts much more rapidly to lower temperatures (Fig. 2). This is a clear sign for Pauli limitation of the upper critical field. Indeed, the Pauli-limiting field can be determined quite reliably from specific-heat data. As mentioned, $H_P$ is directly proportional to $\Delta_0$. This superconducting energy gap at zero temperature is given by the jump height of the specific-heat anomaly at zero field. Assuming a BCS-like temperature dependence of the energy gap [30] the complete temperature dependence of the specific-heat difference, $\Delta C(T)$ can be described by the so-called $\alpha$ model [31]. Thereby, the temperature dependence of the energy gap, $\Delta_0(T)$, is scaled by an appropriate parameter $\alpha = \Delta_0(T)/k_B T_c$. For κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, $\alpha$ values between 2.4 [32] and 2.8 [33] have been found. Using the smaller value results in $\mu_0 H_P = 23$ T. This nicely agrees with ~21 T estimated from the specific-heat and magnetic-torque data discussed below.

At 21 T, the specific-heat anomaly sharpens indicating a possible first-order transition. For fields above 21 T, a second, very sharp anomaly just below the first one appears. This can be seen much better in Fig. 3(a). Since the relaxation technique allows to record data during heating and cooling, this was utilized at these high magnetic fields to search for hysteresis. Indeed, as seen in Fig. 3(b), a well-resolved hysteresis evolves for the lower-temperature transition, whereas for the main superconducting transition a small hysteresis might be present, but the effect is barely above the resolution limit. Anyway, the existence of an additional anomaly and the upturn of the upper critical field at low temperatures are strong evidence for the existence of an FFLO state in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

Further support for the occurrence of the FFLO state was found in magnetic-torque data. The magnetic torque is proportional to the perpendicular component of the magnetization with respect to the magnetic field. Using a capacitive cantilever allows for a highly sensitive detection of magnetization changes. In the experiment discussed below, the cantilever could be rotated allowing an alignment of the sample with precision of about 0.01 deg in the applied magnetic field. For in-plane field, the magnetic-torque data shown in Fig. 4(a) have been obtained [18]. Upon lowering the temperature, an increasingly sharp transition appears at $\mu_0 H_{c2}$. This may be taken as an indication that the Pauli limit is reached. Indeed, this sharp transition occurs at about 21 T fitting nicely to the estimated Pauli limit and the specific-heat data.

When lowering the temperature further, superconductivity survives even beyond this field. In addition, a second dip-like feature appears in the torque data below $\mu_0 H_{c2}$ [vertical arrows in Fig. 4(a)], signaling the emergence of the FFLO phase. These results nicely confirm the specific-heat data for the upper critical field. There is, however, a distinctive difference in the extension of the phase between the two anomalies. Whereas the specific-heat data suggest a very narrow region for the additional thermodynamic phase, the dip-like feature in the torque data stays almost constant in magnetic field at about the Pauli limit. This might be related to the much better in-plane alignment of the magnetic field in the torque measurements as for the specific-heat experiment. This will be discussed in more detail below.

