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Spatially Nonuniform Superconductivity in Quasi-Two-Dimensional Organic Charge-Transfer Salts

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Abstract: In the following, a brief overview on the recently found robust experimental evidence for the existence of the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state in layered organic superconductors is given. These electronically quasi-two-dimensional (2D) clean-limit superconductors are ideally suited for observing FFLO states. Applying a magnetic field parallel to the layers suppresses orbital effects and superconductivity is observed beyond the Pauli paramagnetic limit. Both, thermodynamic as well as microscopic experimental data show the existence of an additional high-field low-temperature superconducting state having a one-dimensionally modulated order parameter.

Keywords: organic superconductors; FFLO state; specific heat; NMR

1. Introduction

In most cases, superconductivity is destroyed at high magnetic fields. For spin-singlet pairing, the highest field where this phase change can occur is at the Pauli paramagnetic limit when the Zeeman energy of the itinerant electrons becomes larger than the condensation energy [1,2]. There may, however, exist superconductivity even beyond the Pauli limit with a spatially modulated superconducting order parameter. This was predicted already in 1964, independently by Fulde and Ferrell [3] as well as Larkin and Ovchinnikov [4]. Such now-called FFLO (or LOFF) states can appear in superconductors with very large orbital critical field, B_{orb} , that is, when the usually dominant orbital pair breaking is of minor importance. Only then, superconductivity is eventually suppressed at the Pauli limit $B_P = \Delta_0 / (\sqrt{2}\mu_B)$, where μ_B is the Bohr magneton and Δ_0 the zero-temperature superconducting energy gap [1,2]. According to Gruenberg and Gunther, the Maki parameter [5], $\sqrt{2}B_{orb}/B_P$, has to be larger than 1.8 for the possible occurrence of an FFLO state [6]. Further to that, the mean free path of the charge carriers needs to be larger than the coherence length, i.e., clean-limit superconductors are needed [7–9]. For the latter point, however, some theory works suggest that FFLO phases may survive even with some disorder [10–13]. (For related experimental work see [14–16].)

When applying a magnetic field, the Fermi surface splits into two with spin-up and spin-down electrons. If this splitting is not too large, that is for fields below B_P , still the usual BCS-like pairing with opposite spin and momentum is energetically favourable (left part of Figure 1). Beyond the Pauli limit, however, pairing with finite total momentum, q , becomes the more stable ground state (right part of Figure 1), until the normal state finally is reached at a higher field beyond B_P . In the most simple of the possible FFLO states, the Cooper-pair wave function oscillates with $q \propto B$, leading to an equally oscillating Cooper-pair density also in real space (for possible more elaborated FFLO phases see [8,9]). By that, part of the superconducting volume becomes normal, namely at the wave-function zeros where the excess spins accumulate, allowing the superconducting state to survive even beyond the Pauli limit.

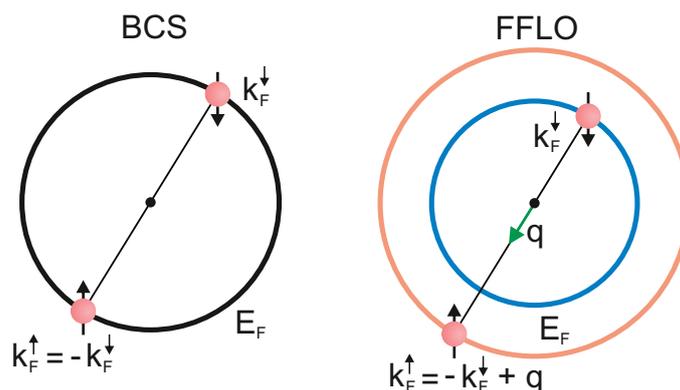


Figure 1. Schematic sketch of (left) the usual BCS pairing state with zero resulting momentum and spin and (right) the FFLO pairing state with a finite center-of-mass momentum, q . The circles represent the Fermi surfaces for spin-up and spin-down electrons.

