Nematic response of the Fulde–Ferrell–Larkin–Ovchinnikov state

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Exotic superconductivity is formed by unconventional electron pairing and exhibits various unique properties that cannot be explained by the basic theory of superconductivity. The Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state, which was proposed in 1964 [1,2], is known as an exotic superconducting state in that the electron pairs have a finite center-of-mass momentum leading to a spatially modulated pattern of superconductivity. The spatial modulation breaks the rotational symmetry of the underlying lattice, and therefore, the FFLO state is categorized as nematic superconductivity. However, the nematicity of the spatial modulation has never been experimentally verified despite numerous efforts over the years. Here, we report detection of nematicity of the FFLO state in a two-dimensional organic superconductor by high-field multidirectional ultrasound measurements. Our results demonstrate that anisotropic acoustic properties depending on the sound propagation direction appear above the Pauli limit. This nematicity reveals that the two-dimensional FFLO state has a center-of-mass momentum parallel to one of the predominant nesting vectors on the Fermi surface. Since the concept of the FFLO state is now applied to a wide range of fields [3], such as astrophysics, nuclear physics, and quantum chromodynamics, the present findings will facilitate our understanding of not only superconductivity in solids but also exotic pairings of various particles.
As theorized by Bardeen, Cooper, and Schrieffer (BCS), superconductivity occurs when itinerant electrons form pairs, so-called Cooper pairs, via an attractive force. Although many superconducting properties are well described by BCS theory, long-standing studies have found various superconductors beyond the BCS framework and many intriguing open questions. One of the exotic unconventional superconducting states, the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state, was independently theorized by Fulde & Ferrell [1] and Larkin & Ovchinnikov [2] in 1964. An up-spin electron with momentum $k$ is coupled with a down-spin electron with momentum $-k+q$ in an FFLO pairing, leading to a finite center-of-mass momentum of Cooper pairs $q \neq 0$, whereas a conventional BCS state is formed by electrons whose momenta are $k$ and $-k$, as illustrated in Fig. 1a. For BCS-type superconductivity, in which spins in paired electrons are antiparallel to each other, a magnetic field destabilizes the superconductivity through the Zeeman effect. In the field where the Zeeman splitting energy reaches the superconducting energy gap $\Delta$, known as the Pauli paramagnetic limit $H_P$, the BCS superconducting state is destroyed. In contrast, the FFLO state is stable even above $H_P$ and more favorable than the BCS state due to a gain in spin polarization energy of the nonzero $q$. This finite $q$ adds a term, $\cos(qr)$, to the order parameter of the superconductivity $\Lambda$. The modified gap function $\Delta \cos(qr)$ indicates that the order parameter spatially oscillates in real space, as shown in Fig. 1b [4-8]. The anisotropic pattern composed of the normal state and the superconductivity breaks the rotational symmetry of the lattice and endows the FFLO state with quantum nematicity depending on the $q$ vector. Since disorder stunts the formation of the spatial modulation, the FFLO state appears only in the clean limit [4]. Superconductivity is suppressed by the orbital effect caused by the Lorentz force of vortices, and therefore, the emergence of the FFLO state is allowed when the orbital effect is sufficiently weaker than the paramagnetic effect, as characterized by the Maki parameter $\alpha_M > 1.8$ [5]. Consequently, these restrictions narrow the candidate materials in the search for FFLO superconductivity [7-13] and have disturbed experimental examination of FFLO physics despite numerous theoretical studies [1-6,14-18]. In particular, spatial anisotropy, the main feature of the FFLO state, has never been experimentally observed.

The organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ (BEDT-TTF is an abbreviation of bis(ethylenedithio)tetrathiafulvalene) is known as the prime candidate for exhibiting the FFLO state and has been examined by various measurements [9,19-25]. As displayed in Fig. 1c, the layered crystal structure formed by alternating stacking of conducting and insulating layers provides a quasi-two-dimensional (quasi-2D) electronic structure. This compound undergoes a superconducting transition at ~9.5 K and changes into a $d$-wave superconducting state [26,27] with nesting vectors including $Q_1$, as shown in Fig. 1d [28,29]. Based on the existence of an additional superconducting phase with an upturn in its field-temperature superconducting phase diagram, earlier works suggest that a putative FFLO phase should appear in a high-field region when the magnetic field is parallel to the conducting plane. Indeed, the emergence of FFLO pairing is highly expected in $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ because of the large Maki parameter, relatively long mean-free path in a clean system [9], and quasi-2D Fermi surface. The heat capacity data [20] show a 1st-order thermodynamic anomaly at $H_{FFLO} \approx 21$ T. Tunnel diode oscillator (TDO) measurements [21] and torque magnetometry [22,23] also detect this
anomaly, which is smeared out by a slight field misalignment. A nuclear magnetic resonance (NMR) study [25] suggests the formation of Andreev bound states in this state, which is more likely due to a phase twist of the order parameter. These features are in good agreement with theoretical predictions for the FFLO state; however, conclusive evidence for anisotropy related to the nematicity of the spatial modulation is still missing. Employing multidirectional ultrasound propagation, we examine the plausible FFLO state of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and establish that this state certainly exhibits an anisotropic response, which is a hallmark of rotational symmetry breaking in the FFLO state.

