Nematic superconductivity in topological semimetal CaSn$_3$

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We report a detailed study of upper critical field in superconducting topological semimetal CaSn$_3$ with the AuCu$_3$-type cubic structure (point group: $O_h$). We find that the anisotropy of the upper critical field shows two-fold symmetry about a $C_4$ axis, breaking the rotational symmetry of the underlying crystal lattice. The rotational symmetry breaking cannot be explained either by the Ginzburg-Landau anisotropic effective mass framework or by flux flow due to the Lorentz force. Instead, the two-fold anisotropy can be ascribed to the unconventional superconducting pairing state characterized by a multi-dimensional representation, or nematic superconductivity. Besides the anisotropy, the temperature dependence of upper critical field strongly deviates from that of conventional depairing field described by Werthamer-Helfand-Hohenberg theory, suggesting odd-parity pairing. The odd-parity nematic superconducting state in CaSn$_3$ provides a unique opportunity to elucidate topological superconductivity.

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Topological superconductors (TSCs) hosting Majorana fermions on the boundary have recently attracted much attention because of the potential application such as quantum computing[1]. Topological aspects of the topological superconducting states are closely linked with the pairing symmetry and the Fermi surface topology. In time-reversal-invariant inversion-symmetric systems, topological superconductivity requires odd-parity pairing with the superconducting gap described by $\Delta(-k) = \Delta(k)$ and Fermi surfaces that enclose an odd number of time reversal invariant momenta [2,4]. In spin-rotational-invariant systems, odd-parity superconductivity arises from spin triplet pairing, mediated by ferromagnetic instabilities as observed in UPt$_3$[5]. On the other hand, in spin-orbit-coupled systems, odd-parity pairing can be stabilized even in the absence of magnetic instabilities[2].

The most extensively studied candidate for TSCs is doped Bi-based topological insulator $M_x$Bi$_2$Se$_3$ ($M = \text{Cu, Sr, Nb}$) with strong spin-orbit coupling (SOC) [6,8]. Confirmed by angle resolved photoemission spectroscopy (ARPES) measurements, the topological nature of the electronic structure remains unchanged upon doping [9]. In the superconducting state, several bulk probes, including field-angle-resolved resistivity [10, 11], heat capacity [12], and nuclear magnetic resonance (NMR) measurements [13], exhibit two-fold anisotropy in the basal plane, in spite of the three-fold symmetry of the lattice with point group $D_{3h}$. Besides the bulk measurements, surface sensitive scanning tunneling microscopy (STM) measurements reveal the superconducting gap with two-fold symmetry pinned by a mirror plane under in-plane magnetic fields [14]. The observation of two-fold anisotropy of the superconducting gap indicates odd-parity superconductivity breaking the rotational symmetry of the underlying lattice, or nematic superconductivity, analogue to liquid crystals breaking the rotational symmetry but preserving the translational symmetry [15].

However, there is a discrepancy concerning the existence of Majorana zero modes (MZMs) in these materials: While point contact spectroscopy on Cu$_2$Bi$_2$Se$_3$ shows a zero-bias conductance peak, suggestive of the presence of MZMs [16], Andreev reflection spectroscopy and STM measurements demonstrate fully gapped superconductivity with no in-gap states, indicative of the absence of MZMs [17,18]. These differences between the conclusions drawn from two surface sensitive measurements raises questions about the realization of topological superconductivity in $M_x$Bi$_2$Se$_3$.

Recently, the ternary stannide semimetal CaSn$_3$ crystallizing the cubic AuCu$_3$-type structure with point group $O_h$ (fig.1a inset) has been proposed to be a prime candidate for realizing topological superconductivity [19]. This stoichiometric compound undergoes a superconducting transition at $T_c = 4.2$ K [20], and is predicted to be a topologically non-trivial semimetal by theoretical calculations [19]. The non-trivial electronic structure hosts topological nodal lines in the absence of spin-orbit coupling (SOC). Upon turning on SOC, the nodal lines unexpectedly evolve into Weyl nodes, despite the time-reversal-invariant centrosymmetric system. The non-trivial Berry phase associated with the topological nature of CaSn$_3$ is experimentally confirmed by recent quantum oscillation measurements [21].