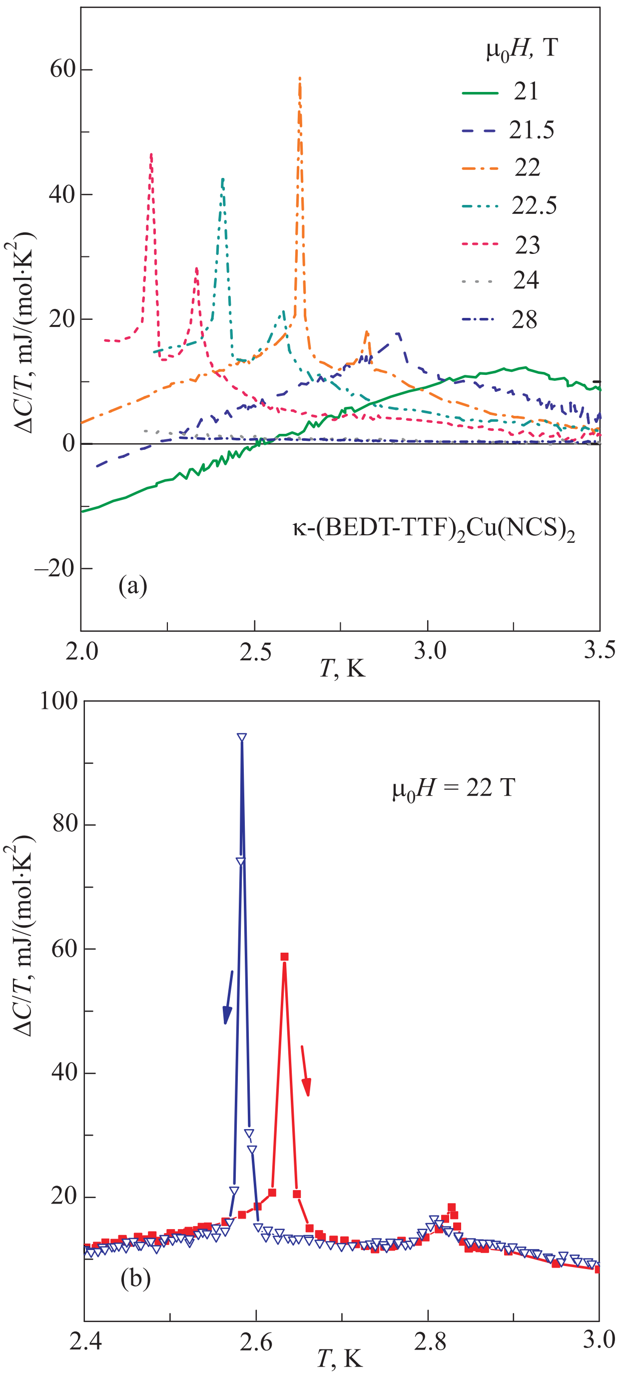


*Fig. 3.* (Color online) (a) High-field data shown in Fig. 2 in an expanded scale. (b) Specific-heat data measured at 22 T during warming and cooling.

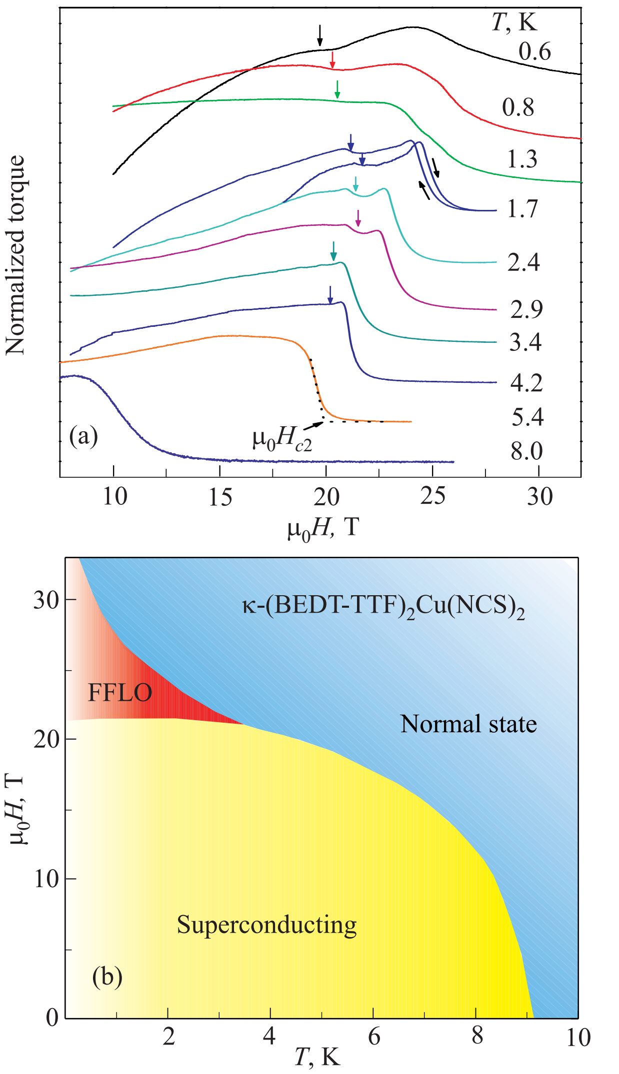


*Fig. 4*. (Color online) (a) Magnetic-torque data of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at various temperatures for in-plane magnetic fields. For $T$ = 1.7 K, data for both up and down field sweeps, otherwise only down sweeps are shown. The vertical arrows mark the small dip-like features, which are associated with the transition into the FFLO state. (b) Schematic phase diagram deduced from the data shown in (a) and Fig. 2 [18].