To discuss the nematicity in the FFLO state, we arranged two pairs of transducers, generating and detecting longitudinal ultrasonic waves, on all sides of a cuboid-shaped single crystal, as shown in Fig. 1e. First, in Fig. 1f, we show the relative change in sound velocity $\Delta v/v$ and ultrasonic attenuation $\Delta a$ at 1.6 K in magnetic fields perpendicular to the conducting plane $\theta=90^\circ$. The polarization vector $\textbf{u}$ (parallel to the ultrasound propagation vector for longitudinal waves) is along the $b$-axis. At low fields, the obtained data reproduce the reported behavior [30]. As indicated by the arrow, $\Delta v/v$ exhibits an anomaly accompanied by suppression of the superconductivity at 3 T ($=H_c2(90^\circ)$). The lattice softening in most of its superconducting region in a perpendicular field (Fig. 1f) agrees with the fact that the vortex lattice melts at a much lower field ($<0.5$ T) when $H||a^*$ [31]. From the equation $H_{c2}(90^\circ)=\phi_0/(2\pi \xi_0^2)$, where $\phi_0$ is the flux quantum, an in-plane coherence length of $\xi_0 \approx 10$ nm is determined. The gradual increase in $\Delta v/v$ between 3 T and 7 T indicates that a fluctuating superconducting state without macroscopic phase coherence exists in this region, as reported [22,32]. At higher fields, both properties exhibit the acoustic de Haas–van Alphen (acoustic dHvA) oscillations mainly composed of two orbits, whose frequencies are estimated to be approximately 610 T and 3300 T. The obtained frequencies well coincide with the reported values of the $\alpha$ orbit (blue area in Fig. 1d) and the $\beta-\alpha$ orbit [33,34].

Detailed analyses and discussions are described in the Supplementary Materials. For the $\alpha$ orbit, an estimation of the mean-free path $l$ from a fit to the typical Lifshitz-Kosevich formula leads to $l \approx 90$ nm. This value sufficiently larger than $\xi_0 \approx 10$ nm indicates that the electronic system is in the clean limit, which meets one of the requirements for the emergence of the FFLO state. For the Maki parameter, the phase diagram, which is consistent with our results discussed later, indicates $\alpha_m \approx 8$ [9], which is approximately 4 times larger than required [5]. Thus, the present sample satisfies the conditions required to form the FFLO state.

Since the FFLO state appears at low temperatures when the orbital effect is sufficiently suppressed, in Fig. 2, we show the magnetic field dependence of the elastic properties ($u||b$) at 2.1 K near the parallel direction, with $\theta<1.2^\circ$. At $\theta=0^\circ$, the field dependence of $\Delta v/v$ has two dips at ~21.3 T (blue circle) and ~24.5 T (black triangle), as indicated by the symbols in Fig. 2a. These anomalies are observed as peaks in $\Delta a$ in Fig. 2b. Based on the results of previous studies [9,19-25], these characteristic fields correspond to $H_{FFLO}$ and $H_{c2}$, respectively, and the FFLO state appears between $H_{FFLO}$ and $H_{c2}$. Upon tilting the sample away from $0^\circ$, $H_{c2}$ abruptly decreases, whereas $H_{FFLO}$ shows barely any change. Since these two anomalies finally merge into one sharp anomaly at $\theta \approx 1.2^\circ$, the FFLO state is completely suppressed by this slight tilt. This result is perfectly consistent with the
report that the FFLO state at 2.0 K only exists for $\theta<1.2^\circ$ [22]. To closely examine the ultrasonic properties of the FFLO state, the datasets of $\theta=0^\circ$ and $\theta=1.2^\circ$ are enlarged in Fig. 2c and 2d. The light green area corresponds to the contribution of the FFLO state. In the superconducting state, vortices have a strong influence on elastic properties [35-37]. Typically, suppression of vortex motion results in lattice hardening. The enhancement of $\Delta v/v$ with increasing magnetic field in the lower-field region indicates compression of the flux-line lattice, which reduces the vortex dynamics. When the vortex lattice melts, $\Delta v/v$ decreases and shows a minimum. In Fig. 2c, the lattice hardening in $\Delta v/v$ indicates that the FFLO state reinforces pinning of the flux lines. For $\Delta a$ in Fig. 2d, attenuation of the sound wave propagation by FFLO formation is natural because of the spatially inhomogeneity. Near $H_{c2}$, a flux flow gives excess attenuation appearing as a peak in $\Delta a$ [35,36], and therefore, the overlap of the two peaks at $H_{FFLO}$ and $H_{c2}$ produces the observed behavior above $H_{FFLO}$. Note that the difference below $H_{c2}$ (gray area) originates from perpendicular components of the applied fields. With increasing $\theta$, the perpendicular component, which penetrates the conducting plane, induces lattice softening and increases the number of scattering centers, leading to a larger $\Delta a$.

