Observation of the Fulde-Ferrell-Larkin-Ovchinnikov state in the quasi-two-dimensional organic superconductor κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ (BEDT-TTF=bis(ethylene-dithio)tetrathiafulvalene)

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LETTER TO THE EDITOR

Observation of the Fulde–Ferrell–Larkin–Ovchinnikov state in the quasi-two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (BEDT-TTF $\equiv$ bis(ethylene-dithio)tetrathiafulvalene)

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Abstract. Single crystals of the quasi-two-dimensional organic type II superconductor, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, have been studied in magnetic fields of up to 33 T and at temperatures between 0.5 K and 11 K using a compact differential susceptometer. When the magnetic field lies precisely in the quasi-two-dimensional planes of the material, there is strong evidence for a phase transition from the superconducting mixed state into a Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state, manifested as a change in the rigidity of the vortex system. The behaviour of the transition as a function of temperature is in good agreement with theoretical predictions.

There has been recent renewed interest in the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) [1] state in superconductors subjected to high magnetic fields (for a summary, see references [2, 3] and references therein). In a metal in a magnetic field, the normal quasiparticles have separate spin-up and spin-down Fermi surfaces (FSs) which are displaced due to the Zeeman energy. In the FFLO state, attractive interactions of quasiparticles with opposite spin on opposite sides of the two FSs lead to the formation of pairs with nonzero total momentum [1]; the phase of the gap function varies spatially with the total momentum, leading to an inhomogeneous superconducting state. Calculations show that in anisotropic superconductors the FFLO state might lead to an enhancement of the upper critical field B_{c2} to between 1.5 and 2.5 times the Pauli paramagnetic limit [2, 3].

Impetus was added to this theoretical work by experimental data from the heavy-fermion compounds $CeRu_2$ [4], UBe_{13} [5] and UPd_2Al_3 [6], which were initially interpreted as indications of a FFLO state. However, subsequent work cast doubt on such claims. In the case of $CeRu_2$, the feature in the magnetization ascribed to the FFLO state was shown to be due to flux-pinning mechanisms involving disorder [7]. Norman [8] also pointed out that the suggested phase boundary in UPd_2Al_3 between the superconducting state and the FFLO state does not follow the expected dependence on temperature (T).

In this letter we describe studies of the resistance and magnetic behaviour of single crystals of the quasi-two-dimensional (Q2D) organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ which indicate a phase transition within the zero-resistance state. In contrast to the case for the heavy-fermion data [4–6], the T-dependence of this transition is similar to that predicted for the phase boundaries between the superconducting and FFLO states.

To induce a FFLO state one needs a suppression of interactions involving the orbital moment (which otherwise destroy the superconductivity) [2], a FS shape conducive to nesting (but not enough to induce density-wave states [9]) and a low impurity scattering rate (clean limit) [9]. The first criterion may be achieved in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in an *exactly* in-plane magnetic field. The FS of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ consists of a warped Q2D cylinder and two quasi-one-dimensional sheets [10, 11]; in an in-plane field virtually all the quasiparticle paths on the FS are open orbits [2, 3, 11–13]. Furthermore, it is known that the FS of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is prone to nesting [14]; however, the nesting is insufficient to cause density-wave states, as shown by the measured FS topology [10, 11]. Finally, the scattering rates and band parameters of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ suggest that it is in the clean limit [15].