Nonuniform FFLO states can appear only at temperatures much lower than the superconducting zero-field transition at T_c , namely below $T^* = 0.56T_c$ [5]. For temperatures between T^* and T_c , only the uniform superconducting state can exist below the upper critical field B_{c2} . Below T^* , marking a tricritical point, the FFLO phase may emerge. Here, a first-order phase transition may occur, whereas above T^* the phase transition to the normal state is second order. For three-dimensional (3D) superconductors the stability region for FFLO states is rather limited but enlarges considerably for electronically highly anisotropic materials [9]. This stability region depends on the dimensionality and becomes much larger for lower dimensions (see e.g., [8,9,17]). Indeed, Figure 2 shows the calculated phase diagram for a two-dimensional (2D) superconductor with isotropic in-plane Fermi velocity [9]. For a more general in-plane anisotropy the FFLO-phase region becomes even larger [18].

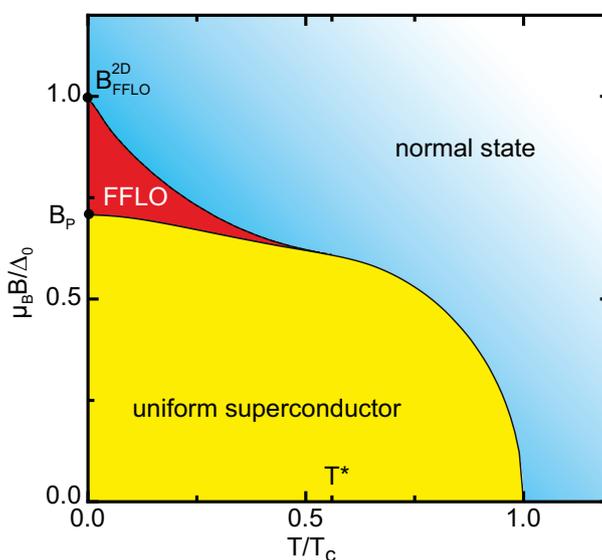


Figure 2. Calculated phase diagram of a Pauli-limited two-dimensional superconductor. Above $T^* = 0.56T_c$ only the uniform superconducting (yellow region) or, above B_{c2} , the normal state (blue) can exist. Below T^* , the FFLO state (red) may evolve up to $\mu_B B_{\text{FFLO}}^{2\text{D}} = \Delta_0$.

It is worthwhile to mention that the notion of FFLO states is of much broader importance than for superconductivity in condensed matter. These exotic states are predicted to exist in general in polarized, spin-imbalanced Fermi systems, such as ultra-cold atomic gases [19], nuclear matter, and dense quark matter [20]. Although there have been some reports on the observation of FFLO states in cold atomic gases [21,22] these results are questioned and solid evidence for FFLO states has, so far, only been

found in condensed-matter systems, such as the organic superconductors discussed in the following chapter. Other candidate materials, such as heavy-fermion and iron-based superconductors, are briefly mentioned in Section 3.

2. FFLO Evidence in Layered Organic Superconductors

For FFLO states to occur certain restrictions apply. As mentioned, the superconductor has to be strongly Pauli limited, with a Maki parameter larger than 1.8, and needs to be in the clean limit. Further, the stability region of FFLO states is rather limited in 3D but is large and experimentally more easily accessible in 2D electron systems. Prime candidate materials are, therefore, quasi-2D organic superconductors, for instance, with the molecular building blocks bisethylenedithio-tetrathiafulvalene (BEDT-TTF or ET for short) or bisethylenedithio-tetraselenafulvalene (BETS). Although there exist controversies on the nature of the superconducting state, with nuclear magnetic resonance (NMR) results evidencing node-like *d*-wave symmetries [23,24] and, on the other side, specific-heat data showing an *s*-wave-like fully gapped order parameter [25], the singlet nature of the pairing, important here, is proven by above NMR data. A more detailed discussion on the nature of the superconducting state can be found in [26]. In any case, the organic materials are well-studied, high-quality crystals with nearly ideal 2D electronic structure and strong type-II spin-singlet superconductors, usually in the clean limit with long mean free paths [26–30]. When aligning the magnetic field parallel to the highly conducting layers, orbital pair breaking is largely reduced and Pauli limitation becomes dominant.

There indeed have been a number of studies for such field orientation reporting evidence for the existence of FFLO states in these 2D organic superconductors. These claims were mainly based on transport data, such as on thermal-conductivity [31], interplane-resistance [32,33], and penetration-depth measurements [34–36]. Clear thermodynamic and microscopic evidence for a high-field FFLO phase was missing until 2011.