In Fig. 3a and 3b, we show the $H_{FFLO}$ and $H_{c2}$ of the detected anomalies at 2.1 K and 6.3 K as an $H$ vs. $\theta$ plot. The cusp-like angular dependence of $H_{c2}$ at 6.3 K can be described by the Tinkham 2D model [38]. This anisotropic behavior and the values of $H_{c2}$ agree well with the results reported in Ref. [21,23,31]. However, this model cannot reproduce $H_{c2}$ at 2.1 K because of the emergence of the FFLO state. The $H_{c2}$ determined by the resistivity (see Supplementary Materials) at 1.6 K also exhibits similar behavior, as shown by the pink triangles (right axis) in Fig. 3a. The abrupt suppression of $H_{c2}$ when moving away from $\theta=0^\circ$ means that the FFLO state is easily destabilized even by the small orbital effect induced by the slight tilt. This fragility to the orbital effect is also a well-known characteristic peculiar to the FFLO state [5,17,39]. In contrast, the angle dependence of $H_{FFLO}$ is not significant. As $H_{FFLO}$ corresponds to $H_B$ determined by the paramagnetic effect, the angle-insensitive behavior is suggestive of isotropic Pauli paramagnetism. This fact is also consistent with the almost isotropic $g$-factor in the organic compounds composed of light atoms with weak spin-orbit coupling.

In Fig. 3c, we organize the present results as the obtained $H$-$T$ superconducting phase diagram at $\theta=0^\circ$. For comparison, we additionally show the data of earlier reports (unfilled symbols) [9,19-25]. Our results are in good agreement with the reported data. In addition, the temperature dependence of the reduced superconducting gap amplitude $\Delta(T)/\Delta(0\ K)$ calculated by the basic BCS theory is also shown on the right axis. Since the $\alpha$ model, a simple extension of the BCS theory, well describes the thermal variation in $|\Delta(T)/\Delta(0\ K)|$ [40], the behavior roughly reconciling with the temperature dependence of $H_f$ for the homogeneous superconducting state is reasonable. This consistency also suggests that the BCS-type superconductivity is suppressed at $H_f$ and that the FFLO state appears above $H_f$ instead.

Apart from the phase diagram, examination in further detail of the pinning effect enhanced in the FFLO state is interesting. In Fig. 4a, we compare the field dependence of $\Delta v/v$ ($\theta=0^\circ$) taken for the parallel ($u|c$) and perpendicular ($u||b$) configurations under the same conditions. There is a small difference depending on the sound wave direction below $H_{FFLO}$ due to the anisotropy of the flux-line lattice. The difference becomes significantly larger in the FFLO region $H_{FFLO}<H<H_{c2}$ (green area).
This behavior is absent when $\theta=90^\circ$, as shown in Fig. 4b. The anisotropic response indicates breaking of the rotational symmetry, which is clear evidence for the nematicity of the FFLO state. The augmentation of the pinning effect only in the $u\parallel b$ configuration suggests that the flux lines are trapped in the spatially modulated pattern along the $b$-axis—the $q$ vector is oriented along the $b$-axis, perpendicular to the field direction in the present setup. Our out-of-plane electrical resistivity data (see Supplementary Materials) agree with the direction of the $q$ vector because of observation of the commensurability effect of the Josephson vortices inside the insulating layers [39,41,42] when $H\parallel c$.

The present results, including nematicity, demonstrate the emergence of the FFLO state above $H_P$. However, we need to consider the question of why the orientation of the $q$ vector is mainly along the $b$-axis, perpendicular to the field direction in the present configuration. In the case of isotropic 3D superconductors, the $q$ vector always points in the field direction [1,2]. Since the $q$ vector can be oriented in any direction in 3D, the nematicity can be treated in the framework of the Heisenberg model. According to this framework, in the present measurement with $H\parallel c$, the $q$ vector should be parallel to the $c$-axis, not the $b$-axis. However, the present superconductivity is described by the 2D model (Fig. 3b). For 2D superconductors, the better nesting vectors on the Fermi surface make the FFLO state more stable, and the anisotropy of the Fermi surface often locks the direction of the $q$ vector according to the predominant nesting vectors [42,43]. Namely, the FFLO state in the anisotropic 2D superconductor is expected to have Ising nematicity. Indeed, theoretical studies [28,29] suggest that the nesting vector $Q_1$, parallel to the $k_B$-axis (green arrow in Fig. 1d), always strongly relates to the Cooper pairing in $\kappa$-type organic salts regardless of the emergent pairing symmetry. Thus, Ising nematicity with the $q$ vector locked parallel to the $b$-axis in the FFLO state should be reasonable for the present 2D superconductor. This result suggests that the direction of the nematicity and the model describing the nematicity, such as Ising, XY, and Heisenberg, can be controlled by changing the shape of the Fermi surface and dimensionality.

The present multidirectional ultrasound measurements demonstrate the nematicity of the FFLO state induced by the spatial modulation of the order parameter through the vortex-pinning effect. Since $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ is a 2D clean superconductor, the FFLO state shows Ising nematicity originating from the anisotropic Fermi surface. Further studies of other FFLO candidates with various features, such as 3D and slight dirtiness, will facilitate a deeper understanding of the FFLO state.

