Calorimetric Measurements of Magnetic-Field-Induced Inhomogeneous Superconductivity Above the Paramagnetic Limit

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We report the first magnetocaloric and calorimetric observations of a magnetic-field-induced phase transition within a superconducting state to the long-sought exotic Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) superconducting state, first predicted over 50 years ago. Through the combination of bulk thermodynamic calorimetric and magnetocaloric measurements in the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ as a function of temperature, magnetic field strength, and magnetic field orientation, we establish for the first time that this field-induced first-order phase transition at the paramagnetic limit $H_p$ is a transition to a higher-entropy superconducting phase, uniquely characteristic of the FFLO state. We also establish that this high-field superconducting state displays the bulk paramagnetic ordering of spin domains required of the FFLO state. These results rule out the alternate possibility of spin-density wave ordering in the high-field superconducting phase. The phase diagram determined from our measurements—including the observation of a phase transition into the FFLO phase at $H_p$—is in good agreement with recent NMR results and our own earlier tunnel-diode magnetic penetration depth experiments but is in disagreement with the only previous calorimetric report.

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Magnetic fields destroy superconductivity. In most cases, this occurs due to the formation of magnetic vortices—nonsuperconducting regions containing a magnetic field flux line shielded by circulating electrons—which increase in density as the magnetic field strength increases, ultimately displacing the superconducting phase. In the absence of magnetic vortices, the paramagnetic spin susceptibility of the electrons making up the superconducting “Cooper pairs” places another upper limit on superconductivity in magnetic fields. Because the electrons in these pairs have oppositely aligned magnetic moments (spins), the reduction in magnetic energy due to flipping the spin of an individual electron will exceed the reduction in electronic energy available from the formation of the Cooper pairs above a critical magnetic field $H_p$, known as the Clogston-Chandrasakar paramagnetic limit [1,2]. A phase transition from the superconducting to the normal metallic state is therefore expected at $H_p$.

Some 50 years ago, however, Fulde and Ferrell [3] and Larkin and Ovchinnikov [4] predicted that there might instead be a phase transition at $H_p$ to a different superconducting phase (often called the “FFLO” state) in which paramagnetic spin domains coexist with a spatially inhomogeneous superconducting phase. This FFLO state is expected to exist at fields above $H_p$ in electronically clean anisotropic superconducting materials [5–7].

The search for inhomogeneous superconductivity has spanned many years and began in low-dimensional single layers of superconducting materials [8]. The first clear calorimetric observations of a bulk-field-induced phase transition between two superconducting phases were observed in the heavy fermion compound CeCoIn$_5$ [9,10]. This transition was initially attributed to FFLO superconductivity but is now known to correspond to the onset of spin-density wave (SDW) ordering within the superconducting state [11–14]. Details of the SDW ordering observed by NMR have led to suggestions of a lower-field FFLO transition [15] and/or coupling of a FFLO phase along $\vec{H}$ to this SDW transition [15–17], but there is no clear thermodynamic evidence for these proposals [14,18,19]. The possibility remains of a more complex coupling of the SDW transition to a modified FFLO phase or pair density wave [15,19]. More recently, an analog of the FFLO state in the continuously variable parameter space of trapped atoms has caught the interest of theorists and experimentalists, stimulating a rich new area of research [20–22].

A cartoon of a FFLO state in a quasi-2D superconductor is shown in Fig. 1 for the simplest possible case: one in which the spatial modulation of the order parameter occurs in the direction of the applied magnetic field. Paramagnetic spin domains form in normal state regions existing at the nodes in the superconducting order parameter, while sheetlike coreless Josephson vortices form between the 2D superconducting layers. At least two criteria must be
satisfied to create this inhomogeneous superconducting state. The first is the suppression or exclusion of vortices as vortices normally destroy superconductivity at magnetic fields lower than the $H_P$ limit. The second criteria is that the materials need to be sufficiently electronically clean for a coherent superconducting wave function to persist over distances on the order of the FFLO wave vector (corresponding to the distance between the nodes in Fig. 1).

Quasi-2D layered organic superconductors should, therefore, be perfect candidates for forming a FFLO state: they have long electronic mean free paths, as shown by large quantum oscillations [23], and they are highly two dimensional, so the vortices can be confined to the least-conducting layers [24]. As a consequence, the vortices become Josephson coupled [25] and only weakly interact with the superconducting layers [26]. Phase diagrams suggesting the existence of a higher-field superconducting phase in $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($T_c$ of 9.5 K) and other superconductors have been established using rf penetration depth [27], tunnel diode oscillator (TDO) rf penetration depth [24,28–30], resistivity [31], thermal conductivity [32], heat capacity [33], torque magnetometry [31,34], and NMR [35,36], but the claimed location, slope, and curvature of the phase boundary between the two superconducting states varies dramatically.