A schematic magnetic phase diagram constructed from the specific-heat and magnetic-torque data is shown in Fig. 4(b). After the very steep initial increase of $\mu_0 H_{c2}$ this slope quickly levels off at higher fields upon reaching the Pauli limit. At lower temperatures, a strong upturn of the $\mu_0 H_{c2}$ line occurs. Together with this upturn, the second phase transition appears. This agrees favorably well with the FFLO scenario. Recent NMR data have given further strong support for the existence of an additional superconducting phase above the Pauli limit in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [20].

In an effort to find further superconductors revealing an FFLO phase and to study this phase in more detail, we investigated the specific heat of the organic superconductor β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ [19]. This superconductor has a modest critical temperature of 4.3 K and a corresponding low Pauli-limiting field of 9.73 T (see below). This allows for a thorough investigation of the phase diagram in readily available commercial superconducting magnets.

The specific heat of the β″ material in zero field and with 10 T applied perpendicular to the BEDT-TTF planes, i.e., along $c^*$, is shown in Fig. 5(a) on a double-logarithmic scale. Due to the strong phonon contribution to the specific heat the anomaly at $T_c$ = 4.3 K (arrow) is hardly visible in

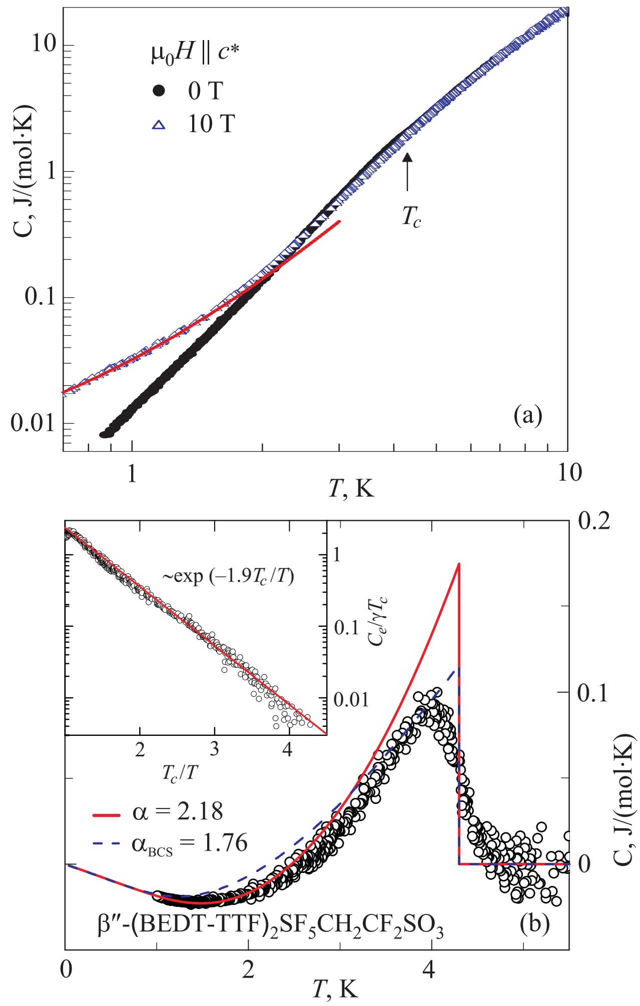


*Fig. 5*. (a) Temperature dependence of the specific heat of β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ in a double-logarithmic scale. Data in the superconducting state in zero field and in the normal state at 10 T applied perpendicular to the BEDT-TTF planes are shown. The solid line is a fit to the 10-T data below 2 K using a linear and cubic term. (b) Temperature dependence of the specific-heat difference between the superconducting and normal state. The lines show the BCS behavior for weak coupling (dashed) [30] and moderately strong coupling (solid) [31]. The inset shows the electronic part of the specific heat, $C_e$, divided by $\gamma T_c$ as function of $T_c/T$. The solid line shows the exponential vanishing of $C_e$ towards low $T$.

