Conventional isotope effect in BiS₂-based superconductor (Sr,La)FBiS₂: possible pairing mechanism switching driven by structural symmetry breaking

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Abstract
Investigation of isotope effects on superconducting transition temperature ($T_c$) is one of the most useful methods to examine whether electron–phonon interaction is essential for pairing mechanisms. The layered BiCh₂-based (Ch: S, Se) superconductor family is a candidate for unconventional superconductors, because unconventional isotope effects have previously been observed in La(O,F)BiSSe and Bi₄O₄S₃. In this study, we investigated the isotope effects of $^{32}$S and $^{34}$S in the high-pressure phase of (Sr,La)FBiS₂, which has a monoclinic crystal structure and a higher $T_c$ of ~10 K under high pressures, and observed conventional isotope shifts in $T_c$. The obtained results suggest that the pairing mechanisms of BiCh₂-based superconductors could be switched by a structural-symmetry change in the superconducting layers induced by pressure effects.
Introduction

In conventional superconductors, electron–phonon interactions are essential for the formation of Cooper pairs\(^1\). According to BCS (Bardeen-Cooper-Schrieffer) theory\(^1\), the transition temperature \((T_c)\) of a phonon-mediated superconductor is proportional to its phonon energy \(\hbar \omega\), where \(\hbar\) and \(\omega\) are the Planck constant and the phonon frequency, respectively. Therefore, \(T_c\) of conventional superconductors is sensitive to the phonon frequency, and modifications of the isotope mass \((M)\) of the constituent elements, the so-called isotope effect, have been used to investigate the importance of electron–phonon interactions in the pairing of various superconductors. The isotope exponent \(\alpha\) is defined by \(T_c \sim M^\alpha\), and \(\alpha \approx 0.5\) is expected according to BCS theory\(^1\). For instance, \(\alpha\) values close to 0.5 have been detected in (Ba,K)BiO\(_3\) \((\alpha_0 \approx 0.5)^2\), MgB\(_2\) \((\alpha_0 \approx 0.3)^3\), and borocarbides \((\alpha_0 \approx 0.3)^4\). In addition, the hydrides \((\text{H}_2\text{S and LaH}_{10})\) high-\(T_c\) superconductors also showed a conventional shift in \(T_c\) with \(\alpha_{\text{H}_2\text{S and LaH}_{10}} = 0.3–0.5\) in isotope effect investigations\(^5,6\). In contrast, in superconductors with unconventional mechanisms, the isotope effect is not consistent with the BCS theory, and \(\alpha\) values deviated from 0.5\(^7,8\).

The target system of this study, layered BiCh\(_2\)-based \((\text{Ch: S, Se})\) superconductors, has been extensively studied since its discovery in 2012\(^9,10\). Because of its layered structure composed of alternate stacking of a superconducting layer and a blocking (insulating) layer, which resembles those of high-\(T_c\) superconductors\(^12,13\), many studies have been performed on material development and on pairing mechanisms\(^13\). Although non-doped (parent) BiCh\(_2\)-based compounds are semiconductors with a band gap, electron doping of the BiCh\(_2\) layers makes the system metallic, and superconductivity is induced. An example of this is F substitution in REOBiCh\(_2\) \((\text{RE: rare earth})^9,11\). In addition, the superconducting properties of BiCh\(_2\)-based systems are very sensitive to the effects of external (physical) and/or chemical pressures\(^14,17\). When external pressures are applied, the crystal structures of REOBiCh\(_2\)-based systems tend to distort into a monoclinic \((P2_1/m)\) structure, and a higher-\(T_c\) phase \((T_c > 10 \text{ K})\) is induced\(^16\). Instead, by applying in-plane chemical pressure (shrinkage of the Bi-Ch conducting plane) via isovalent-element substitutions at the RE and/or Ch sites, a tetragonal \((P4/nmm)\) phase is maintained, and bulk superconductivity is induced in the tetragonal phase. The emergence of bulk superconductivity due to chemical pressure effects can be explained by the suppression of local structural disorder, which is caused by the presence of Bi lone pair electrons\(^18,20\).