2.1. Thermodynamic Data and Phase Diagrams

The first thermodynamic evidence for the appearance of an FFLO state was found for the organic superconductor κ -(BEDT-TTF)₂Cu(NCS)₂ by use of specific-heat measurements [37]. Figure 3 shows the obtained data for in-plane field alignment after subtracting the phonon part of the specific heat. The latter was extracted by measuring the normal-state specific heat separately in a field of 14 T applied perpendicular to the layers. At $T_c = 9.1$ K, a clear λ -like anomaly is resolved which reduces in size and shifts to lower temperatures with increasing magnetic field. Above 21 T, however, the anomaly sharpens and a second transition appears at somewhat lower temperatures in fields up to 23 T. This latter anomaly showed a hysteresis in the specific-heat data evidencing the first-order nature of the transition [37].

This second anomaly was not observed in later work that measured the penetration depth using a tunnel-diode-oscillator technique [36], magnetic torque [38], or magnetic-field-dependent calorimetry [39]. A possibly reason for this discrepancy could have been a small misalignment of the investigated crystal in the work reported in Ref. [37]. The measurements were performed on a fixed platform in a 28-T magnet at the Grenoble High Magnetic Field Laboratory (LNCMI-Grenoble). Although the crystal was aligned in the best possible way, an out-of-plane orientation of the magnetic field on the sub-degree level cannot be excluded. Indeed, as was shown later, rotating the magnetic field by a small amount (of the order of 1 degree) immediately suppresses the FFLO state. Detailed angular-dependent specific-heat studies of another organic superconductor, β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃ discussed further below, showed that a second anomaly just below B_{c2} appears when the magnetic field is aligned by about 0.2–0.3 degree off the in-plane orientation [40,41]. This makes it rather likely that the sharp first-order transition shown in Figure 3 for κ -(BEDT-TTF)₂Cu(NCS)₂ is an artifact due to a small out-of-plane component of the magnetic field.

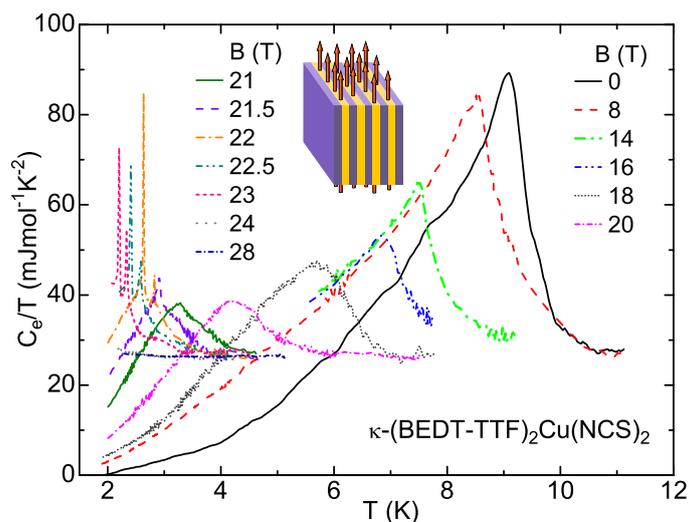


Figure 3. Electronic part of the specific heat of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$, divided by temperature, vs. temperature in parallel magnetic fields (inset) up to 28 T.

The B_{c2} data extracted from the specific heat (Figure 3) are shown as black circles in Figure 4. From the specific-heat data, it is possible to determine the Maki parameter. The orbital critical field can be estimated from the initial critical-field slope at T_c , yielding $dB_{c2}/dT \approx 20$ T/K using the data points at 0 and 8 T, and the Werthamer–Helfand–Hohenberg (WHH) extrapolation [42], $B_{orb} = 0.7T_c dB_{c2}/dT \approx 130$ T. The Pauli limit can reliably be estimated from the jump height and temperature dependence of the specific-heat anomaly resulting in the strong-coupling value $\Delta_0/k_B T_c \approx 2.4$ [43] and, finally, in $B_P = 22(1)$ T. Together with $B_{orb} \approx 130$ T, this leads to a Maki parameter of about 8.4, comfortably larger than the 1.8 required for FFLO states to occur.