Here we report a detailed study on the upper critical field $H_{c2}$ for superconducting topological semimetal CaSn$_3$, revealing the remarkable two-fold anisotropy around a $C_4$ axis in the crystal structure with point group.
Crystal structure and bulk superconductivity in CaSn₃. a, Inset: CaSn₃ crystallizes in the AuCu₃-type cubic structure with four-fold-symmetry around the ⟨100⟩-axes. Main panel: Temperature dependence of resistivity with the high residual resistivity ratio RRR ∼ 60. b, Low temperature resistivity of CaSn₃ below 6 K, showing a superconducting transition at $T_s = 4.15$ K, consistent with the previous reported value [20]. c, The dc magnetic susceptibility of CaSn₃, showing the full diamagnetic screening.

The two-fold anisotropy in the superconducting state cannot be attributed to either anisotropic effective mass or to flux flow depinning due to the Lorentz force. Together with the peculiar temperature dependence of $H_{c2}$, the observation of spontaneous rotational symmetry breaking in the superconducting state for CaSn₃ clearly evinces the realization of nematic superconductivity, opening up a promising pathway to the investigation of topological superconductivity.

Single crystals of CaSn₃ were grown with Sn-self flux. We confirm the AuCu₃-type cubic structure via powder X-ray diffraction. Cut from the same starting piece, bar-shape samples #2a and #2b (~ $1.5 \times 0.50 \times 0.075$ mm³) were used for the field-angle-dependent magnetotransport measurements with a four-wire configuration in a dilution refrigerator with a Swedish rotator.

Upon cooling temperatures, the resistivity for CaSn₃ shows metallic behavior, followed by a sharp superconducting transition at $T_s = 4.15$ K, close to the previously reported value (figs.1a and b). Explicated by the small residual resistivity $\rho_0 \sim 0.5 \ \mu\Omega \ cm$ and the high residual resistivity ratio RRR ∼ 60, our single crystalline sample has less disorder, in contrast to the high residual resistivity for doped topological insulator $M_x$Bi₂Se₃. Consistent with the resistive transition, the dc magnetic susceptibility shows large diamagnetic screening at ~ $4.0$ K (fig.1c), corresponding to the full superconducting volume fraction within the margin of errors from the estimated demagnetizing factor. The full volume fraction in CaSn₃ accompanied by the sizable heat capacity jump [20] suggests bulk superconductivity in CaSn₃, in contrast to the small superconducting volume fractions observed in Cu-doped Bi₂Se₃ [6].

Exotic superconductivity in CaSn₃ is evidenced by the upper critical field $H_{c2}$. Surprisingly, the field-angle-dependent magnetoresistance of CaSn₃ shows salient rotational symmetry breaking of the underlying crystal lattice. Since the AuCu₃-type cubic structure with point group $O_h$ has four-fold rotational symmetry about ⟨100⟩-axes, i.e., the $C_4$ axes, we expect four-fold oscillations in the angular variation of physical quantities such as upper critical field. However, the obtained angular variation of the resistivity $\rho(\theta)$, where $\theta$ is a relative angle between the applied current $I || [001]$ and the applied magnetic field $H$, reveals clear two-fold anisotropy at $\mu_0 H = 0.4$ T as plotted in fig.2a. Whereas no distinct anisotropy of $\rho(\theta)$ is observed in the normal state at $T = 3.34$ K, the two-fold anisotropy appears at lower temperatures. For instance, while being resistive at $\theta = 0^\circ$ ($H || I || [001]$) at $T = 3.08$ K, the sample is superconducting around $\theta = \pm 90^\circ$ ($H || [010] \perp I$), indicating $H_{c2}$ at $\theta = \pm 90^\circ$ is notably higher than that at $\theta = 0^\circ$. The spontaneous rotational symmetry breaking is more clear in the polar plot of $\rho(\theta)$, indicative of the realization of nematic superconductivity (fig.2b).