Fig. 5(a). Below 2 K, the data in the normal state at 10 T can be ell described by $C = \gamma T + \beta T^3$, resulting in a Sommerfeld coefficient $\gamma = 19.0(5)$ mJ/(mol·K$^2$) and a Debye contribution with $\beta = 12.8(4)$ mJ/(mol·K$^4$) (corresponding to a Debye temperature of 218(3) K). This is in excellent agreement with previous results [34]. We used the normal-state data set in 10 T applied along the $c^*$ direction to determine all the specific-heat differences, $\Delta C$, discussed in the following.

The specific-heat difference between the superconducting (0 T) and normal (10 T) state is shown in Fig. 5(b). Here, the anomaly at $T_c$ is well resolved now, although it is rather broad due to fluctuation effects. The idealized specific-heat jump at $T_c$ and the temperature dependence of $\Delta C(T)$ does not follow the weak-coupling BCS behavior [dashed line in Fig. 5(b)] [30]. However, by use of the mentioned $\alpha$ model [31] a reasonable description of the data is possible assuming a moderately strong coupling with a gap ratio $\alpha = \Delta(0)/k_B T_c = 2.18$, where $\alpha = 1.76$ in the weak-coupling limit. From that, we can extract the Pauli limiting field $\mu_0 H_P = 9.73(3)$ T.

The inset of Fig. 5(b) shows the exponential vanishing of $C_e \propto \exp(-1.9T_c/T)$ without any indication of a residual electronic contribution in the superconducting state. This fit line agrees perfectly with the $\alpha$-model description of the data shown in the main panel. Such exponential dependences have as well been found for three other organic superconductors [32,35,36] in line with reports by other groups [33,37]. These specific-heat results, therefore, prove the existence of a complete superconducting gap and are strictly against any unconventional nodal order parameter. A recent report indicating a $T^2$ dependence of the electronic specific-heat contribution at low temperatures is questionable since different Sommerfeld coefficients in the normal and superconducting state have been used to describe the data [38].

The differences between the specific heat for selected in-plane fields and the normal-state specific heat is shown in Fig. 6. By using an equal-entropy construction the field-dependent transition temperatures have been extracted (Fig. 7). Starting at $T_c = 4.3$ K for zero field, the specific-heat anomaly first shifts only slightly with increasing field. From the initial slope of the critical field, $H'_{c2} \approx 25$ T/K, we obtain the orbital critical field $\mu_0 H_{\text{orb}} = -0.7 T_c H'_{c2} \approx 75$ T. As for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, this field is much larger than $\mu_0 H_P$. Consequently, the Pauli-limiting effect becomes dominant at higher magnetic fields. This leads to the rapid decrease of the critical-field slope. Then again, below about 1.6 K (above 9.3 T), $H_{c2}$ rises steeply to values considerably larger than the Pauli limit (dashed line in Fig. 7). As for the κ-phase material, this is a clear indication for the emergence of the FFLO phase.

There are, however, also remarkable differences to the results obtained for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Figs. 2 and 3). For the κ-phase material, the anomaly from the

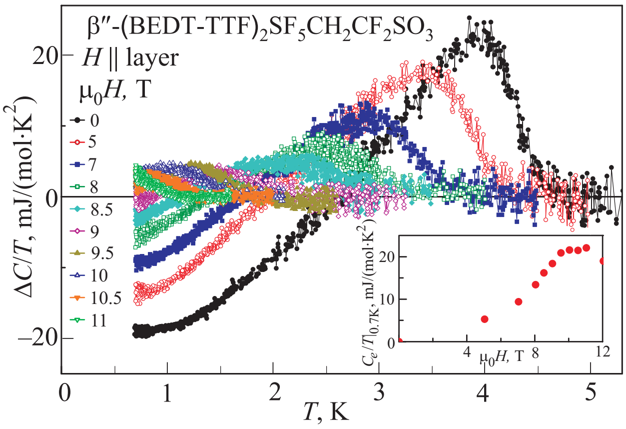


*Fig. 6.* (Color online) Difference between the specific heat for selected in-plane magnetic fields and the normal-state specific heat divided by temperature as a function of temperature for β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$. The inset shows the field-dependent evolution of the electronic part of the specific heat, $C_e$, divided by temperature.

normal to the superconducting state becomes very sharp, whereas it remains rather broad for the β″-phase superconductor. In addition, in the latter material no indication for a second phase transition is found, in sharp contrast to the clear first-order transition in the κ-phase compound.

