Emerging Superconductivity and Topological States in Bismuth Chalcogenides

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Abstract

In this chapter, we review the recent experimental work in emerging superconductors, i.e., bismuth chalcogenides, including the newly discovered BiS(e)$_2$-based layered superconductors and some topological superconductor candidates. Their crystal structure and various physical properties are reviewed in detail, with the correlation between structure and superconductivity as the main clue throughout this chapter. Bi$_2$Os$_2$ is the simplest structure in Bi–O–S compounds and probably the parent compound of this series. Superconductivity emerges when carriers are introduced by intercalation or chemical substitution. The superconducting layer is extended to BiSe$_2$ layer in LaO$_{1-x}$F$_x$BiSe$_2$, which has an improved superconductivity. Moreover, the topological insulator Bi$_2$Se$_3$ can be turned into superconductors by intercalating metal atoms into van der Waals space, e.g., Sr$_x$Bi$_2$Se$_3$, a potential topological superconductor, whose quantum oscillations reveal a possible topological surface state. The intermediate external pressure can efficiently suppress superconductivity, which reemerges when pressure is further increased, while $T_c$ is nearly invariant in high-pressure region, indicating an unconventional pairing state.

Keywords: bismuth chalcogenides, BiS(e)$_2$-based superconductors, crystal structure, intercalation, topological superconductors, high pressure

1. Introduction

Superconductivity was first discovered in the resistivity measurement of mercury by Kamerlingh Onnes in 1911. Its resistance abruptly vanishes at 4.1 K. Zero resistance means no energy loss in electric transport, which could greatly solve the energy crisis in the future. Since then, superconductivity has been a long-lasting hot topic in condensed matter physics. Exploring room temperature superconductors is one of the ultimate dreams.
However, so far, only two kinds of unconventional superconducting systems have exceeded the Macmillan limit at ambient pressure, i.e., the cuprate and iron-based superconductors. In general, the correlation of structure and typical properties is always a useful guideline for effectively searching for special functional materials. In fact, the structure of both cuprate and iron-based superconductors can be characterized as a sandwiched “hamburger” model. It consists of superconducting layers (\(\text{CuO}_2\) plane, \(\text{Fe}_2\text{M}_2\) (\(\text{M} = \text{As}, \text{P}, \text{S}, \text{Se}, \text{and Te}\)) layer) and spacer layers, which stack alternatively along the c-axis [1, 2]. Superconductivity occurs when the charged carriers are generated by the defects or substitution in superconducting layers or more commonly provided by the space layers; namely, a new superconducting layer probably means a new superconducting system. The spacer layer can be easily tuned by doping, substitution, intercalation, and pressure, which could affect superconductivity [3]. Therefore, materials with layered structure have been regarded as the most promising playground for exploring new high-\(T_c\) superconductors.

In 2010, superconductivity arising from the topological insulator \(\text{Bi}_2\text{Se}_3\) by Cu intercalation was first reported [4]. It has drawn much attention since \(\text{Cu}_x\text{Bi}_2\text{Se}_3\) is proposed as a topological superconductor candidate, as evidenced by the zero-bias conductance peak and quantum oscillation experiment [5, 6]. Very recently, superconductivity with topological states was also reported in its isostructural compounds, \(\text{Sr}_x\text{Bi}_2\text{Se}_3\) and \(\text{Nb}_x\text{Bi}_2\text{Se}_3\) [7, 8]. In 2012, an exotic superconductivity was discovered in a new layered structure \(\text{Bi}_4\text{O}_4\text{S}_3\) with zero-resistance superconducting temperature at about 4.5 K [9]. Soon, another new BiS-based superconductor \(\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2\) was reported, whose structure is more definite and the zero-resistance superconducting temperature is about 8 K for the samples annealed under high pressure [10]. As its structure is very similar to the iron-based superconductor \(\text{LaOFeAs}\), this system has been intensively researched, and lots of isostructural superconductors have been synthesized, including \(\text{ReO}_{1-x}\text{F}_x\text{BiS}_2\) (\(\text{Re}: \text{Ce}, \text{Pr}, \text{Nd}, \text{Yb}\)), \(\text{Sr}_{1-x}\text{Re}_x\text{FBiS}_2\) (\(\text{Re}: \text{La}, \text{Ce}\)), \(\text{EuBiS}_2\), and \(\text{Eu}_3\text{Bi}_3\text{S}_4\) [11–15]. These researches are focused on tuning the spacer layers. The attempts to explore new superconducting layers only succeed in \(\text{LaO}_{x}\text{F}_{x}\text{BiSe}_2\) and \(\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2\) [16–18]. So far, the superconducting layer of this system has been extended to \(\text{BiCh}_2\) (\(\text{Ch}: \text{S}, \text{Se}\)). In this chapter, the crystal structure and superconducting properties of Bi–O–S superconductors, \(\text{LaO}_{1-x}\text{F}_x\text{BiSe}_2\) single crystals, and \(\text{Sr}_x\text{Bi}_2\text{Se}_3\) single crystals are briefly reviewed.