Single crystals ($\sim 1 \times 0.5 \times 0.1$ mm^3; mosaic spread $\lesssim 0.1^\circ$) of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ were produced using electrocrystallization [13]. Electrical contacts (resistance $\leqslant 10\ \Omega$) were made to the two large faces of each crystal (parallel to the $\boldsymbol{b}$–$\boldsymbol{c}$ (Q2D) planes) by attaching 25 μm Au wires or 12.5 μm Pt wires using graphite paint. The resistance was measured by driving an AC current (5–25 μA, 17–200 Hz) between contacts on the upper and lower surfaces; the voltage was measured on an adjacent pair of contacts using a lock-in amplifier. In this configuration, the resistance is proportional to the interplane resistivity component ρ_{zz} [16]. Care was taken to ensure that the measured resistance was neither frequency nor current dependent. Individual crystals were mounted in or on the coil of a tuned-circuit differential susceptometer (TCDS) [17]; we shall return to the function of the coil below. The coil was mounted in a cryostat which allowed it (and the sample) to be rotated to all possible orientations in the magnetic field $\boldsymbol{B}$ [13]. The orientation of the sample is defined by the polar angle θ between $\boldsymbol{B}$ and the normal to the sample's $\boldsymbol{b}$–$\boldsymbol{c}$ planes and the azimuthal angle ϕ ($\phi = 0$ is a plane of rotation of $\boldsymbol{B}$ containing $\boldsymbol{b}$ and the normal to the $\boldsymbol{b}$–$\boldsymbol{c}$ plane). The cryostat was placed in 31 and 33 T Bitter coils at NHMFL, Tallahassee.

Figure 1(a) shows the superconducting-to-normal transition measured in the resistance of a crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at $T = 4.22$ K and $\theta = 90.0^\circ$. Note that the change from zero resistance to normal-state magnetoresistance occurs over a range of about 5 T. This broadened transition region appears to be an intrinsic feature of (BEDT-TTF)-based superconductors [18]; it has been attributed to dissipation due to superconducting weak links in inhomogeneous samples [19, 20], magnetoresistance due to a lattice distortion via coupling with the quantized vortices [21] and dissipation caused by fluctuations characteristic of a d-wave superconductor [22]. All of the models mentioned regard the broadened transition region as an artefact of the superconducting state; in common with others [13, 18], we therefore choose a field B_p at which the extrapolations of the normal-state magnetoresistance and the transition region intercept (figure 1(a)) as a measure of the upper critical field, B_{c2}.

The detection of the FFLO state depends upon the very precise orientation of the crystal within the magnetic field, and figure 1(b), which displays the resistance of a κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ sample at $B = 26.5$ T and $T = 1.45$ K as a function of θ, shows how this is accomplished. In addition to the angle-dependent magnetoresistance oscillations, which allow one to determine ϕ [10], there is a very sharp dip at $\theta = \pm 90^\circ$. The dip occurs because the θ-dependence of the upper critical field is very sharply peaked at $\theta = 90^\circ$ [13, 15]; B_{c2} is less than 26.5 T except at angles very close to $\theta = 90^\circ$. At exactly 90°, B_p approaches 30.5 T at $T = 1.45$ K, but the wide superconducting-to-normal transition (see figure 1(a)) means that zero resistance is not attained in figure 1(b). This effect was used to orientate the crystal; in

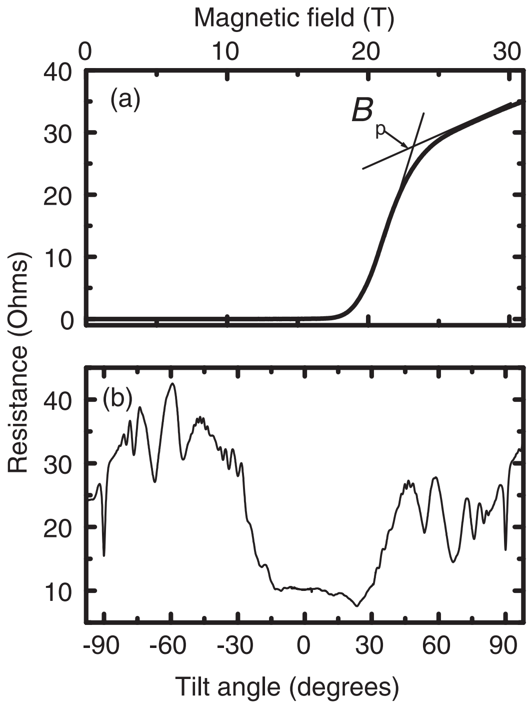

Figure 1. (a) Resistance of a single crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ as a function of magnetic field at $T = 4.22$ K and $\theta = 90.0°$. Note the broadened transition from zero resistance to normal-state magnetoresistance. The intersection of the straight lines defines the critical field B_p. (b) Resistance of a κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal at $\phi = 150°$, $B = 26.5$ T and $T = 1.45$ K, as a function of tilt angle θ. The data show behaviour typical of the normal-state magnetoresistance (e.g. angle-dependent magnetoresistance oscillations and an asymmetric rise in resistance as θ increases from 0 towards 90°) [11, 12] except very close to $\theta = 90°$, where the sharp dips indicate the onset of superconductivity.