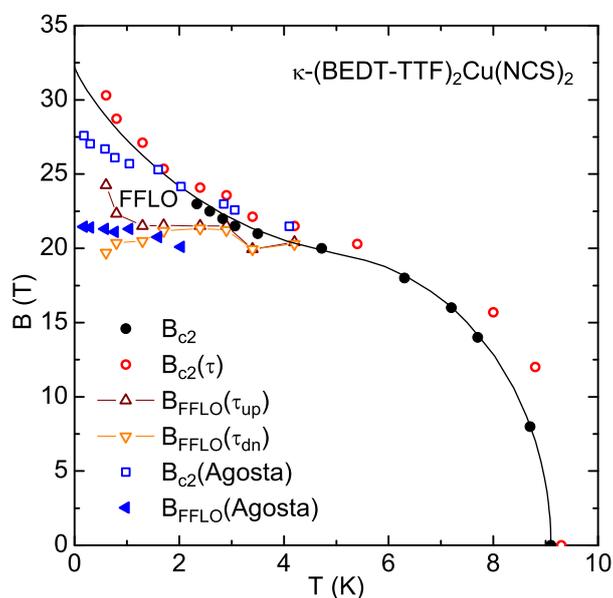


Figure 4. Superconducting phase diagram of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ as obtained from the specific-heat data shown in Figure 3 (black circles), torque, τ , data (open circles and triangles) [38], as well as data taken from the work of Agosta et al. (blue squares and triangles) [39]. The solid line is the calculated B_{c2} for an isotropic in-plane Fermi velocity.

The solid line in Figure 4 represents B_{c2} , the calculated phase transition from the normal to the superconducting state for a 2D superconductor with isotropic in-plane Fermi surface, as shown in

Figure 2. Very good agreement with the specific-heat data is found. The phase diagram in Figure 4 further includes data from magnetic-torque measurements, where a rotator made possible precise alignment of the magnetic field parallel to the layers [38]. These data overestimate somewhat the more reliable specific-heat B_{c2} values. The torque measurements, however, done with sweeping the magnetic field, allowed to resolve the hysteretic phase transition from the uniform to the FFLO superconducting state (open triangles).

In a very recent ac-specific-heat and magnetocaloric-effect measurement the phase transition from the uniform to the FFLO phase was verified thermodynamically by performing field sweeps (closed blue triangles in Figure 4) [39]. At low temperatures, the B_{c2} values in this experiment (open blue squares) lie clearly above the Pauli limit, again consistent with the existence of the FFLO phase, however, they fall somewhat below the torque data and the calculated line. Here, more work is necessary for a more reliable determination of the B_{c2} line at lowest temperature.

There exist a large number of quasi-2D organic superconductors [27,28] most of which are candidates for showing FFLO states. However, for practical reasons, T_c should be in a range, so that not too low temperatures or too high magnetic fields are needed to reach these states. Further, high-quality crystals of sufficient size are required for resolving the phase transitions in bulk experiments. These conditions are favorably fulfilled in the electronically nearly ideal 2D material β'' -(BEDT-TTF) $_2$ SF $_5$ CH $_2$ CF $_2$ SO $_3$ [44–46].

For this superconductor, specific heat [40] showed a strong upward curvature of the superconducting phase boundary above B_p , consistent with the existence of an FFLO state, even though a transition from the uniform to the FFLO phase was not directly observed. The electronic part of the specific heat divided by temperature is shown in the relevant temperature range in Figure 5. Here, 10-T specific-heat data in perpendicular field were used to subtract the phonon contribution. From an equal-entropy construction of the zero-field data, the bulk $T_c = 4.3$ K can be determined. From the idealized jump at T_c and the temperature dependence of the specific heat the zero-temperature energy gap $\Delta_0/k_B T_c = 2.18$, evidencing a moderately enhanced coupling strength, and the Pauli limit $B_p = 9.73(3)$ T is found [40]. When applying magnetic fields by use of a rotator precisely aligned parallel to the conducting layers, the specific-heat anomaly shifts to lower temperatures and remains resolvable at least up to 11 T (Figure 5). As evident from the data, superconductivity persists clearly beyond the Pauli limit.