In this Letter, we report results of magnetic-field-dependent heat capacity and magnetocaloric effect measurements as a function of field strength, direction, and temperature between 0.15 and 4.2 K. The heat capacity measurements allow us to discern the locations of the phase boundaries and determine the order of the transitions. The magnetocaloric effect measurements allow us to infer whether a phase is paramagnetic, diamagnetic, or fully polarized and, for first-order transitions, observe the sign of the change in entropy at the transition.

To carry out these measurements, we have made use of a recently developed rotatable calorimeter [18], designed for use in the portable dilution refrigerator and 32-mm bore high-field resistive magnets at the National High Magnetic Field Laboratory DC field facility. The calorimeter fits into a top-loading single-axis probe [37], capable of 360° rotation at base temperature, with a resolution of 0.02°. The sample is weakly thermally linked to a temperature-controlled platform inside the vacuum calorimeter, which is, in turn, weakly linked to the cryogenic mixture. When inserted into a dilution refrigerator, measurements can be made from 100 mK to 10 K during a single experiment. The heat capacity was measured as a function of the magnetic field for a series of fixed temperatures and field orientations using an ac calorimetric method [38] after corrections for the magnetic-field dependence of the resistive thermometers [39]. The sample layers were oriented parallel to the applied magnetic field to within 0.1° through the calorimetric determination of $H_{c2}(\theta)$.

Figure 2 shows the measured magnetic-field-dependent heat capacity between 15 and 32 T in the low temperature limit for an applied field parallel to the conducting layers. The results reveal the presence of a hysteretic and, therefore, first-order phase transition between two different superconducting states at $H \approx H_P = 20.7$ T, followed by a phase transition to the normal nonsuperconducting state at a temperature-dependent field $H_{c2}(T)$. In addition, we note that this transition to a high-field superconducting state is strongly angle dependent, disappearing for angles $\theta \geq 1^\circ$, as shown in Fig. 3. The rapid disappearance of the
transition at \( H_p \) as the sample is rotated away from the field; parallel orientation is as expected for an FFLO transition in a 2D superconductor such as BEDT-TTF, a phase would readily be destroyed by spin-orbit scattering once the sample is tilted enough for Abrikosov vortices to begin to penetrate the superconducting planes.

The overall increase in specific heat with an increasing applied field is expected because the magnetic field is breaking Cooper pairs (and when in the FFLO phase, creating paramagnetic spin domains), thereby increasing the number of quasiparticles that can carry entropy. The steep upward curvature to the field dependence of \( C_p(H) \) that arises at high fields within the superconducting state is characteristic of strongly Pauli-paramagnetic superconducting materials [40,41]. At higher temperatures, we observe a broad peak in the specific heat \( C_p(H) \) due to the transition from the high-field superconducting to normal state at \( H_{c2}(T) \). At lower temperatures, however, the peak diminishes in height, disappearing by 0.3 K. For consistency, we therefore take \( H_{c2}(T) \) to correspond to the inflection point between the normal and superconducting state, as shown by arrows in Fig. 2.

The superconducting phase diagram thus determined from our calorimetric measurements is shown in Fig. 4. For comparison, we also include data points from earlier NMR [35,36], rf penetration depth [24], and specific heat measurements [33]. Our \( H_{c2}(T) \) phase boundary is in agreement with previous measurements. The location and curvature of our phase boundary between the low-field superconducting states and suggested FFLO state at \( H_p \) is in good experimental agreement with our earlier tunnel diode oscillator (TDO) rf penetration measurements [24] and NMR [35,36] but in strong disagreement with previous penetration depth [27] and calorimetric [33] claims for observation of an FFLO phase boundary.

The size of the specific heat jump \( \Delta C/T \) we observe at \( H_{c2} \) is governed by the magnetic Ehrenfest relation [42] for a second-order phase boundary

\[
\frac{\Delta C}{T} = \left( \frac{\partial M}{\partial H} \right) \left( \frac{\partial H_{c2}}{\partial T} \right)^2. 
\]

For traditional superconductors, the first term in this product remains finite, but the second term—the slope of the \( H_{c2}(T) \) phase boundary—starts high, then flattens out as \( T \to 0 \) [43], leading to a decrease in \( \Delta C/T \) as \( T \to 0 \). In contrast, in the FFLO state, the slope of \( H_{c2}(T) \) remains high [44], while the first term in the product approaches zero as \( T \to 0 \) [35,45], leading to the observed change in the field position of the specific heat jump and the absence of a discernible jump by 0.3 K.