This unusual anisotropy of $H_{c2}$ does not originate from lowering the crystallographic symmetry associated with structural phase transitions. Indeed, we observe no discernible anomaly associated with such phase transitions in the temperature dependence of resistivity (fig.1) as well as in the previously reported heat capacity study [20], suggesting the crystallographic symmetry remains the same point group $O_h$ at low temperatures.

The observed angular dependence of $H_{c2}$ cannot be explained by the anisotropic Ginzburg-Landau (GL) model, attributed to the anisotropy of the effective mass. In the anisotropic GL model, the angular dependence of upper critical field can be written by

$$H_{c2}(\theta) = \frac{H_{c2}(0^\circ)}{\sqrt{\cos^2 \theta + 2 \Gamma^2 \sin^2 \theta}},$$

where the anisotropy ratio $\Gamma$ is given by $\Gamma = H_{c2}(0^\circ)/H_{c2}(90^\circ) = \sqrt{m_{010}/m_{001}}$. Here $m_{010}$ and $m_{001}$ are the effective masses for the energy dispersion along [010] and [001] directions, respectively. The extracted $\Gamma$ from the measured angular variation of $H_{c2}(\theta)$ is 1.17, yielding unusually large mass anisotropy of $\Gamma^2 = m_{010}/m_{001} \sim 1.37$ (fig.3). However, in cubic systems with point group $O_h$, the effective masses along the main orthogonal axes are isotropic, i.e., $m_{010} = m_{001}$, incompatible with the obtained $\Gamma$ of CaSn₃. Moreover, the calculated $H_{c2}(\theta)$ using eq.(1) represented by the solid line in fig.3 clearly departs from the observed $H_{c2}(\theta)$, excluding the anisotropy of $H_{c2}$ arising from the anisotropic effective mass.

Another possible explanation of the measured anisotropy in $H_{c2}$ of CaSn₃ is lowering the symmetry due
to flux flow resistance. Because of the Lorenz force depending on the relative angle between $H$ and $I$, flux lines in type-II superconductors can be depinned from pinning centers. In the longitudinal configuration ($H \parallel I$), no Lorentz force is produced by the applying magnetic field. By contrast, in the transverse configurations ($H \perp I$), applied field induces the Lorentz force, leading to finite flux flow resistance that reduces $H_{c2}$, accompanied by broadening of the superconducting transition. While large orbital magnetoresistance caused by the Lorentz force is observed in the normal state of CaSn$_3$ in the transverse configuration (fig.4b), $H_{c2}(90^\circ) (H \perp I)$ is higher than $H_{c2}(0^\circ) (H \parallel I)$, inconsistent with the flux flow depinning. Together with the absence of broadening of the resistive transition in the transverse configuration as shown in figs.4a and b, we can exclude the flux flow scenario for the observed anisotropy.

Excluding the GL anisotropic model and flux flow scenario, we attribute the unexpected rotational symmetry breaking in the superconducting state of CaSn$_3$ to the unconventional pairing symmetry. Indeed, very similar spontaneous rotational symmetry breaking in the superconducting state, or nematic superconductivity, has previously been observed in putative TSC $MxBiSe_3$ via field-angle-resolved resistivity [10, 11]. The nematic symmetry involves the odd-parity pairing symmetry described by two dimensional $E_u$ representation in the trigonal $D_{3d}$ point group of $M_xBiSe_3$ [23].