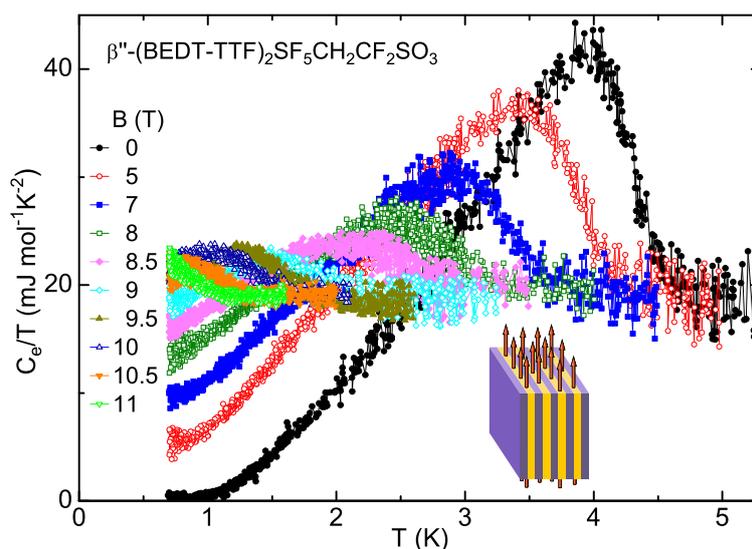


Figure 5. Temperature dependence of the electronic part of the specific heat, divided by temperature, of β'' -(BEDT-TTF) $_2$ SF $_5$ CH $_2$ CF $_2$ SO $_3$ in various parallel magnetic fields up to 11 T.

The superconducting phase diagram determined from these specific-heat measurements is shown in Figure 6. Again, the initial slope of the critical field at T_c (approximately 25 T/K) allows to estimate

$B_{orb} \approx 75$ T, that is much larger than B_p and results in a Maki parameter close to 11. The data show the typical behavior of a Pauli-limited superconductor. The very steep slope of the B_{c2} line near T_c rapidly becomes shallow at higher magnetic fields when the Pauli limit is approached. The dotted line in Figure 6 depicts the estimated B_{c2} line without the appearance of an FFLO state. Obviously, the specific-heat data lie clearly above this estimate with a changed curvature of the B_{c2} line: Strongly suggesting the emergence of an FFLO state.

The relative increase of the upper critical field, B_{c2} , at low temperatures is clearly larger than for κ -(BEDT-TTF)₂Cu(NCS)₂. The blue dashed line in Figure 6 is equivalent to the solid line shown in Figure 4, just normalized for T_c and B_p . As mentioned, this theory line was calculated assuming an isotropic in-plane Fermi velocity. Earlier investigations of the Fermi-surface topology of β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃, however, showed that the electronically 2D material has as well a pronounced anisotropy of the Fermi surface within the planes (inset of Figure 6) [47]. The experimental aspect ratio of the in-plane Fermi-surface ellipse is 9. Calculating the critical-field line for the same Fermi-velocity ratio yields the dotted line in Figure 6. The experimental data lie just between this line and the calculations for the isotropic in-plane case. For the aspect ratio 2.25, excellent agreement with the experimental data is obtained (solid line in Figure 6). In view of the rather simple mean-field theory used for the calculations, neglecting any kind of fluctuations, the description of the experimental data is superb [18,48].

It is worthwhile to mention that the phase diagram of β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃ is independent of in-plane orientation of the magnetic field, in contrast to out-of-plane rotations. When measuring the specific heat for three different in-plane field alignments, the extracted B_{c2} lines fall on top of each other within error bars [18]. This suggests negligible orbital effects [49] and a pinning of the FFLO modulation vector q at some optimum position, most probably parallel to the short axis of the Fermi-surface ellipse depicted in the inset of Figure 6.

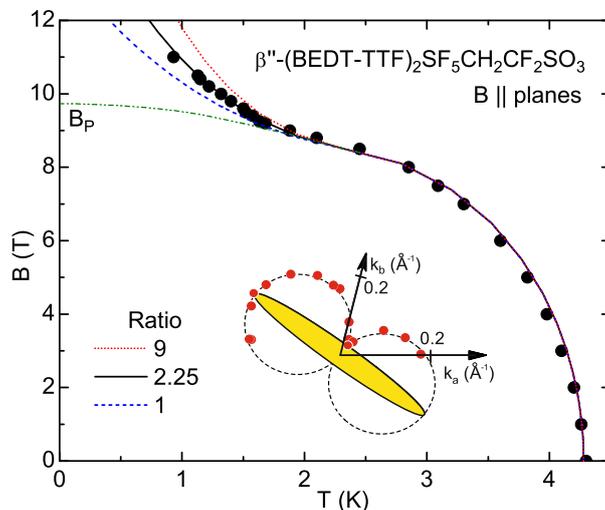


Figure 6. Phase diagram of β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃ as extracted from the data in Figure 5. Three lines show the calculated B_{c2} for different Fermi-velocity ratios of elliptical Fermi surfaces. The dotted line is a rough extrapolation of the high-temperature data towards the Pauli limit at $T = 0$, estimating the transition from the uniform to the FFLO superconductivity. The inset depicts the measured in-plane Fermi surface [47].