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[1] P. Fulde and R. A. Ferrell, Superconductivity in a Strong Spin-Exchange Field. *Phys. Rev.* **35**, A550 (1964).

[2] A. I. Larkin and Y. N. Ovchinnikov, Nonuniform state of superconductors. *Zh. Eksp. Teor. Fiz.* **47**, 1136 (1964).

[3] R. Casalbuoni and G. Nardulli, Inhomogeneous superconductivity in condensed matter and QCD. *Rev. Mod. Phys.* **76**, 263 (2004).

[4] L. G. Aslamazov, Influence of Impurities on the Existence of an Inhomogeneous State in a Ferromagnetic Superconductor. *Sov. Phys. JETP* **28**, 773 (1969).

[5] L. W. Gruenberg and L. Gunther, Fulde-Ferrell Effect in Type-II Superconductors. *Phys. Rev. Lett.* **16**, 996 (1966).

[6] Y. Matsuda and H. Shimahara, Fulde–Ferrell–Larkin–Ovchinnikov State in Heavy Fermion Superconductors. *J. Phys. Soc. Jpn.* **76**, 051005 (2007).

[7] J. Wosnitza, FFLO States in Layered Organic Superconductors. *Ann. Phys.* **530**, 1700282 (2018).

[8] C. C. Agosta, Inhomogeneous Superconductivity in Organic and Related Superconductors. *Crystals* **8**, 285 (2018).

[9] R. Lortz, et al. Calorimetric Evidence for a Fulde-Ferrell-Larkin-Ovchinnikov Superconducting State in the Layered Organic Superconductor κ-(BEDT-TTF)₂Cu(NCS)$_₂$. *Phys. Rev. Lett.* **99**, 187002 (2007).

[10] H. Radovan, et al. Magnetic enhancement of superconductivity from electron spin domains. *Nature* **425**, 51 (2003).

[11] C.-w. Cho, et al. R. Thermodynamic Evidence for the Fulde-Ferrell-Larkin-Ovchinnikov State in the KFe$_2$As$_2$ Superconductor. *Phys. Rev. Lett.* **119**, 217002 (2017).

[12] S. Kitagawa, et al. Evidence for the Presence of the Fulde-Ferrell-Larkin-Ovchinnikov State in CeCu$_2$Si$_2$ Revealed Using $^{63}$Cu NMR. *Phys. Rev. Lett.* **121**, 157004 (2018).

[13] S. Kasahara, et al. Evidence for an Fulde-Ferrell-Larkin-Ovchinnikov State with Segmented Vortices in the BCS-BEC-Crossover Superconductor FeSe. *Phys. Rev. Lett.* **124**, 107001 (2020).

[14] A. Buzdin and M. L. Kulic, Unusual behavior of superconductors near the tricritical Lifshitz point. *J. Low Temp. Phys.* **54**, 203 (1984).

[15] H. Shimahara and D. Rainer, Crossover from Vortex States to the Fulde-Ferrell- Larkin-Ovchinnikov State in Two-Dimensional s- and d-Wave Superconductors. *J. Phys. Soc. Jpn.* **66**, 3591 (1997).

[16] H. Shimahara, Fulde–Ferrell–Larkin–Ovchinnikov State and Field-Induced Superconductivity in an Organic Superconductor. *J. Phys. Soc. Jpn.* **71**, 1644 (2002).

[17] U. Klein, Two-dimensional superconductor in a tilted magnetic field: States with finite Cooper-pair momentum. *Phys. Rev. B* **69**, 134518 (2004).

[18] T. Mizushima, K. Machida, and M. Ichioda, Topological Structure of a Vortex in the Fulde-Ferrell-Larkin-Ovchinnikov State. *Phys. Rev. Lett.* **95**, 117003 (2005).

[19] J. Singleton, et al. Observation of the Fulde-Ferrell-Larkin-Ovchinnikov state in the quasi-two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (BEDT-TTF=bis(ethylene-dithio)tetrathiafulvalene). *J. Phys.: Condens. Matter* **12**, 641 (2000).

[20] C. C. Agosta, et al. Calorimetric Measurements of Magnetic-Field-Induced Inhomogeneous Superconductivity Above the Paramagnetic Limit. *Phys. Rev. Lett.* **118**, 267001 (2017).

[21] C. C. Agosta, et al. Experimental and semiempirical method to determine the Pauli-limiting field in quasi-two-dimensional superconductors as applied to κ-(BEDT-TTF)$_2$Cu(NCS)$_2$: Strong evidence of a FFLO state. *Phys. Rev. B* **85**, 214514 (2012).

[22] B. Bergk, et al. Magnetic torque evidence for the Fulde-Ferrell-Larkin-Ovchinnikov state in the layered organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. *Phys. Rev. B* **83**, 064506 (2011).
[23] S. Tsuchiya, et al. Phase Boundary in a Superconducting State of \( \kappa \)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\): Evidence of the Fulde–Ferrell–Larkin–Ovchinnikov Phase. *J. Phys. Soc. Jpn.* **84**, 034703 (2015).