a fixed applied field which is less than the maximum possible upper critical field, but greater than the maximum possible zero-resistance field, higher values of B_{c2} lead to lower measured resistances and vice versa.

In order to get the true in-plane critical field, we found it essential to align the crystal to better than $\pm 0.1°$ using the sharp dip at $\theta = 90°$; misalignment by a fraction of a degree lowers the measured critical field by ~1–2 T. We have also found it necessary to work with *small* crystals, as the magnetic forces have proved capable of bending larger platelets at orientations close to $\theta = 90°$, resulting in the broadening of the superconducting–normal transition. In a previous work [13], we showed that the critical fields of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, whilst varying strongly with θ, are almost completely independent of ϕ.

Having orientated the sample, one must detect the transition between the mixed state and the FFLO state. Ideally, one would use a thermodynamic measurement of a quantity such as the specific heat, or detect the change in the vortex arrangement using neutron scattering or magnetic force microscopy [23]. However, very considerable difficulties are inherent in using such techniques on a tiny single-crystal sample which is orientated to better than $\pm 0.05°$ in a magnetic field ~30 T at temperatures down to 500 mK. Moreover, conventional magnetometry is unhelpful in this context, as there is no discontinuous change in the amount of flux penetrating the sample at the transition [2, 23].

We have chosen instead to examine the *rigidity* of the vortex arrangement, which has been predicted to change on going from the mixed state to the FFLO state [23]. The sample is mounted with its Q2D planes perpendicular to the axis of the TCDS coil. When the quasistatic magnetic field is in the sample planes ($\theta = 90°$), the TCDS coil provides a small oscillating magnetic field *perpendicular* to the static field (and the vortices) which exerts a torque on the vortices. The coil in the TCDS forms part of a tank circuit operating at ~3 MHz, so changes in the rigidity of the vortices (i.e. their resistance to the torque) affect the effective 'stiffness' of the circuit and therefore shift its resonant frequency [17].

Figure 2(a) shows simultaneous measurements of the TCDS frequency and sample resistance as a function of magnetic field ($\theta = 90.00 \pm 0.05°$, $\phi = 0$). The resistive