2.2. Microscopic Evidence

The thermodynamic measurements discussed above give strong evidence in favor for the existence of FFLO states, but they cannot supply microscopic insight into the spatially modulated order parameter. This was finally provided by sophisticated ¹³C NMR experiments. First, such measurements were performed for κ -(BEDT-TTF)₂Cu(NCS)₂ in resistive magnets of the high-field laboratories in

Tallahassee [50] and, later, in Grenoble [51]. The NMR spectra taken in Tallahassee at 0.35 K showed, up to about 21.3 T, only a gradual field-dependent broadening. Beyond this field, i.e., above the estimated Pauli limit, the spectra broaden considerably until, at about 25 T, the linewidth of the spectra is indistinguishable from that of the normal state [50]. The abrupt change of the NMR spectra around the Pauli limit is taken as evidence for a Zeeman-driven phase transition into another superconducting state, giving further evidence for the FFLO state.

In the other mentioned NMR work by the group in Grenoble, a very strong enhancement of the spin-lattice relaxation rate, T_1^{-1} , was found when going from the normal-conducting to the FFLO state as a function of temperature [51]. A similar enhancement was found when going from the uniform superconducting to the FFLO state as a function of magnetic field. This was attributed to excess low-energy density of states due to Andreev bound states formed near the nodes of the FFLO order parameter and was taken as a direct evidence for a modulated FFLO order parameter [51]. Figure 7 shows the field evolution of the NMR relaxation rate divided by temperature, $(T_1 T)^{-1}$, at various temperatures (see the Supplemental Information in Ref. [52]). At 1.1 K, similar as reported in Ref. [51], a large enhancement of $(T_1 T)^{-1}$, compared to the normal-state value, is seen when entering the FFLO state above and around the zero-temperature Pauli limit (dashed vertical line in Figure 7). However, at 0.35 K, a temperature much lower than investigated in [51], no enhancement in $(T_1 T)^{-1}$ is found. This may be explained by an Andreev bound-state energy larger than the thermal energy and a concomitant reduced influence of these states on the relaxation rate.

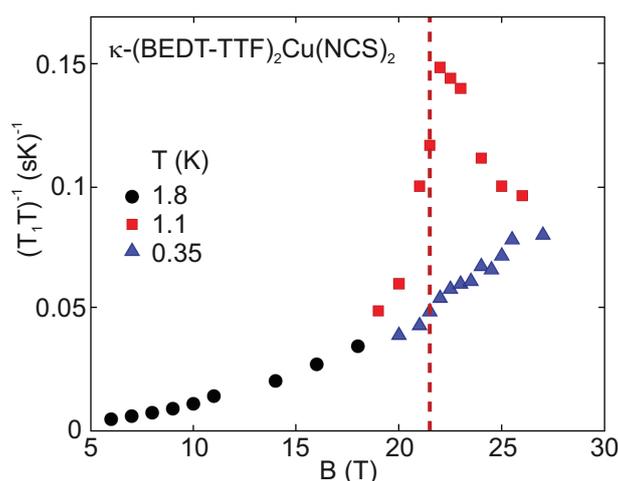


Figure 7. Field dependence of the spin-lattice relaxation rate, T_1^{-1} , divided by temperature of κ -(BEDT-TTF)₂Cu(NCS)₂. The data taken at 1.1 K exhibit an increase much beyond the normal-state value in the region where the FFLO phase occurs, whereas the effect is quenched at the lower temperature of 0.35 K. The dashed vertical line depicts the Pauli limit.