[24] J. A. Wright, et al. Zeeman-Driven Phase Transition within the Superconducting State of \( \kappa \)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\). *Phys. Rev. Lett.* **107**, 087002 (2011).

[25] H. Mayaffre, et al. Evidence of Andreev bound states as a hallmark of the FFLO phase in \( \kappa \)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\). *Nat. Phys.* **10**, 928 (2014).

[26] K. Izawa, et al. Superconducting Gap Structure of \( \kappa \)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\) Probed by Thermal Conductivity Tensor. *Phys. Rev. Lett.* **88**, 027002 (2001).

[27] S. Imajo, et al. Superconducting Phase Diagram of the Organic Superconductor \( \kappa \)-(BEDT-TTF)\(_2\)Cu[N(CN)\(_2\)]Br above 30 T. *J. Phys. Soc. Jpn.* **87**, 123704 (2018).

[28] D. Guterding, et al. Near-degeneracy of extended \( s^\pm d_{x^2-y^2} \) and \( d_{xy} \) order parameters in quasi-two-dimensional organic superconductors. *Phys. Rev. B* **94**, 024515 (2016).

[29] K. Zantout, et al. Superconductivity in correlated BEDT-TTF molecular conductors: Critical temperatures and gap symmetries. *Phys. Rev. B* **97**, 014530 (2018).

[30] M. Yoshizawa, et al. Sound velocity change at superconducting transition in \( \kappa \)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\). *Solid State Commun.* **89**, 701 (1994).

[31] S. Uji, et al. Quantum vortex melting and phase diagram in the layered organic superconductor \( \kappa \)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\). *Phys. Rev. B* **97**, 024505 (2018).

[32] M.-S. Nam, et al. Fluctuating superconductivity in organic molecular metals close to the Mott transition. *Nature* **449**, 584 (2007).

[33] S. Uji, et al. Effective mass and combination frequencies of de Haas-van Alphen oscillations in \( \kappa \)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\). *Synth. Met.* **85**, 1573, (1997).

[34] V. M. Gvozdikov, et al. de Haas–van Alphen and chemical potential oscillations in the magnetic-breakdown quasi-two-dimensional organic conductor \( \kappa \)-(BEDT-TTF)\(_2\)Cu(NCS)\(_2\). *Phys. Rev. B* **70**, 245114 (2004).

[35] Y. Shapira, and L. J. Neuringer, Magnetoacoustic Attenuation in High-Field Superconductors. *Phys. Rev.* **154**, 375 (1967).

[36] J. Pankert, et al. Ultrasonic Attenuation by the Vortex Lattice of High-\( T \) Superconductors. *Phys. Rev. Lett.* **65**, 3052, (1990).

[37] T. Watanabe, et al. High-field state of the flux-line lattice in the unconventional superconductor CeCoIn\(_5\). *Phys. Rev. B* **70**, 020506(R) (2004).

[38] M. Tinkham, M. Effect of Fluxoid Quantization on Transitions of Superconducting Films. *Phys. Rev.* **129**, 2413 (1963).

[39] S. Uji, et al. Vortex Dynamics and the Fulde-Ferrell-Larkin-Ovchinnikov State in a Magnetic-Field-Induced Organic Superconductor. *Phys. Rev. Lett.* **97**, 157001 (2006).

[40] O. J. Taylor, et al. Specific-Heat Measurements of the Gap Structure of the Organic Superconductors \( \kappa \)-(ET)\(_2\)Cu[N(CN)\(_2\)]Br and \( \kappa \)-(ET)\(_2\)Cu(NCS)\(_2\). *Phys. Rev. Lett.* **99**, 057001 (2007).

[41] L. Bulaevskii, A. Buzdin, and M. Maley, Intrinsic Pinning of Vortices as a Direct Probe of the Nonuniform Larkin-Ovchinnikov-Fulde-Ferrell State in Layered Superconductors. *Phys. Rev. Lett.* **90**, 067003 (2003).

[42] S. Sugiura, et al. Josephson vortex dynamics and Fulde-Ferrell-Larkin-Ovchinnikov superconductivity in the layered organic superconductor \( \beta^0 \)-(BEDT-TTF)\(_2\)SF\(_2\)CH\(_2\)CF\(_2\)SO\(_3\)). *Phys. Rev. B* **100**, 014515 (2019).
Figure 1  Schematics of the FFLO state, crystal structure, and experimental setup.  