A remarkable feature for Pauli-limited superconductors is the restoration of the electronic part of the specific heat, $C_e$, with applied magnetic field. As was analyzed by Machida and Ichioka [39], a concave shape of the field-dependent Sommerfeld coefficient, $\gamma(H)$, is expected.

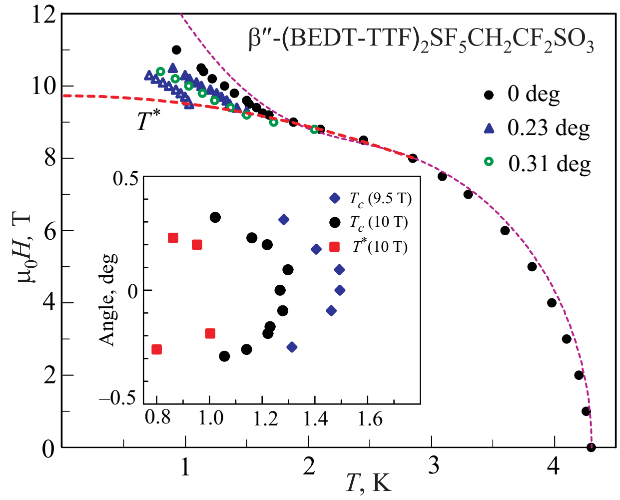


*Fig. 7.* (Color online) Superconducting phase diagram of β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ for fields aligned parallel to and by 0.23 and 0.31 deg out of the superconducting layers. The data of the second anomaly observed at 0.23 deg [Fig. 9(b)] are labeled by $T^*$ (open blue triangles). The dashed line is a rough extrapolation of the data between 2 and 3 K to the Pauli limit of 9.73 T. The dotted line represents the calculated $H_{c2}$ (see text for details). The inset shows the angular dependence of $T_c$ and $T^*$ at 9.5 and 10 T.

Since we could not determine $\gamma(H)$, i.e., $C_e/T$ extrapolated to $T = 0$ for all magnetic fields, we extracted $C_e/T$ at $T = 0.7$ K as a function of field (inset of Fig. 6). The clear concave shape of the data is obvious proving the Pauli limitation once again. A similar field-dependent $C_e/T$ appears for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ as well. The appearance of the maximum in $C_e/T$ at about 11 T beyond the normal-state $\gamma = 19.0(5)$ mJ/(mol·K$^2$) is caused by the determination of $C_e/T$ at finite temperature.

By use of the highly accurate rotation mechanism, we intentionally rotated the sample by 0.31 deg out of the in-plane field orientation. For this field alignment, we measured the temperature dependence of the specific heat close to $T_c$ for a number of different magnetic fields around the Pauli limit. The specific-heat differences are shown in Fig. 8 in comparison to the data for accurate in-plane field orientation. At 8.8 T, there is hardly any difference in the specific heat for the two orientations discernible. At higher fields, the superconducting phase transition shifts notably to lower temperatures and, concomitantly, the anomaly becomes considerably sharper for the data at 0.31 deg. This might indicate a first-order-like transition for slight out-of-plane alignments. However, we could not resolve any clear latent heat in our relaxation data. The critical temperatures extracted from the data at 0.31 deg are plotted as well in Fig. 7. Here, it becomes clear that the upturn of the $H_{c2}$ line is highly sensitive to the precise in-plane alignment of the magnetic field; the upturn at 0.31 deg is much less pronounced than for 0 deg. Indeed, when rotating the crystal at 9.5 T to out-of-plane angles of 0.4 deg, the phase transition could not be resolved any more in the available temperature window (see Fig. 2 in Ref. 19).