For β' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃, more detailed NMR studies are possible due to the field-temperature range easier accessible with superconducting magnets and available cryostat systems. For the measurements, as before, ¹³C isotopes were introduced on the two central carbon sites of the BEDT-TTF molecules [52]. These sites are the most sensitive to the conducting electrons in the 2D BEDT-TTF-based materials. In [52], NMR spectra were taken for a number of accurately in-plane aligned magnetic fields at 0.13 and 1.7 K. Figure 8a shows the field-dependent shift of the NMR spectra, or more precisely the first moments of the NMR spectral positions, at these temperatures. At low fields, below about 9 T in the Shubnikov phase, only a moderate increase of the shift due to orbital contributions is visible. In the normal state, above 10 T at 1.7 K, the NMR line shift is constant and caused by the hyperfine fields associated with the paramagnetic spin susceptibility. Between these two limits, the hyperfine fields at the ¹³C sites increase steeply evidencing the appearance of the nonuniform electron polarization expected for the FFLO state. These line shifts are accompanied

by considerable line broadenings of the NMR spectra (see [18,52]). The onsets of the rapid line-shift increase fits favorably to the dotted line plotted in Figure 6. The NMR data at 1.7 K indicate that the FFLO state appears at 9 and is present at 9.5 T, whereas at 0.13 K, the nonuniform superconductivity evolves above 9 T and remains up to the highest measured field of 11.9 T, in agreement with the specific-heat data.

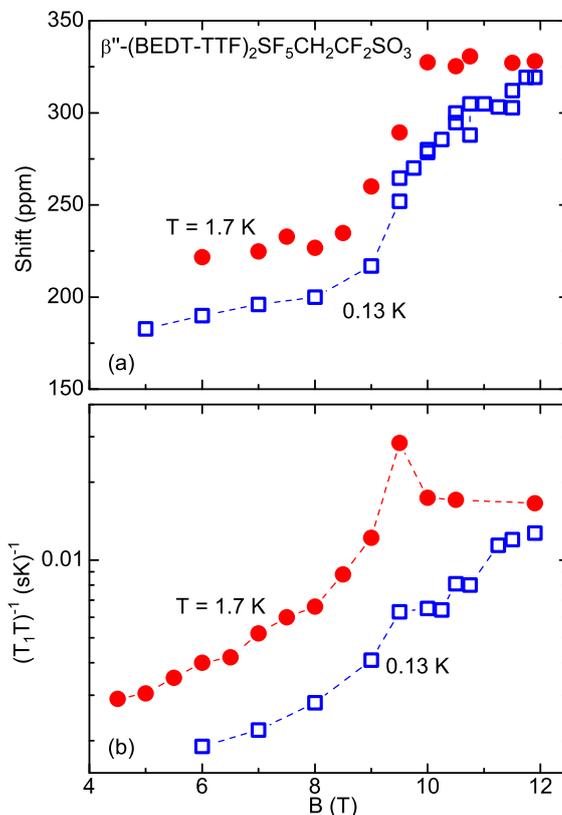


Figure 8. (a) Field dependence of the ¹³C NMR shift in β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃. (b) Spin-lattice relaxation rate divided by temperature, $(T_1T)^{-1}$, vs magnetic field. The data taken at $T = 1.7$ K show an increase at 9.3 T greater than the normal-state value, similar as visible in Figure 7 for κ -(BEDT-TTF)₂Cu(NCS)₂ and discussed in connection with the occurrence of the FFLO phase. The dashed lines connecting the data points are guides to the eye.

Complementary field-dependent data of the spin-lattice relaxation rate are shown in Figure 8b. Similar as for κ -(BEDT-TTF)₂Cu(NCS)₂ (Figure 7), a clear enhancement of $(T_1T)^{-1}$ appears at 1.7 K indicating as well the existence of the FFLO state even at this higher temperature. At 0.13 K, no enhancement in $(T_1T)^{-1}$ is detected, equally consistent for both investigated organic superconductors. As mentioned, this may be a signature of Andreev bound states in the FFLO phase. However, whether this assignment is correct needs further proof.

In the FFLO state, several types of periodic structures of the order parameter, one or two dimensional, may occur [8,9,53–55]. Accordingly, nonuniform electron-spin polarizations appear that lead to spatially oscillating local fields at the ¹³C nuclei sites and corresponding characteristic broadenings of the NMR spectra. Assuming the simplest modulation of the order parameter with a single- q (i.e., one-wavelength) sinusoidal oscillation, the NMR line broadens to a double-horn structure, in case the original NMR line is not already too wide due to other sample-inherent local-field inhomogeneities [18]. In the present case, the two inequivalent BEDT-TTF molecules per unit cell with two ¹³C each lead to four main NMR lines (ignoring dipole-dipole splitting) that can be well resolved in the normal state [52].