2. Crystal structure and superconducting properties

2.1. Bi–O–S superconductors

The element composition of \(\text{Bi}_4\text{O}_4\text{S}_3\) is the same as \(\text{Bi}_x\text{O}_y(\text{SO}_4)\text{Bi}_z\text{S}_4\) (\(x = 0.5\)), and its parent \(\text{Bi}_8\text{O}_{18}\text{S}_3\) is an oxide insulator composed of alternatively stacked \(\text{BiS}_2\) and \(\text{Bi}_2\text{O}_2 + \text{SO}_4 + \text{Bi}_2\text{O}_2\) layers along the c-axis. It has a tetragonal structure with I4/mmm space group and its schematic crystal structure is shown in Figure 1(c). Band calculations demonstrate that the half vacancy of \(\text{SO}_4\) layer generates electron carriers into \(\text{BiS}_2\) layer. The normal state of \(\text{Bi}_4\text{O}_4\text{S}_3\) is metallic and the superconductivity mainly originates from the Bi 6p\(_x\) and 6p\(_y\) orbitals in \(\text{BiS}_2\) layers. Therefore, the \(\text{BiS}_2\) layer is called the superconducting layer in this family.
However, the chemical composition studies show that it probably contains two new Bi–O–S phases, i.e., Bi$_2$OS$_2$ and Bi$_3$O$_2$S$_3$. Their schematic structures can be seen in Figure 1(a) and (b). Bi$_2$OS$_2$ is an insulating phase and its content is less than 10%. Bi$_3$O$_2$S$_3$ is the main phase and likely accounts for the 4.5 K superconductivity in Bi$_4$O$_4$S$_3$. And the superconductivity can be suppressed by the amount of Bi$_2$OS$_2$-like stacking faults [19]. Once the quality of Bi$_3$O$_2$S$_3$ sample is improved, the superconducting volume fraction will be enhanced with its zero-resistance superconducting temperature increased up to 4.9 K [20].

The crystal structure of Bi$_3$O$_2$S$_3$ is similar to Bi$_4$O$_4$S$_3$ with the same I4/mmm space group, $a = 3.9674$ Å and $b = 41.2825$ Å. The electron carriers are believed to be generated from S$_2^-$ layers replacing the vacancy of SO$_4^{2-}$ layers in Bi$_4$O$_4$S$_3$. The chemical composition of Bi$_2$OS$_2$ can also be expressed as BiOBiS$_2$. Then we can see it is isostructural with LaOBiS$_2$ with P4/nmm space group, $a = b = 3.9744$ Å and $c = 13.7497$ Å. BiOBiS$_2$ has the simplest structure and composition, then it is probably the parent compound of this BiS$_2$-based family. Besides, superconductivity is likely to be induced by introducing carriers into spacer layer. In fact, F-doped Bi$_2$OS$_2$ has been reported to exhibit bulk superconductivity below 5 K [21, 22].

Figure 2 shows the powder XRD patterns of Bi$_3$O$_2$S$_3$, Bi$_4$O$_4$F BiS$_2$ and Bi$_2$OS$_2$ samples. We can see that samples of Bi–O–S compounds tend to contain impurities such as Bi$_2$O$_4$, Bi, and BiS$_2$ because their synthesis temperature is relatively low (520°C for Bi$_4$O$_4$S$_3$ and Bi$_3$O$_2$S$_3$, and 400°C for Bi$_2$(O,F)S$_2$) [9, 19–21]. Besides, these samples can only be synthesized in a narrow temperature region. Another difficulty in detecting their actual composition and structure is that several strong diffraction peaks in the powder XRD patterns are very close to each other.
Hence, bulk superconductivity is very important in this system. Up to now, high-quality samples, especially single crystals, are still needed to investigate the relationship of structure and properties, in view of the multiple competing low-energy crystal structures in this system.