Regarding the mechanisms of superconductivity in the BiCh\(_2\)-based family, the pairing mechanisms of the BiCh\(_2\)-based superconductor family are still controversial\(^19\), owing to superconducting properties that are tunable by external and/or chemical pressure effects, which sometimes causes scattered results. Although earlier theoretical and experimental studies suggested conventional mechanisms with fully gapped s-wave pairing states\(^21,23\), recent theoretical calculations of \(T_c\) indicated that a \(T_c\) of an order of several K to 10 K in BiS\(_2\)-based
superconductors cannot be explained within phonon-mediated models. Furthermore, angle-resolved photoemission spectroscopy (ARPES) proposed unconventional pairing mechanisms owing to the observation of a highly anisotropic superconducting gap in \( \text{NdO}_{0.71}\text{F}_{0.29}\text{BiS}_{2} \). In addition, a study on the Se isotope effect with \(^{76}\text{Se}\) and \(^{34}\text{Se}\) in \( \text{LaO}_{0.06}\text{F}_{0.4}\text{BiSSe} \) indicated the possibility of unconventional (non-phonon) mechanisms with \( \alpha_{\text{Se}} \) close to 0. In addition, we have recently reported on an unconventional isotope effect with \(^{32}\text{S}\) and \(^{34}\text{S}\) in \( \text{Bi}_{2}\text{O}_{4}\text{S}_{3} \) \((-0.1 < \alpha_{\text{S}} < 0.1)^{27}\). These two superconductors have a tetragonal crystal structure and show a relatively low \( T_{c} \) of 3.8 K for \( \text{LaO}_{0.06}\text{F}_{0.4}\text{BiSSe} \) and 4.7 K for \( \text{Bi}_{2}\text{O}_{4}\text{S}_{3} \). As mentioned above, the BiS\(_2\)-based superconductor has a high-pressure (high-\( P \)) phase, which exhibits a higher \( T_{c} \) of over 10 K. Therefore, this background encouraged us to plan an isotope effect study for a high-\( P \) (monoclinic) phase with a higher \( T_{c} \), in order to find a way to design new BiCh\(_2\)-based superconductors with a higher \( T_{c} \) and to elucidate the mechanisms of superconductivity in the system.

Herein, we show experimental evidence of phonon-mediated superconductivity in a high-\( P \) phase of BiS\(_2\)-based superconductors (Sr,La)FBiS\(_2\). We have investigated the sulphur isotope effects (\(^{32}\text{S}\) and \(^{34}\text{S}\)) on \( T_{c} \) for a high-\( P \) phase of (Sr,La)FBiS\(_2\) with \( T_{c} \sim 10 \) K\(^{28-30}\). Conventional shifts in \( T_{c} \) between samples synthesised with \(^{32}\text{S}\) and \(^{34}\text{S}\) were observed, which suggests the importance of phonons for the pairing mechanisms in the compound. The conventional isotope effects in (Sr,La)FBiS, which has a monoclinic structure, are in contrast to the unconventional isotope effects observed in \( \text{La}(\text{O,F})\text{BiSSe} \) and \( \text{Bi}_{2}\text{O}_{4}\text{S}_{3} \), which have a tetragonal structure\(^{26,27}\). Based on a combination of the discussion of previous and present isotope studies, we suggest that the structural difference between the tetragonal and monoclinic structures could be a switch of the pairing mechanisms in BiCh\(_2\)-based superconductors.

**Results**

**Characterisation of isotope samples**

In general, the shift in \( T_{c} \) due to isotope effects is very small, even with \( \alpha \sim 0.5 \) for low-\( T_{c} \) superconductors. Therefore, examining the isotope effects with sets of samples with comparable superconducting properties is important to reach a reliable conclusion. However, precise control of the superconducting characteristics of BiCh\(_2\)-based compounds is the challenge of this study, because the \( T_{c} \) of BiCh\(_2\)-based superconductors depends on the carrier concentration. From among the BiCh\(_2\)-based compounds, we selected the Sr\(_{1-x}\)La\(_x\)FBiS\(_2\) system, because the carrier concentration in this system is essentially determined by the La concentration \( (x) \), and \( x \) can easily be analysed by compositional analysis, such as energy dispersive X-ray spectroscopy (EDX). Here, we synthesised polycrystalline samples of Sr\(_{1-x}\)La\(_x\)FBiS\(_2\) using \(^{32}\text{S}\) and \(^{34}\text{S}\) isotope
chemicals for the investigation of sulphur isotope effects. We confirmed that the structural characteristics (particularly lattice constants) of the examined samples are comparable on the basis of powder X-ray diffraction (XRD) analyses (Figs. 1a and 1b). Detailed Rietveld analysis results are summarised in the Supplementary file. Although small impurity peaks were observed for #34-1, the lattice constants for the examined samples were comparable as shown in Fig. 1b. The La concentration (x) analysed by EDX was \(x = 0.36\)–0.38, which is plotted in Fig. 1c. Among these samples, the carrier concentrations of samples #32-2, #34-1, and #34-2 were comparable, and that of #32-1 was slightly higher, where the sample labels indicate isotope mass (32 or 34) and batch number (1 or 2).