The blue line in Figure 9 shows a measured NMR spectrum for β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃ at 0.13 K and 10.25 T. This spectrum can be simulated using the mentioned simple 1D sinusoidal modulation of the spin polarization (green line in Figure 9). Thereby, the different orbital parts and hyperfine couplings of the four independent, Gaussian-broadened main NMR lines (red and orange lines) have been taken into account (see Ref. [52] for details). The simulated total NMR line nicely agrees with the measured data. Indeed, assuming a 2D order-parameter modulation for the NMR-line simulation fails to describe the measured data. The NMR spectra, therefore, give clear microscopic evidence for a spatially single- q 1D modulated nonuniform superconducting state, fully in line with the long-sought FFLO prediction.

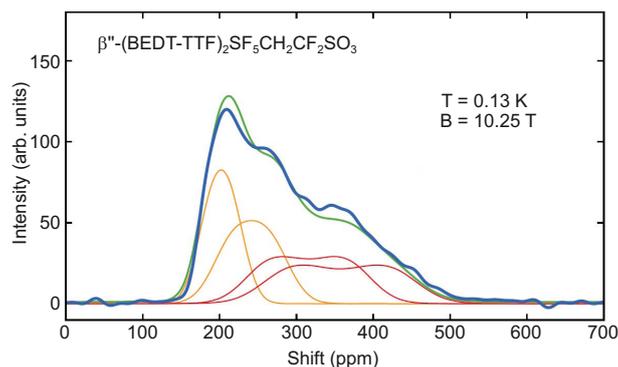


Figure 9. Experimental NMR spectrum (blue) of β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃ at 0.13 K and 10.25 T compared with that generated by assuming a 1D sinusoidal modulation of the spin polarization (green). The orange and red lines depict the four independent contributions.

3. Other FFLO Candidate Materials

The question arises as to whether FFLO states are unique for 2D organic superconductors. Indeed, the conditions to observe FFLO states are ideal in these molecular conductors, namely high crystal quality with long mean-free paths, very large orbital critical fields with corresponding large Maki parameters for in-plane aligned magnetic fields, and a rather extended stability region of the FFLO phases in the $B - T$ phase diagram due to the two dimensionality. However, other material classes as well fulfil these conditions and FFLO states are to be expected.

Heavy-fermion materials, for example, are good candidates for showing FFLO states: The orbital critical fields are often high and may exceed the Pauli limit due to the large effective masses and anisotropies favor the occurrence of nonuniform pairing. Indeed, in the heavy-fermion superconductor CeCoIn₅ clear thermodynamic and microscopic evidence for the existence of an additional superconducting state at low temperatures and high magnetic fields was found [56–58]. Initially, this state was suggested to be a realization of a FFLO state. This, however, was revised a few years later when neutron-scattering data revealed clearly the existence of incommensurate antiferromagnetic order just inside this superconducting state. Thereby, the incommensurate antiferromagnetic wave vector Q was proven to be field independent [59]. This now-called Q phase certainly is a unique and fascinating state of matter, but clearly not a realization of the originally proposed FFLO states [60–63]. Whether it is a more complicated version of such a state [64] or is of completely different origin is still the subject of intense research.

Recently, specific-heat and magnetic-torque experiments revealed compelling evidence for the existence of a superconducting high-field low-temperature state above the Pauli limit in KFe₂As₂ [65]. The anisotropic iron-pnictide superconductors, therefore, appear to be the second material class in which thermodynamic data strongly suggest the existence of an FFLO state. Further work is needed to establish this finding with additional evidence.

4. Conclusions and Outlook

More than 50 years after the theoretical work of Fulde–Ferrell and Larkin–Ovchinnikov, there is now solid evidence for the realization of FFLO states in organic superconductors. Various experiments have provided strong support for this notion. In particular, specific-heat and NMR experiments helped to determine the superconducting phase diagram and to gain microscopic insight into the nonuniform modulation of the order parameter. A 1D sinusoidally oscillating spin polarization can favorably explain the NMR spectra. Further experiments that would allow one to directly determine the modulation wave vector, such as neutron scattering or scanning tunneling microscopy, would be highly desirable. In addition, there are predictions for the existence of a quantum critical point at the transition from the FFLO to the normal state [66] for which experimental evidence would be needed. Finally, first indication for the existence of an FFLO state was found very recently in an iron-pnictide superconductor widening the possibility to further study the nature of these nonuniform superconducting states in different material classes.

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