The physical properties of Bi–O–S superconductors are introduced, taking Bi$_3$O$_2$S$_3$ and F-doped Bi$_2$O$_2$S$_2$ for instance [20, 21]. Figure 3(a) shows the temperature dependence of resistivity and magnetoresistivity under different applied magnetic fields for Bi$_3$O$_2$S$_3$. Its normal state is metallic-like and a sharp drop in resistivity appears at 5.8 K and quickly down to zero at 4.9 K. The upper critical field is estimated from resistivity versus temperature curves under different applied magnetic fields perpendicular to the sample surface, as seen in the insets of Figure 3(a). According to the Werthamer-Helfand-Hohenberg (WHH) formula, the upper critical field $\mu_0 H_{c2}(0)$ is evaluated to be about 4.84 T.

The shielding volume fraction is about 100%, revealing bulk superconductivity, as seen in Figure 3(b). The divergence in temperature dependence of magnetic susceptibility and the M-H curves characterize Bi$_3$O$_2$S$_3$ as a type-II superconductor. The Hall effect shows a remarkable nonlinear magnetic field dependence of transverse resistivity, which means it is likely a multiband superconductor [23]. However, the Hall resistivity at different temperatures is all negative, indicating that the dominant charge carriers are electron-type. The evaluated charge carrier density is about $1.5 \times 10^{19} \text{ cm}^{-3}$. It is much lower than those of cuprate and iron-based superconductors, implying a low superfluid density. Chemical substitution effects seem to increase the charge carrier density, but ultimately inhibit the superconductivity [24–26].

A clear specific heat anomaly appears around the superconducting transition temperature, as seen in Figure 3(d), confirming the bulk superconductivity in Bi$_3$O$_2$S$_3$. The electronic specific

![Figure 2. Powder XRD patterns of Bi$_3$O$_2$S$_3$, Bi$_2$O$_2$S$_2$ and Bi$_2$O$_{1-x}$F$_x$S$_2$ polycrystalline samples. The special characters (*, #) represent the impurity phases.](image)
heat coefficient $\gamma$ and phonon specific heat coefficient $\beta$ for the normal state under 9 T are obtained as $1.65 \text{ mJ/(mol K}^2\text{)}$ and $2.6 \text{ mJ/(mol K}^4\text{)}$, respectively, using linear fitting of $C/T$ versus $T^2$. As the phononic contribution to the heat capacity is generally independent of the external magnetic field, the electronic specific heat of superconducting state can be expressed by the equation

$$C_e(T) = C(T, H = 0) - C(T, H = 9T) + \gamma T.$$  \hspace{1cm} (1)

The estimated value of $\Delta C_e / \gamma T_c$ is comparable to the BCS weak-coupling limit 1.43.

Undoped Bi$_2$O$_2$S$_2$ was predicted to be an insulating oxide by the band structure calculations. However, we can see it is almost metallic from 300 K to 30 K, and a weak semiconductor behavior emerges below 30 K, which may be originating from the impurities. The F-doping can significantly decrease the normal state resistivity and increase the shielding volume fraction, as shown in Figure 4. The best doping ratio is about 0.24. From the temperature dependence of magnetic susceptibility, the best doped sample has a bulk type-II-like
superconductivity. When doping content exceeds 0.27, superconductivity disappears and the resistivity increases quickly. Besides, the quality of samples (x > 0.27) synthesized by conventional solid state reaction method begins to deteriorate with increasing doping content [21]. In fact, the Bi$_2$(O,F)S$_2$ samples synthesized by topotactic fluorination using XeF$_2$ also contain bismuth impurity [22]. It is difficult to get pure samples because the optimal synthesis temperature is only around 400°C.

2.2. Re(O,F)BiCh$_2$ (Ch: S, Se) superconductors

Re(O,F)BiS$_2$ (Re: La, Ce, Pr, Nd, Yb) superconductors have been intensively studied since the report of LaO$_{0.5}$F$_{0.5}$BiS$_2$. Their structure is more definite and similar to “1111” phase of iron-based superconductors. Single crystals of this structure have been successfully synthesized [27]. Structure tuning is mainly concentrated on the spacer layers rather than the superconducting layer. And only the electron-doping into the insulating parent can induce superconductivity [28]. Here, we introduce the crystal structure and various physical properties of LaO$_{1-x}$F$_x$BiSe$_2$ single crystals, which also firstly extend the superconducting layer to BiSe$_2$ layer.