The dotted line in Fig. 7 is the calculated phase-transition line assuming *s*-wave superconductivity, which, however, is not an essential ingredient, and modeling the system by a stack of 2D superconducting planes with negligibly small interplane conductivity [40]. In Fig. 7, we used the phase line calculated for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [16] by simply rescaling for the different critical temperatures and Pauli-limiting fields. Very good agreement between the experimental data for 0 deg and the calculation is obtained which might become even better when the more correct electronic parameters for β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ would be used.

At 10 T, we as well measured the specific heat close to the phase transition at constant magnetic fields by rotating the sample in small steps around in-plane ($\Theta = 90$ deg) alignment. Similar as for 9.5 T, $T_c$ reduces quickly and the anomaly sharpens clearly as seen in Fig. 9(a). In addition, a second sharp anomaly, just below $T_c$, emerges when the magnetic field is rotated out of plane by a mere of ±0.2 deg. The anomalies move out of the available temperature window for slightly larger angles. The angular dependences of the observed anomalies for 9.5 (Fig. 2 in Ref. 19) and 10 T are shown in the inset of Fig. 7. The second anomaly below $T_c$ is labeled $T^*$. Thereby, as the criterion determining $T^*$, we used the maximum of the specific-heat anomaly in the $\Delta C/T$ data.

We investigated this second anomaly in more detail by measuring the specific heat for different magnetic fields close to and above the Pauli limit at the out-of-plane angle of 0.23 deg [Fig. 9(b)]. The $T^*$ anomaly appears at about 9.4 T. With increasing field, the two anomalies move almost parallel to each other towards lower temperatures keeping a distance of about 0.3 K. At 10.5 T, the $T^*$ anomaly is moved out of the accessible temperature window.

These data resemble the specific-heat anomalies observed in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Figs. 2 and 3). The temperature difference between the two anomalies there has a similar value of about 0.2 K. This indicates that for the experiment on the κ-phase material the magnetic field probably had a small out-of-plane component.

All thermodynamically determined phase-transition points are shown in Fig. 7. The hypothetical low-temperature upper critical field without an FFLO state is visualized by the dashed line. For that, we extrapolated the data between 2 and 3 K to the Pauli limit of 9.73 T at $T = 0$. For in-plane field alignment (0 deg), an upturn of the $H_{c2}$ line almost as predicted (dotted line in Fig. 7) is found. For the out-of-plane angles 0.23 and 0.31 deg, the upturn is strongly reduced. In addition, for 0.23 deg the second $T^*$ anomaly appears. For angles larger than about 0.5 deg, no upturn of $H_{c2}$, i.e., no FFLO state appears.

A puzzle is still the origin of the $T^*$ anomaly. It most likely is not related to the transition from the FFLO to the homogeneous state since that should appear at the Pauli-limiting field (dashed line in Fig. 7). It may be speculated that the $T^*$ anomaly is caused by a commensurability effect of the wavelength of the superconducting order parameter in the FFLO state and the distance of a line parallel

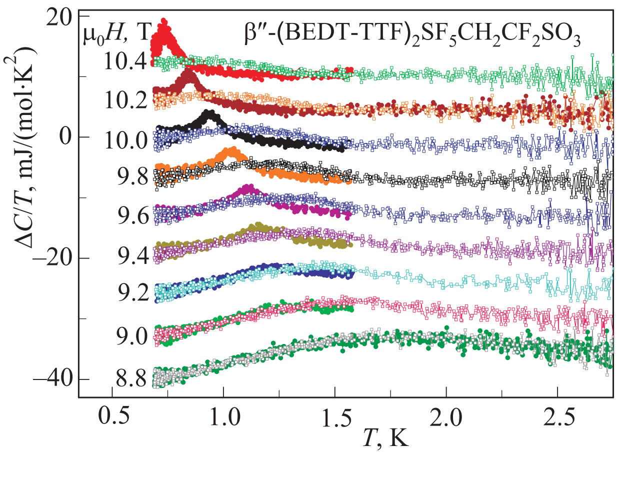


*Fig. 8.* (Color online) Specific-heat differences divided by temperature of β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ measured in different magnetic fields aligned parallel (open symbols) and 0.31 deg out of the conducting plane (closed symbols). The data are plotted offset for clarity.