**a** Schematics of BCS pairing and FFLO pairing. $k$ and $\sigma$ represent the momentum and spin of the electrons. **b** Spatial modulation of order parameter $\Delta(r)$ in the FFLO state (dashed curve). The normal state (blue) appears at nodes of the superconducting (SC) order parameter $\Delta \cos(qr)$. **c** Quasi-2D crystal structure of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$. **d** Fermi surface of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$. The solid and dashed black lines are the folded and unfolded Brillouin zones, respectively. The blue and red curves show the Fermi surfaces, and the green arrow indicates the most predominant nesting vector. **e** Experimental setup for the multidirectional ultrasound measurements using longitudinal sound waves. The magnetic field was rotated from the $c$-axis to the $a^*$-axis. $\theta$ is the polar angle from the $c$-axis. **f** Relative change in the sound velocity $\Delta v/v$ (red, left axis) and attenuation coefficient $\Delta \alpha$ (blue, right axis) at $T=1.6$ K and $\theta=90^\circ$ as a function of magnetic field. The black arrow indicates the upper critical field of the superconductivity $H_{c2}$.  

\[ \Delta \alpha = \Delta \alpha(10^3 \text{ dB/m}) \]  

\[ \Delta v/v = \Delta v/v(10^{-3}) \]
Figure 2  Low-temperature and high-field ultrasonic properties when $\theta \sim 0^\circ$.

**a, b** Magnetic field dependence of $\Delta v/v$ (a) and $\Delta \alpha$ (b) at 2.1 K. The blue and black symbols indicate the dips in $\Delta v/v$ and the peaks in $\Delta \alpha$. **c, d** Enlarged plot of the datasets at $0^\circ$ and $1.2^\circ$. The green area indicates the difference between the $0^\circ$ and $1.2^\circ$ data, which reflects the contribution of the FFLO state.
Figure 3  

$H$-$\theta$ and $H$-$T$ superconducting phase diagrams.  

a, b $H_{c2}$ (black triangles) as a function of the absolute value of the field angle $|\theta|$ at (a) 2.1 K and (b) 6.3 K. The blue circles in (a) indicate $H_{\text{FFLO}}$. The green and red areas represent the regions for the FFLO phase and BCS phase, respectively. The dotted curves in (a) and (b) are fits to the Tinkham 2D model.  

c $H$-$T$ superconducting phase diagram obtained in this work (filled symbols) and previous reports (blank symbols) [9,20,21,25]. The dashed curve (right axis) is the temperature dependence of the reduced superconducting gap amplitude $\Delta(T)/\Delta(0 \text{ K})$ calculated by the basic BCS theory.
Figure 4  Nematicity in the FFLO state.

\(a,b\)  \(\Delta v/v\) at 1.6 K for \(u||b\) (pink) and \(u||c\) (light blue) in magnetic fields (a) parallel (\(\theta=0^\circ\)) and (b) perpendicular (\(\theta=90^\circ\)) to the 2D conducting plane. Significant nematic behavior, namely, direction dependence of the longitudinal sound wave propagation, is observed only in the FFLO state (green area), whereas the direction dependence of \(\Delta v/v\) in the BCS state and the normal state is not large. The inset schematics show the electronic states (red: superconductivity, blue: normal state), directions of applied fields (light green arrows), and sound polarization vectors (striped arrows).
Sample preparation.
Single crystals of κ-(BEDT-TTF)₂Cu(NCS)₂ measured in this study were synthesized by typical electrochemical process and crystallized as black hexagonally-shaped blocks. The shape of the crystals used in the ultrasonic measurements was modified as described in the Supplementary Materials.

Ultrasonic measurements.
Using the typical pulse-echo methods, the ultrasonic properties were measured. Longitudinal ultrasound waves, whose frequencies were in the range of 37-39 MHz, were generated and detected by LiNbO₃ piezoelectric transducers (90 µm thickness) attached on side surfaces of the crystals. Further details of the setup are presented in the Supplementary Materials.
Supplementary Materials

1. Details of our multidirectional ultrasound measurements

In this study, we implemented multidirectional ultrasound measurements using four LiNbO$_3$ piezoelectric transducers. Figure S1a shows a photo of the sample setup for the measurements. The sample shape is indicated by the red dotted line, and the transducers are highlighted in blue. The gold wires in the picture are the electrical wiring to the transducers to apply and detect sound waves. Rotating magnetic fields are applied in the $a^*\cdot c$ plane. As shown in Fig. S1b, the crystal used in this study was sliced and formed into a square shape to attach the transducers with epoxy resin because typical crystals of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ were obtained in a hexagonal shape. Longitudinal sound waves were generated from one of the transducers and detected from another. The sound velocity $v$ is approximately 2.4 km/s at 10 K and has no significant in-plane anisotropy. Figure S1c shows the temperature dependence of $\Delta v/v$ for the superconducting state (0 T) and the normal state (5 T, applied perpendicular to the conducting plane) of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$. The data are well consistent with the reported data [S1]. Notably, measuring the temperature dependence with the above pulsed-field ultrasound measurement setup was difficult due to the temperature control, and therefore, the temperature dependence was measured using another probe and another crystal.