The powder XRD pattern and crystal structure of LaO$_{0.59}$F$_{0.41}$BiSe$_2$ superconducting single crystal are presented in Figure 5. No impurity phase is found and each peak is indexed. It has a P4/nmm tetragonal lattice with the refined lattice constants a = b = 4.1377 Å and c = 14.1566 Å, which are larger than those of LaO$_{0.5}$F$_{0.5}$BiS$_2$ for the larger ionic radius of Se$^{2-}$. Figure 6 shows a comparison of the temperature dependence of resistivity for La(O,F)BiS$_2$ and La(O,F)BiSe$_2$ samples. LaOBiS$_2$ can be described as an insulator while LaOBiSe$_2$ is metallic. For LaO$_{0.5}$F$_{0.5}$BiS$_2$, it exhibits a semiconducting behavior before the superconducting transition begins. The transport property of LaO$_{0.5}$F$_{0.5}$BiSe$_2$ is similar to Bi$_2$O$_2$S$_2$ but with a lower residual resistivity. Other isostructural compounds such as LaO$_{0.5}$F$_{0.5}$BiTe$_2$ and LaO$_{0.5}$SbS$_2$ are also reported, but no superconductivity can be observed down to 1.7 K [16].

![Figure 4](image-url)
Fluorine doping effect on the superconductivity of LaO$_{1-x}$F$_x$BiSe$_2$ single crystals is shown in Figure 7(a) and (b). F-doping can significantly decrease the resistivity of normal state and increase the superconducting transition temperature and shielding volume fraction. Unfortunately, the flux method can only grow single crystals with the largest F content of about 0.5. For example, the sample with F-doping amount of 0.52 was grown by a nominal component of 0.9. The magnetic susceptibility measurement shows LaO$_{1-x}$F$_x$BiSe$_2$ has a bulk superconductivity and belongs to the type-II superconductors. Upper critical magnetic field can be evaluated from the resistivity versus temperature under various magnetic fields. As seen in Figure 7(c) and (d), the upper critical fields at zero temperature are estimated to be 29 T and 1 T for H$\parallel$ab and H$\perp$ab, respectively, which indicate large anisotropy.

Figure 5. (a) Powder XRD pattern (black circles) with the Rietveld refinement (red curve) and Miller indices for LaO$_{0.59}$F$_{0.41}$BiSe$_2$. The inset table summarizes the structural parameters. (b) Crystal structure of LaO$_{0.59}$F$_{0.41}$BiSe$_2$. The rectangle indicates the unit cell [17].

Figure 6. A comparison of the temperature dependence of resistivity between (a) La(O,F)BiS$_2$ and (b) La(O,F)BiSe$_2$.
The anisotropy parameter $\gamma_s$ of the LaO$_{1-x}$F$_x$BiSe$_2$ superconducting single crystal is investigated by measuring the angular dependence of resistivity under various magnetic fields at 3 K (see Figure 8). Note that the angle $\theta$ describes the deviation of magnetic field with respect to the ab-plane of single crystal. Only the data with magnetic field below 1 T are selected for the reduced magnetic field, because the $H^{\text{c2}}(0)$ for $H \perp \text{ab}$ is about 1 T. The reduced magnetic field is calculated by the equation

$$H_{\text{red}} = H \sqrt{\sin^2 \theta + \gamma_s^2 \cos^2 \theta}. \quad (2)$$

According to the Ginzburg-Landau theory [29], the curves of resistivity versus reduced magnetic field under different magnetic fields should merge into one. The resultant anisotropy parameter at 3 K is about 30 (see Figure 8(b)), which is close to the result of upper critical field within the ab-plane.