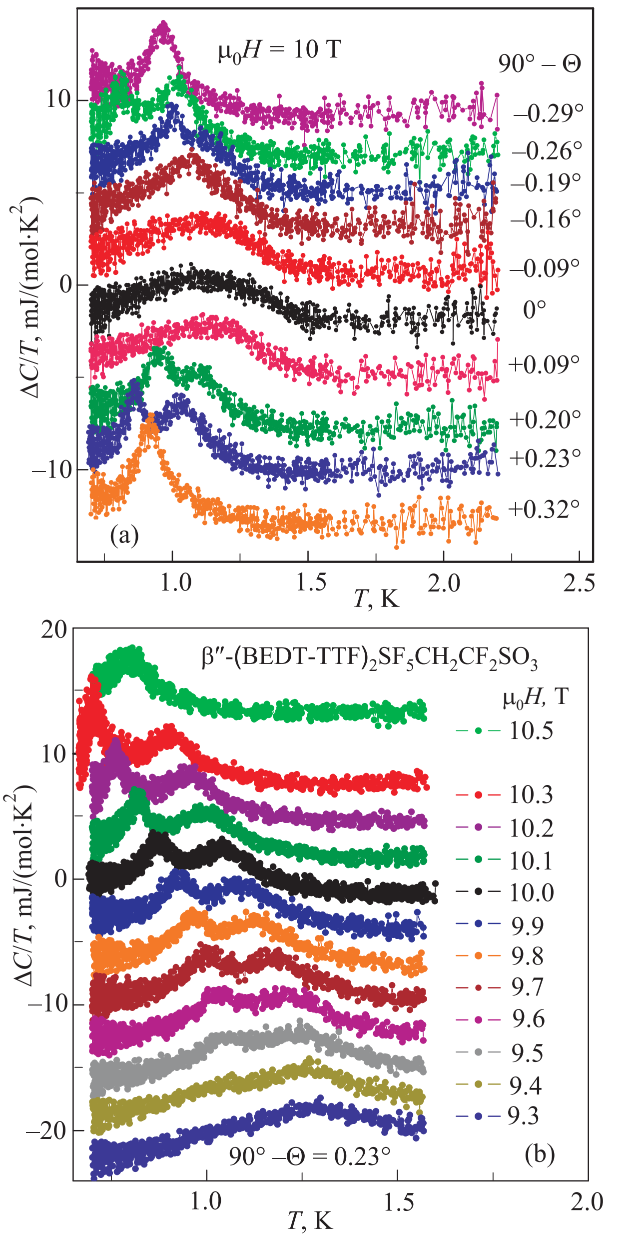


*Fig. 9.* (Color online) Specific-heat differences, $\Delta C/T$, of β″-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ measured (a) at 10 T for different angles close to in-plane field orientation and (b) in different magnetic fields aligned 0.23 deg out of the conducting plane.

to the applied field crossing two superconducting layers. By that, zeros of the order parameter could accommodate in the non-superconducting anion layers.

In the specific-heat measurements no feature at the dashed line in Fig. 7, i.e., at the expected transition from the FFLO state to the homogeneous superconducting state was observed. However, our kind of specific-heat measurements are not well suited to detect such a transition line. When sweeping the temperature at constant magnetic field, in the best case, one only would cross the transition line at a very shallow angle. Here, magnetocaloric-effect experiments, i.e., sweeping the magnetic field at constant temperature while measuring the heat tone of the sample, would be the method of choice. Such experiments are, however, rather challenging due to the small heat capacity of the samples.

### Summary

High-resolution specific-heat experiments as well as torque-magnetization data have allowed to extract reliable thermodynamic phase diagrams for two 2D organic superconductors based on BEDT-TTF. The very steep initial critical-field slopes for in-plane magnetic fields reflect the very short out-of-plane coherence lengths and very high orbital critical fields. Towards lower temperatures, the upper critical fields become Pauli limited. Reducing the temperature even further, clear upturns of the critical-field lines appear, giving evidence, for the emergence of FFLO states. The occurrence of a second phase transition inside the superconducting state in a very narrow angular range close to optimum in-plane alignment is puzzling so far. Further experiments are under way to search for a microscopic evidence of modulated FFLO order parameters.

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