![Fig. S1](image-url) **a** Photo of the sample setup with piezoelectric transducers (blue). The red dotted curve emphasizes the outline of the sample. Rotating magnetic fields are applied in the $a^*-c$ plane. **b** Schematic illustration of the treatment for attaching the transducers to the crystal. **c** Temperature dependence of $\Delta v/v$ at 0 T and 5 T when $u||b$ and $H||a^*$.
2. Acoustic de Haas oscillations

Figure S2a shows the oscillatory part of $\Delta\alpha$, $\Delta\alpha_{\text{osc}}$, originating from the acoustic de Haas oscillation at 1.6 K. The black curve is a fit to the Lifshitz-Kosevich formula with the frequencies of the $\alpha$ orbit $F_\alpha=610$ T and the $\beta-\alpha$ orbit $F_{\beta-\alpha}=3300$ T. The Fourier spectrum of $\Delta\alpha_{\text{osc}}$ is shown in Fig. S2b. This spectrum clearly indicates the absence of the $\beta$ orbit component with $F_\beta=3900$ T and the presence of the $\beta-\alpha$ orbit, known as the forbidden orbit, component in the acoustic de Haas signal. The absence of the $\beta$ orbit component is reasonable since the measurement temperature is relatively high ($T>1.6$ K) to detect the heavy-mass $\beta$ orbit ($m_\beta\sim6m_e$). Figure S3 shows the mass plot in $\ln(A/T)$ vs. $T$ format, where $A$ represents the Fourier amplitude estimated in the range from 30 T to 50 T. Both orbits show similar temperature dependence, and an effective mass of $m^*\sim3.0m_e$ is obtained for both. For the $\alpha$ orbit, the result shows good agreement with the reported data, $m_\alpha\sim3.2m_e$ [S2,S3]. This agreement is natural because the effective mass is determined by the band structure and the electronic correlation. However, the value of $m_{\beta-\alpha}$ strongly depends on the measurement technique [S2-S4]. The cause of this strange feature is unclear at present. Although only an empirical trend, the $\beta-\alpha$ orbit often seems to be observed more significantly in high-frequency measurements, such as a GHz electrodynamic response [S3] and sub-MHz ac resistance [S4]. The origin and features of the $\beta-\alpha$ orbit are still open questions.

![Figure S2](image_url)

**Fig. S2** a Acoustic de Haas oscillation observed in $\Delta\alpha$ at 1.6K. The black curve represents a fit to the two-component Lifshitz-Kosevich formula of the $\alpha$ orbit and the $\beta-\alpha$ orbit. b Fourier spectrum of the acoustic de Haas shown in a. The peaks are observed at the frequencies $F_\alpha=610$ T and $F_{\beta-\alpha}=3300$ T. The reported frequency for the $\beta$ orbit $F_\beta=3900$ T [S2] was not detected in the present measurement due to the relatively high temperature. c Mass plot of the detected orbits. Both are well reproduced with effective mass $m^*\sim3.0m_e$, which is consistent with the reported data $m_\alpha\sim3.2m_e$ [S2,S3].
3. Magnetic field dependence of $\Delta v/v$ in parallel fields at various temperatures

The data points $H_{c2}(\theta = 0^\circ)$ shown in Fig. 3 are obtained from the field dependence of $\Delta v/v$ at various temperatures shown in Fig. S3. Above 4 K, an additional anomaly is observed at ~5 T. Since elastic properties are strongly influenced by vortices, this anomaly should be attributable to transitions of the vortices. The Josephson vortex lattices in 2D layered superconductors exhibit several transitions related to their depinning and melting, as reported [S5]. The drastic enhancement of $\Delta v/v$ below 5 T is most likely due to pinning of the flux lines since this anomaly disappears at low temperatures. This is because the interlayer coherence length in 2D superconductors becomes smaller than the interlayer spacing at lower temperatures, and the pinning effect on the Josephson vortices in the insulating layers is strongly suppressed due to interlayer decoupling. For depinned Josephson vortices, the flux-line lattice flows and can be easily deformed in the insulating plane; and therefore, the in-plane anisotropy should be reduced. This suppression of the in-plane anisotropy should correspond to the small sound wave direction dependence below $H_{\text{FFLO}}$, as shown in Fig. 4a.

![Graph showing magnetic field dependence of $\Delta v/v$ at various temperatures](Fig. S3)

**Fig. S3** In-plane magnetic field dependence of $\Delta v/v$ at various temperatures. The dashed lines are guides to make the transition at $H_{\text{FFLO}}$ (blue circle) clearer.
4. Out-of-plane electrical resistance

During the ultrasound measurements, we additionally measured the out-of-plane electrical resistance of another crystal at the same time. The field directions were the same as those shown in Fig. S1 and electric currents were applied parallel to the $a^*$-axis. Figure S4 shows the magnetic field dependence of the resistance at 1.6 K. Since these were just supplementary measurements obtained while performing the main ultrasound measurements, there are no data at $|\theta|=0^\circ$. Nevertheless, the data at $\theta = -0.7^\circ$ and $-0.5^\circ$ show the resistivity data of the FFLO state appearing above $H_{\text{FFLO}}=21$ T. $H_{c2}$ is determined by the deflection points shown by the pink triangles. As indicated by the arrows, these data show some kinks in the FFLO state. Since the finite resistance originates from the vortex dynamics, these kinks should be related to vortex pinning. Similar kink structures of the out-of-plane resistance are reported in other FFLO candidates [S5,S6] and are regarded as the commensurability effect of pinning on the FFLO spatial modulation [S5-S7]. This effect occurs at certain fields where the FFLO wavelength $2\pi/q$ is commensurate with the Josephson vortex lattice constant $d_{Jv}$, which leads to smaller resistances due to the relatively strong pinning at the nodes. This effect also indicates that the $q$ vector is parallel to the $b$-axis because the spatial modulation needs to trap the flux lines, which is consistent with the results obtained by our ultrasound measurements.