Considering that the $T_c$ of LaO$_{0.5}$F$_{0.5}$BiS$_2$ is increased from 2.7 K to 10.6 K under a hydrostatic pressure of 1.68 GPa [30], the highest $T_c$ among the BiS$_2$-based superconductors, higher $T_c$ above 10.6 K...
is expected for LaO$_{0.5}$F$_{0.5}$BiSe$_2$ under external pressure since its zero-resistance temperature is about 3.5 K. However, we find that its superconductivity and shielding volume fraction decrease unexpectedly with increasing pressure below 1 GPa hydrostatic pressure, as seen in Figure 9(a). Another experiment with higher pressure shows that a new superconducting phase emerges at about 1.2 GPa and $T_c$ reaches about 6.5 K at 2.17 GPa [31]. Accompanied by this crossover, the normal state is switched from that with a low temperature resistivity upturning to a metallic one. Accordingly, the normal state resistivity also shows a nonmonotonic change with the external pressure. These facts suggest that the BiSe$_2$-based system is very different from the BiS$_2$-based system.

2.3. M$_x$Bi$_2$Ch$_2$ (Ch: Se, Te) superconductors

Topological insulator has linearly dispersive band structures and its topological surface state exhibits metallic properties while the bulk state is insulating. If its spin-momentum locking effect combines with superconductivity, Majorana fermion may exist, which is useful for quantum computing. At first, the topological superconductors were mostly focused on the proximity-induced
superconductivity. The discovery of Cu$_x$Bi$_2$Se$_3$ superconductor opens a new gate to topological superconductors, i.e., superconductors induced by doping into topological insulators, which are expected to be the candidate of three-dimensional topological superconductors. Recently, a series of superconductors based on the topological insulators have been reported, such as Cu$_x$(PbSe)$_y$(Bi$_2$Se$_3$)$_z$ [32], Sr Bi$_2$Se$_3$ [7], Nb Bi$_2$Se$_3$ [8], and Tl Bi$_2$Te$_3$ [33]. Here, we put emphasis on the crystal structure and physical properties of SrBi$_2$Se$_3$ single crystals.

The structure of Sr$_x$Bi$_2$Se$_3$ is similar to that of Cu$_x$Bi$_2$Se$_3$ and isomorphic to the parent Bi$_2$Se$_3$. Sr atoms may act as a bipolar dopant that can be embedded in the van der Waals space or randomly substitute for Bi. The actual Sr doping content of Sr$_x$Bi$_2$Se$_3$ is very little so that it is hard to define its precise position. Nevertheless, the lattice constants of Sr$_x$Bi$_2$Se$_3$ are a little larger than those of Bi$_2$Se$_3$, while the lattice constants of Bi$_{2-x}$Sr$_x$Se$_3$ are smaller. The c-axis lattice constant of Bi$_{2-x}$Sr$_x$Se$_3$ decreases slightly with increasing doping content (see Figure 10(b)). In addition, all samples grown in Bi$_{2-x}$Sr$_x$Se$_3$ ratio show no signs of superconductivity at 1.8 K, as seen in Figure 11(a). Therefore, we could use Figure 10(a) as the schematic structure diagram.

The linear curves of Hall resistivity versus magnetic field indicate that Sr$_x$Bi$_2$Se$_3$ has only one electron-like bulk carrier. The carrier density increases slightly with decreasing temperature. Its average is around $2.3 \times 10^{19}$ cm$^{-3}$, about 1–2 orders of magnitude lower than Cu$_x$Bi$_2$Se$_3$. Figure 11(d) and (e) shows that the $T_c$ of superconducting samples changes little with different Sr contents, but the shielding volume fraction is very different. Only those samples with Sr content above 0.06 have a large shielding volume fraction. Moreover, the superconductivity is very stable in air, as evidenced by the almost unchanged shielding volume fraction for the sample placed in air even for a month. This provides great convenience for experimental research.

The topological surface state of Sr$_x$Bi$_2$Se$_3$ single crystal has been investigated through Shubnikov-de Haas oscillation measurements. Clear oscillations in resistivity and Hall resistivity can be observed under high magnetic field at different temperatures, as shown in Figure 12(a) and (c). The oscillation amplitudes become more pronounced for higher magnetic field and lower temperature. However, the oscillatory periods measured at different temperatures remain constant, so only the data at 0.35 K with the most noticeable oscillations are selected to deduce the Landau level

![Figure 10](image-url)
indices. In fact, the measured resistivity and Hall resistivity actually contain contributions from both the surface and bulk conductance when a large parallel bulk conduction channel is present. Therefore, the least confusing method is to convert resistivity into conductance to determine the Landau index because its components are additive \[34\]. The following equations are used to calculate conductance

\[
G_{xx} = \frac{R_x}{R_{xx}^2 + R_{xy}^2}, \quad G_{xy} = \frac{R_y}{R_{xx}^2 + R_{xy}^2}.
\] (3)