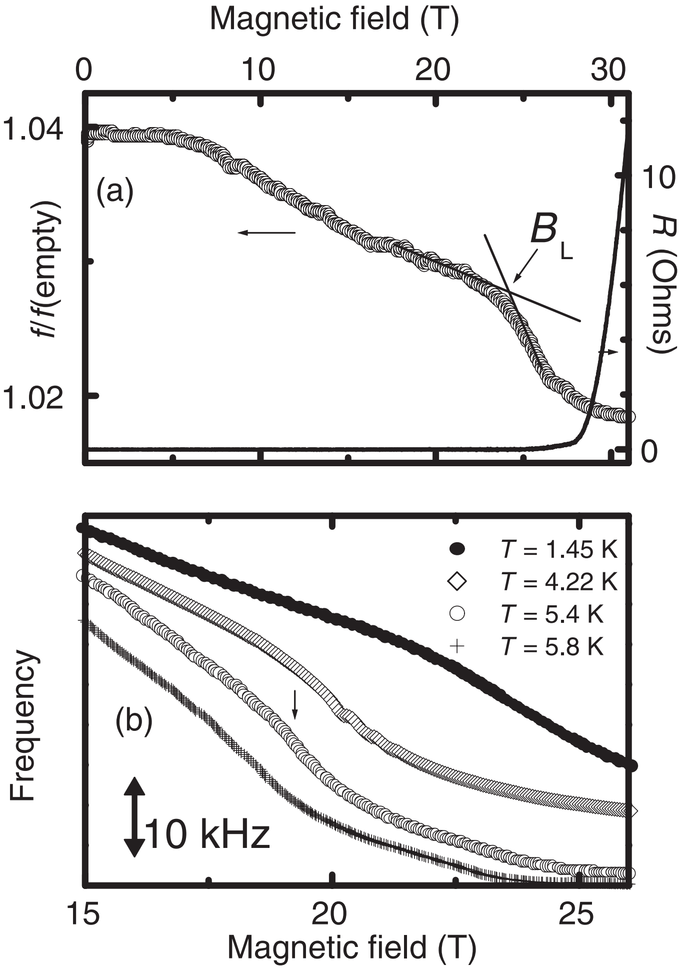

Figure 2. (a) Normalized TCDS frequency (i.e. frequency of loaded coil divided by frequency of the empty coil) (points, left axis) and sample resistance (solid curve, right axis) versus magnetic field; $T = 0.44$ K, $\theta = 90°$, $\phi = 0°$. The intersection of the two lines at the 'elbow' in the TCDS response defines the field B_L. (b) Raw TCDS frequency versus magnetic field for temperatures $T = 1.45$, 4.22, 5.4 and 5.8 K, showing the movement of B_L to higher fields as T decreases ($\phi = 0°$); the data have been vertically offset for clarity. The arrow indicates the 'elbow' in the frequency at $B_L \approx 19$ T for $T = 5.4$ K; for higher temperatures (e.g. 5.8 K) it was not observed.

onset is at ~28 T ($B_p \approx 33.5$ T). The TCDS frequency has been normalized by dividing by the field dependence of the frequency of the empty coil (caused by the magnetoresistance of the copper windings [17]); any remaining field dependence is due to the presence of the sample. Superimposed on the gentle downward trend, which results from the growing flux penetration [17], is a steeper drop, or 'elbow', starting at ~23 T. The drop occurs below the resistive onset (and well below B_p); it therefore represents a change of sample behaviour *within* the superconducting state. We label the field at which the drop occurs B_L, defining it using the intersection of the extrapolations shown in figure 2(a). As the temperature rises, B_L moves to lower magnetic fields, and figure 2(b) shows some representative data. The 'elbow' in the field dependence of the TCDS frequency is visible up to about $T \approx 5.4$ K (the arrow in figure 2(b)), but could not be detected at higher temperatures.

The fields B_p and B_L are shown as a function of T in figure 3 for a number of samples. The B_p-data are in good agreement with previous studies of B_{c2} in in-plane fields [13,24], once one makes allowance for the different methods of defining the upper critical field employed in the earlier works; the high B_p-values obtained in this work ($B_p(T = 0) \approx 35$ T) are indicative of the high quality of our crystals, their precise orientation and their freedom from strain or bending. Note that there were vestiges of the superconducting transition visible at $T \sim 10.4$ K in our samples, although zero resistance was attained only below $T \sim 9.6$ K.

Before discussing figure 3 further, we consider whether the feature at B_L might be explained by the vortex-related instabilities which have been invoked to dismiss claims for the FFLO state in heavy-fermion materials [7, 25]. Such mechanisms were also probably responsible for an earlier erroneous claim of a FFLO state in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [26]. These instabilities are describable by the 'synchronization pinning scenario' (SPS) [27] and may be identified by their history dependence [7,27] and the way in which the T-dependence of the instability field follows that of B_{c2}, falling to zero at, or just below T_c (see also reference [8]). By contrast, the T-dependence of B_L is completely different to that of B_p, and by inference, B_{c2} (figure 3).

Experiments involving a number of different samples, thermal cycling and the application of bias voltages to the samples were carried out to assess whether the SPS has a role in the feature at B_L; data from three samples subjected to different bias and cooling conditions are shown in figure 3. The measured $B_L(T)$ does not seem to be affected by thermal cycling, cooling rate, bias current and route into the superconducting state to within experimental accuracy. This is in sharp contrast to the behaviour of vortex-related (SPS) instabilities [7,27], and strongly suggests that the feature at B_L is an intrinsic effect in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. By contrast, an earlier feature which had been tentatively associated with the FFLO state [26] was found to disappear on thermal cycling.