In CaSn$_3$, in addition to the nematic symmetry, peculiar temperature dependence of $H_{c2}$ supports the realization of unconventional superconducting pairing. Regardless of the applied field configurations $H \parallel I$ or $H \perp I$, $H_{c2}$ for CaSn$_3$ extracted from the midpoints of resistive transitions (figs.4a and b) increases linearly with decreasing temperatures down to $T \sim 0.4T_c$, deviating from the conventional orbital depairing field described by the Werthamer-Helfand-Hohenberg (WHH) theory [24, 25]. According to the WHH theory, $H_{c2}(T)$ at $T = 0$ K is given by $H_{c2}(0) = -\alpha T_c \left( \frac{\partial H_{c2}}{\partial T} \right)_{T=0}$, where $\alpha$ is 0.69 for the dirty limit and 0.74 for the clean limit superconductors (fig.4c) [24, 25]. However, the obtained values of $H_{c2}(0) = 1.4$ T for $\theta = 0^\circ \ (H \parallel I \ || \ [001])$ and 1.6 T for $\theta = 90^\circ \ (H \parallel [010])$ correspond to $\alpha \sim 0.85$ independent of $\theta$, substantially exceeding the orbital limit.
of $\alpha = 0.74$ for clean superconductors (fig. 4c inset). The exceeding orbital limit can be ascribed to several reasons, such as multiband effects. However, the multiband effect is implausible in CaSn$_3$ because $H_{c2}$ observed in CaSn$_3$ lacks peculiar upward curvature in the temperature dependence as observed in multiband superconductor MgB$_2$ [20]. Interestingly, $H_{c2}$ of CaSn$_3$ is in a good agreement with that of the polar p-wave pairing state [27], plotted as the normalized upper critical field $h = -H_{c2}/(T_c \partial H_{c2}/\partial T)_{T= T_c}$ in the inset of fig. 4c, suggestive of the realization of odd-parity pairing states.

The nematic superconducting state in CaSn$_3$ is pinned by the applied current ($I \parallel [001]$) which lowers the symmetry of underlying lattice, resulting in the [001] direction no longer identical to the others. The lowering of symmetry allows creating a single domain or imbalance in multiple domains of the nematic state. Upon rotating magnetic field in the $C_4$ plane perpendicular to the applied current ($\phi$ rotation) from [100] to [010], we observe no two-fold anisotropy, but instead, clear four-fold symmetry in the upper critical field of sam-

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Finally, we briefly comment on the possible superconductor order parameter realized in CaSn$_3$. Armed with group theoretical classifications, we can determine possible pairing symmetry inducing spontaneous rota-

tional symmetry breaking in the superconducting state of CaSn$_3$. Discarding pairing states higher than $f$-wave out of ten irreducible representations of $O_h$, we tabulate the possible superconducting pairing states with the lower symmetry of point group $D_{4h}$, which is a subgroup of $O_h$ and breaks the crystallographic rotational symmetry (table. 1) [28]. Although further parity-sensitive experiments, including NMR Knight shift, are required, together with the observed $H_{c2}$ close in the form to that of polar p-wave pairing state and the fully-gapped state unveiled by low-temperature specific heat [21], the nematicity suggests that two dimensional representation $E_u$ symmetry with the fully-gapped d-vector $2\hat{k}x - \hat{k}y$ can possibly be stabilized in CaSn$_3$, satisfying a key gra-

| $\Gamma$ | $\psi(k)/d(k)$ | Zeros in the gap |
|---|---|---|
| $E_y$ | $k_y^2 - k_y^2$ | L |
| $T_{2y}$ | $k_yk_z$ | L |
| $E_u$ | $\hat{x}k_x - \hat{y}k_y$ | P |
| $T_{1u}$ | $\hat{y}k_x - \hat{z}k_y$ | P |
| $T_{2u}$ | $\hat{x}(k_y + ik_z) + (\hat{y} + iz)k_z$ | P |
| $T_{3u}$ | $\hat{x}(k_y + ik_z) + (\hat{y} + iz)k_z$ | P |
dient for topological superconductivity in time-reversal-invariant inversion-symmetric systems, namely, the fully-gapped odd-parity pairing state.

In summary, we have investigated the anisotropy of upper critical field in topological semimetal CaSn$_3$. We observe unusual two-fold symmetry of $H_{c2}$ about a four-fold symmetric axis, indicative of the realization of nematic superconductivity pinned by the applied current. We also observe anomalous superconducting pairing states. These observations indicate that the pairing symmetry realized in CaSn$_3$ is odd parity, providing a promising platform for realization of topological superconductivity.

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