After removing the nonoscillatory background, the oscillatory components are obtained and plotted as a function of \(1/B\). The frequencies are 146 T for longitudinal conductance and 144.8 T for Hall conductance, which are comparable to those of Bi\(_{2}\)Se\(_3\) but smaller than Cu\(_x\)Bi\(_{2}\)Se\(_3\). The integer Landau index \(n\) corresponds to the valleys in \(\Delta G_{xx}\), while the valleys in \(\Delta G_{xy}\) are assigned to \(n + 1/4\) [see Figure 13(a) and (c)]. The 1/4 shift arises to match the valleys in \(d\Delta G_{xy}/dB\) with the valleys in \(\Delta G_{xx}\) [34]. The obtained intercepts of the linear fittings for \(n\) versus \(1/B\) are both close to the value for an ideal Dirac system, i.e., \(-0.5\) rather than 0 or 1 (see Figure 13(b) and (d)). Thus, it provides transport evidence for the existence of Dirac fermions in Sr\(_x\)Bi\(_{2}\)Se\(_3\) superconductor.
The superconductivity of Sr$_x$Bi$_2$Se$_3$ is very sensitive to external pressure below 1 GPa, as seen in Figure 14(a) and (b). With the increasing applied pressure, the $T_c$ and shielding volume fraction decrease but the normal state resistivity increases. This depression of superconductivity can be

![Figure 12](image1.png)

**Figure 12.** SdH oscillations under high magnetic field for Sr$_x$Bi$_2$Se$_3$ single crystal. (a) and (c) Magnetic field dependence of resistivity and Hall resistivity at different temperatures. (b) and (d) Magnetic field dependence of the fitted longitudinal and Hall conductivity at 0.35 K [7].

![Figure 13](image2.png)

**Figure 13.** (a) and (c) Oscillatory component of the longitudinal and Hall conductivity at 0.35 K plotted against 1/B. (b) The Landau index $n$ versus 1/B, where $n$ and $n + 1/2$ correspond to the valleys and peaks of $\Delta G_{xx}$. (d) $n$ versus 1/B derived from (c), where $n + 1/4$ corresponds to the valleys of $\Delta G_{xy}$ [7].
attributed to the reduction of charge carrier density, which is apparent from the normal state resistivity. However, if the pressure continues to increase, the normal state resistivity begins to decrease and a sign of superconducting transition occurs at 6 GPa. Then, the $T_{c\text{onset}}$ and the charge carrier density estimated from the normal state resistivity gradually increase with the increasing pressure, and $T_{c\text{onset}}$ reaches around 8 K when $P > 14$ GPa. But unfortunately, the $T_{c\text{onset}}$ remains almost constant for the pressure up to 40 GPa, although the normal state resistivity keeps decreasing. The reemerging superconductivity is very robust and the $T_{c\text{onset}}$ still changes little under 80 GPa [35]. In fact, the whole process contains three structural phases, i.e., R-3 m, C2/m, and I4/mmm, as seen in Figure 14(d). The structural transitions and pressure-invariant $T_c$ are very similar to the parent compound $\text{Bi}_2\text{Se}_3$, which needs further investigations.

3. Conclusions

The discovery of superconductivity in layered compound $\text{Bi}_2\text{O}_2\text{S}_3$ brings in a new BiS$_2$-based superconducting family, including the Bi–O–S compounds, Re(O,F)BiS$_2$, and MFBiS$_2$ superconductors. The superconducting layer is extended to BiSe$_2$ layer in LaO$_{1-x}$F$_x$BiSe$_2$ and Sr$_{1-x}$La$_x$FBiSe$_2$. The crystal structure and various superconducting properties are reviewed for selective systems. Hall effect and specific heat suggest that they are probably multiband
superconductors and can be described by BCS weak-coupling theory. Moreover, bismuth chalcogenide topological insulators can be turned into superconductors by doping, which are potential candidates for 3D topological superconductors. For example, the topological surface state of Sr$_x$Bi$_2$Se$_3$ is well supported by SdH oscillations under high magnetic field. The intermediate external pressure can efficiently suppress the superconductivity, which reemerges when pressure is further increased, while $T_c$ is nearly invariant in high-pressure region, indicating an unconventional pairing state.

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Conflict of interest

The authors declare no competing financial interests.

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