A shift in vortex rigidity is one of the key identifying features of the FFLO state [25]. Figure 3 therefore compares B_L and B_p with the calculated FFLO phase diagram of reference [9], derived for a generic Q2D metal. The theoretical curves have been scaled using a $T = 0$ B_{c2} of 35 T and $T_c = 10$ K. Even though there are (not unexpected [19–21]) deviations of B_p from the theoretical dependence of B_{c2}, the experimental data in figure 3 bear a striking similarity to the calculated phase boundaries of reference [9]. In particular, B_L follows the phase boundary between the type-II superconducting state and the FFLO state (dotted curve) closely, extrapolating to B_p at $T \sim T^* = 0.56T_c$. The meeting of the two phase boundaries at $T^* = 0.56_c$ is a robust feature of models of the FFLO state, irrespective of dimensionality [9].

The sensitivity of the FFLO state to orbital effects has been mentioned above. Figure 4 shows the TCDS frequency versus magnetic field for several angles $\theta = 90° \pm \Delta\theta$. It is obvious that the 'elbow' at B_L, identified with the presence of the FFLO state, is only visible for

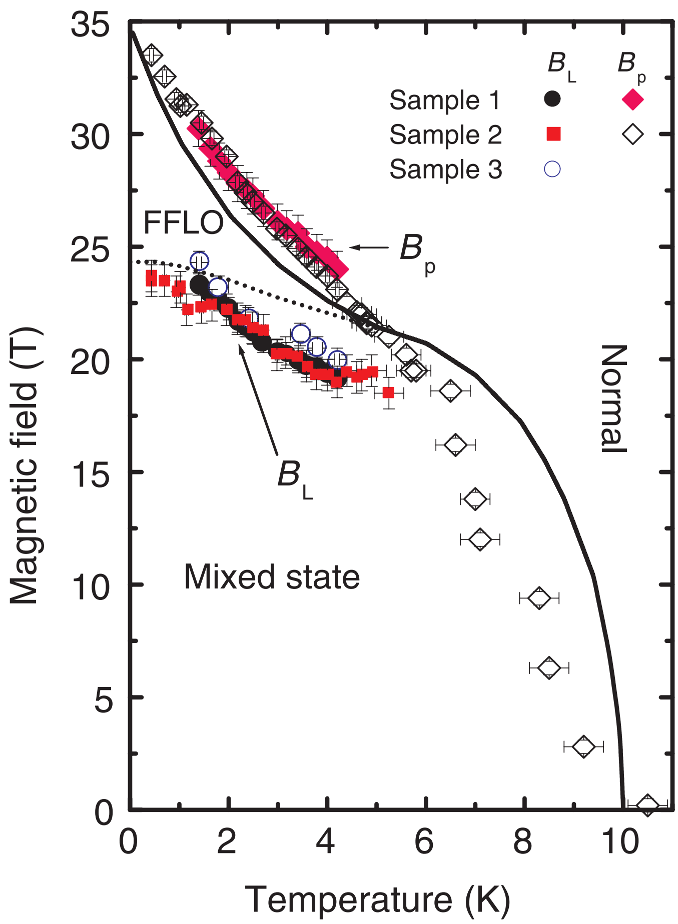

Figure 3. Temperature dependences of the fields B_L and B_p at $\theta = 90°$, $\phi = 0°$, compared with the FFLO phase diagram of reference [10]; the solid curve separates the superconducting and normal states. The boundary between the mixed state and the FFLO state is shown as a dotted line. Data for three samples under differing conditions of bias and thermal cycling are shown.