**Fig. S4 a,b** Out-of-plane magnetoresistance at 1.6 K at various angles. An enlarged plot of the datasets for $\theta = -1.6^\circ$, $-0.7^\circ$, and $-0.5^\circ$ is shown in b. The pink triangle shows $H_{c2}$ at each angle. The arrows point to kinks in the FFLO state.
5. Flux pinning in the FFLO state

In the main text, we discuss flux pinning in the spatial modulation of the FFLO state. Here, we confirm that the FFLO modulation reduces the flux motion via the pinning effect from the viewpoint of the length scale. The Josephson vortices should be pinned at nodes of the spatial modulation of the FFLO state because the Josephson supercurrent is absent at the node positions. Therefore, for the strong pinning effect, the wavelength of the order parameter oscillation $2\pi/q$ ($q=|q|$) should be comparable to or smaller than the Josephson vortex lattice constant $d_{JV} (d_{JV}=\phi_0/\pi H$, where $s$ is the layer spacing) as shown in Fig. S5. Using half the $a$-axis length, 0.8 nm, $d_{JV}$ at 21 T is estimated to be approximately 120 nm. This estimation means that pinning by the FFLO formation requires $q>5*10^7$ m$^{-1}$. In the FFLO state, the energy gain by the momentum $q$ is larger than the Zeeman splitting energy of the up- and down-spin Fermi surfaces. This energy balance gives the relation $q\hbar v_F=g\mu_B H_{FFLO}$. Here, $v_F$, $g$, and $\mu_B$ are the Fermi velocity, the $g$-value, and the Bohr magneton, respectively. This rough approximation leads to $q=6*10^7$ m$^{-1}$ ($2\pi/q$~100 nm) at 21 T. This estimation indicates that the value of $2\pi/q$ is almost comparable to that of $d_{JV}$ around $H_{FFLO}$, and the Josephson vortex lattice is uniformly pinned by the FFLO spatial modulation around $H_{FFLO}$. Since the size of $2\pi/q$ abruptly decreases to $\pi\xi|_{||}$ when approaching $H_{c2}$ [S5,S8], the relation $2\pi/q<d_{JV}$ for the strong pinning effect is satisfied in all of the FFLO regions.

\[2\pi/q \approx \frac{g\mu_B H_{FFLO}}{\hbar v_F} \approx 100 \text{ nm}\]

\[2\pi/q \approx \frac{\pi \xi_{||}}{} \approx 30 \text{ nm}\]

\[d_{JV} \approx 120 \text{ nm}\]

\[d_{JV} \approx 100 \text{ nm}\]

**Fig. S5** Schematic picture of the pinning effect of the Josephson vortices (green circles) in the FFLO modulation (red curves) near the characteristic fields, $H_{FFLO}$~21 T and $H_{c2}$~26 T. The lengths of the modulation and vortex lattice constant are given by the formula described in the text.
References

[S1] M. Yoshizawa, et al. Sound velocity change at superconducting transition in κ-(BEDT-TTF)₂Cu(NCS)₂. Solid State Commun. 89, 701 (1994).

[S2] S. Uji, et al. Effective mass and combination frequencies of de Haas-van Alphen oscillations in κ-(BEDT-TTF)₂Cu(NCS)₂. Synth. Met. 85, 1573, (1997).

[S3] S. Hill, et al. A comparison of the high field quantum oscillations observed by electrodynamic and d.c. transport techniques in the organic superconductor κ-(BEDT-TTF)₂Cu(NCS)₂. Synth. Met. 86, 1955 (1997).

[S4] S. Sugiura, Private communication.

[S5] S. Sugiura, et al. Josephson vortex dynamics and Fulde-Ferrell-Larkin-Ovchinnikov superconductivity in the layered organic superconductor β’-(BEDT-TTF)₂SF₆CH₂CF₂SO₃. Phys. Rev. B 100, 014515 (2019).

[S6] S. Uji, et al. Vortex Dynamics and the Fulde-Ferrell-Larkin-Ovchinnikov State in a Magnetic-Field-Induced Organic Superconductor. Phys. Rev. Lett. 97, 157001 (2006).

[S7] L. Bulaevskii, et al. Intrinsic Pinning of Vortices as a Direct Probe of the Nonuniform Larkin-Ovchinnikov-Fulde-Ferrell State in Layered Superconductors. Phys. Rev. Lett. 90, 067003 (2003).

[S8] H. Shimahara, Fulde-Ferrell state in quasi-two-dimensional superconductors. Phys. Rev. B 50, 12760 (1994).