When we transform our field sweep measurements at fixed \( T \) into temperature sweeps at a fixed field, we find that in the region of overlap \( (T \geq 1.8 \text{ K}) \), the field dependence of our data is self-consistent with an earlier report by Lortz et al. [33], including the broad peak below \( H_{c2} \). The weak temperature dependence of the first-order phase line we observe at \( H_p \) means, however, that this transition would not be expected to be resolved in their temperature sweeps of \( C_p(T) \) at a constant magnetic field [33]. In contrast, their temperature sweep measurements naturally yield sharper peaks at \( H_{c2}(T) \) than field sweeps as \( T \to T_c \).
We now turn to our swept-field magnetocaloric measurements across this low-field to high-field superconducting phase boundary. Magnetocaloric measurements were made in the field parallel \( \theta = 0 \) orientation. In these measurements, as with the specific heat measurements, the sample is thermally linked to a temperature-controlled platform while the magnetic field is swept up or down, but in contrast to the specific heat measurements, no heating is provided by the sample heater. The measured temperature difference \( \Delta T \) between the sample and the platform depends on the field sweep rate \( \dot{H} \), the thermal conductance \( \kappa \) of the wires linking the sample and platform, and the temperature dependence of the magnetization \( (\partial M/\partial T)_H \) \[14\]

\[
\Delta T = -\left[ \frac{T}{\kappa} \left( \frac{\partial M}{\partial T} \right)_H + \tau \frac{d\Delta T}{dH} \right] \dot{H}, \quad (2)
\]

where \( \tau = C/\kappa \) is the sample to platform relaxation time.

For a strongly temperature-dependent paramagnetic phase \( (\partial M/\partial T < 0) \) and sufficiently high sweep rate, the up sweep will, therefore, be warmer than the down sweep. At a first-order transition, additional contributions to the magnetocaloric effect arise from (1) the release of latent heat at a first-order transition upon leaving a higher-entropy phase, (2) the absorption of latent heat upon entering a higher-entropy phase, and (3) the release of heat in both sweep directions due to irreversibility, reflecting the system’s tendency to briefly remain at the boundary in what becomes a metastable state before jumping to the lower-energy thermodynamically preferred state.

The expected change in entropy at the transition depends on the nature of the high-field phase. In the FFLO state, the superconducting gap function is inhomogeneous (being spatially modulated with a wavelength \( 2\pi/q \)); paramagnetic quasiparticles appear periodically at the nodes in the gap function \[14\]. These additional quasiparticles lead to an increase in entropy upon crossing the phase boundary at \( H_p \) for up sweeps into a FFLO phase and a corresponding decrease in entropy at \( H_p \) for down sweeps \[14,47\]. In contrast, spin-density wave ordering within a homogeneous superconducting phase leads to a reduction in the number of degrees of freedom and a corresponding decrease in entropy for the high-field phase \[14\].

As seen in Fig. 5, we find a positive difference in sample temperature \( \Delta T_{ud} = \Delta T_{up} - \Delta T_{down} \), emerging as \( H \rightarrow H_p \), consistent with the emergence of paramagnetic spins. The strong maximum in \( \Delta T_{ud} \) within the paramagnetic high-field state is possibly due to the remarkably strong temperature dependence of the electronic spin polarization (and spin relaxation rate) observed in NMR at these fields \[35,36\]. At a still higher field, \( \Delta T_{ud} \rightarrow 0 \) as \( H \rightarrow H_{c2} \) since \( \partial M/\partial T \rightarrow 0 \) due to the strong polarization of the high-field low-temperature metallic state. Superimposed on that overall positive temperature difference \( \Delta T_{ud} \), we also observe the release of latent heat (plus irreversibility heating) at the \( H_p \) boundary on the down sweep and latent heat absorption (less irreversibility heating) on the up sweep, as expected for the high-field FFLO state. Measurements on a second sample gave the same results.

This directly observed increase in entropy upon entering the high-field superconducting state implies, by the magnetic Clausius-Clapeyron equation, that the phase boundary between the two superconducting states must be at least weakly negatively temperature dependent. This result is in agreement with the FFLO phase diagram presented here in addition to theoretical \[14,43\] and experimental \[48\] expectation.

We have shown (1) that a bulk thermodynamic first-order phase transition occurs within the superconducting state of the molecular superconductor \( \kappa-\text{(BEDT-TTF)}_2\text{Cu(NCS)}_2 \), (2) that this transition occurs at the paramagnetic limit \( H_p \) for traditional superconductivity in this material, (3) that this phase transition occurs only when vortices are excluded from the 2D superconducting planes, (4) that this high-field superconducting state is paramagnetic, and (5) that this high-field superconducting state is higher entropy, even though higher magnetic fields usually decrease entropy. Taken together, these results provide the first thermodynamic case for the existence of an inhomogeneous FFLO superconducting phase with paramagnetic spin domains for \( H \geq H_p \) in highly anisotropic 2D molecular superconductors, such as \( \kappa-\text{(BEDT-TTF)}_2\text{Cu(NCS)}_2 \).

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