(This figure is in colour only in the electronic version, see www.iop.org)

$|\Delta\theta| \lesssim 1.5°$; this is in good agreement with the theoretical calculations of references [23, 28], which predict that the FFLO is only stable in typical organic conductors for $|\Delta\theta| \lesssim 0.3$–$2.3°$. For bigger deviations than this, a substantial number of closed orbits will be possible on the FS [11, 12], leading to suppression of the superconductivity due to orbital effects [13, 23, 24, 28]. It is notable that several groups have found it difficult to fit the angle dependence of B_{c2} close to $\theta = 90°$ (see reference [18] for a discussion and comparison of the various formulae employed); the presence of the FFLO state and the resulting increase in upper critical field may well account for this. Note that the number of closed orbits at a particular value of θ will depend on ϕ [11, 12], so the range of θ over which the FFLO state can exist may depend critically on ϕ. Only a restricted number of values of ϕ have been examined in detail thus far, and it is difficult to make more than a tentative judgment, but we remark that the region of θ over which the feature at B_L is visible appears to become narrower as ϕ increases from 0 towards 90°.

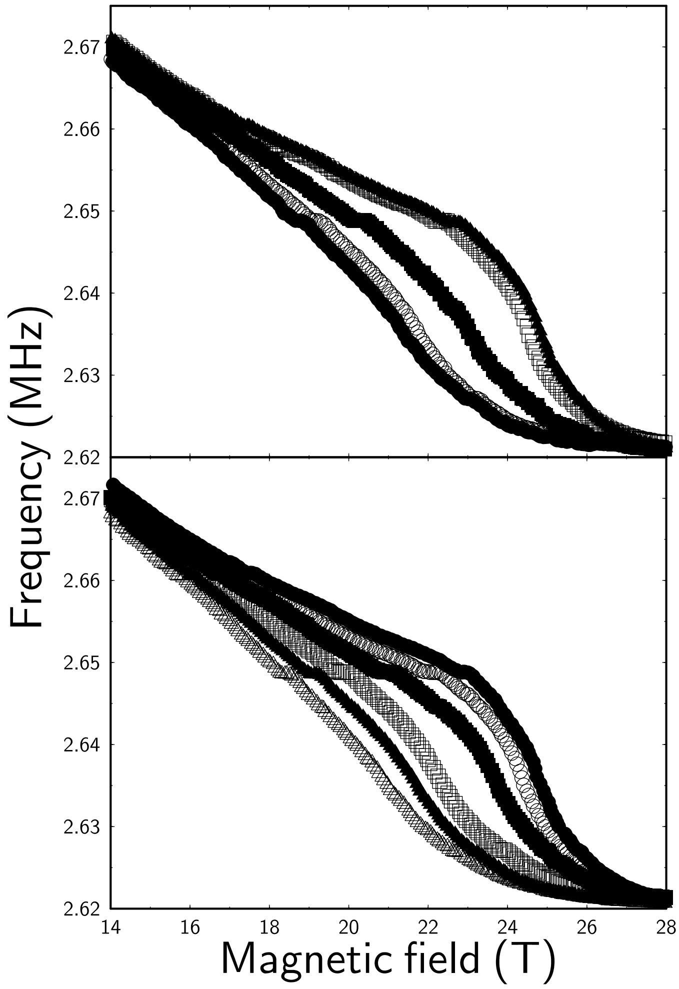

Figure 4. Raw TCDS frequency versus magnetic field for several different values of θ. Upper: black triangles, 90.15°; open squares, 89.74°; black squares, 89.17°; open circles, 88.61°; black circles, 88.33°. Lower: black circles, 90.00°; open circles, 90.35°; black squares, 90.74°; open squares, 91.12°; black triangles, 91.53°; open triangles, 91.92°. ϕ is $-45°$. The elbow at B_L disappears when the angle differs from 90° by more than about $\sim$1.5°. Note that the small step seen in all data just below 2.65 MHz is an artefact of an internal change of range in the electronic frequency meter; it is present under all experimental conditions at the same frequency.

In summary, we have measured the magnetic behaviour and resistivity of single crystals of the organic superconductor, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. When the field lies in the Q2D planes of the material, there is evidence for a phase transition into what we believe is a Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state. The phase transition is in good agreement with theoretical predictions.

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