**Magnetisation measurements under high pressure**

As reported in a recent pressure study\(^{30}\), (Sr,La)FBiS\(_2\) shows a dramatic increase in \(T_c\) from ~3 K for the low-pressure (low-\(P\)) phase to ~10 K for the high-\(P\) phase on application of external pressure of about 1 GPa. The crystal structure of the high-\(P\) phase can be regarded as monoclinic, whereas that for the low-\(P\) phase is tetragonal, as shown in Figs. 1d and 1e, which is similar to the structural evolution of LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) under pressures\(^{16,30}\). Figures 2a-2d show the temperature dependences of magnetisation measured at 10 Oe after zero-field cooling (ZFC). All samples of #32-1, #32-2, #34-1, and #34-2 show the transition from a low-\(P\) phase to a high-\(P\) phase, as plotted in Fig. 2e. Notably, in the high-\(P\) phase after the \(T_c\) jump, \(T_c\) does not behave as a function of pressure in the examined pressure range. This trend enabled us to examine the S isotope effect for the high-\(P\) phase of the samples. Figure 3a shows selected data of the temperature dependence of magnetisation for high-\(P\) phases of #32-1, #32-2, #34-1, and #34-2. Zoomed plots near the onset temperature of the superconducting transition (\(T_c\)) are shown in Fig. 3b. To estimate \(T_c\), the temperature differential of magnetisation (\(dM/dT\)) was calculated and plotted as a function of temperature (Figs. 3c-3f). \(T_c\) was estimated to be the temperature at which linear fitting lines for just above and just below the transition cross, as indicated by the red lines in those figures. The estimated \(T_c\) are 10.40, 10.14, 9.92, and 9.71 K for the high-\(P\) phases of #32-1, #32-2, #34-1, and #34-2, respectively (see Table I). The highest \(T_c\) was observed for #32-1 with a higher La concentration (electron doping amount). For the two samples with \(^{34}\)S, \(x\) for #34-1 is slightly higher than \(x\) for #34-2, while the difference is within the error bars shown in Fig. 1c. The difference in \(T_c\), however, can be seen in Figs. 3e and 3f. The trend that a higher \(T_c\) is observed for a sample with higher \(x\) is consistent with the trend seen for #32-1. When comparing the \(T_c\) between #32-2 and #34-1, a different trend was observed; the \(T_c\) estimated for #32-2 was higher than that of #34-1 with \(x\) slightly higher than \(x\) for #32-2. This fact implies that the isotope effect in the high-\(P\) phase of Sr\(_{1-x}\)La\(_x\)FBiS\(_2\) is conventionally present. When calculating the isotope effect exponent for \(^{32}\)S and \(^{34}\)S from \(T_c\)'s of #32-2 and #34-1, we obtained \(\alpha_S = 0.36\). As La concentrations
for #32-2 and #34-2 are very close, estimation of their $\alpha_S$ may be essential, which gives $\alpha_S = 0.71$. This is a value close to the conventional $\alpha = 0.5$ expected from BCS theory. By averaging the $T_c$s of the two $\text{^{34}S}$ samples, we obtained $\alpha_S = 0.54$. There is uncertainty in the determination of the essential $\alpha_S$ for the high-$P$ phase of (Sr,La)FBiS$_2$ because $T_c$ depends on the carrier concentration in this system, and the expected difference in $T_c$ between samples with $\text{^{32}S}$ and $\text{^{34}S}$ is not large. However, with the results shown here and the systematic analyses of $\alpha_S$, we can reach the conclusion that phonons are essential for the superconductivity pairing mechanisms in the high-$P$ phase of (Sr,La)FBiS$_2$. This is in contrast to the unconventional isotope effects observed in La(O,F)BiSSe$^{26}$ and Bi$_4$O$_4$S$_3$.$^{27}$ We discuss the possible differences in the structural and electronic characteristics of (Sr,La)FBiS$_2$ ($\alpha_S = 0.54$) and La(O,F)BiSSe ($-0.04 < \alpha_{Se} < 0.04$)$^{26}$ in the following section.

**Discussion**

As summarised in Fig. 1, conventional isotope effect was observed for the high-$P$ phase of (Sr,La)FBiS$_2$, whereas unconventional isotope effects were observed in La(O,F)BiSSe and Bi$_4$O$_4$S$_3$. The clear difference between the two groups exhibiting conventional and unconventional isotope effects is the crystal system. The high-$P$ phase of (Sr,La)FBiS$_2$ has a monoclinic structure and a distorted in-plane structure in the BiS$_2$ layers.$^{19}$ In contrast, La(O,F)BiSSe and Bi$_4$O$_4$S$_3$ have tetragonal structures, in which the square Bi-Ch network forms a superconducting plane. Although the low-$P$ phase of (Sr,La)FBiS$_2$ is tetragonal, same as for La(O,F)BiSSe and Bi$_4$O$_4$S$_3$, bulk superconductivity is not observed at ambient pressure because of insufficient in-plane chemical pressure.$^{17-19,30}$ In the low pressure range, bulk superconductivity is induced, but the determination of $T_c$ is difficult because of the contribution of the superconducting states from the growing high-$P$ phase. Based on the isotope effects in the high-$P$ phase of (Sr,La)FBiS$_2$, La(O,F)BiSSe, and Bi$_4$O$_4$S$_3$, we suggest that structural symmetry breaking in the superconducting BiCh$_2$ layer is an essential factor in the switching of the isotope effect from unconventional to conventional.

We calculated the band structures of (Sr,La)FBiS$_2$ and La(O,F)BiSSe (see Supplementary file). Note that the calculated results for (Sr,La)FBiS$_2$ are based on the tetragonal structure of the low-$P$ phase, because structural parameters for the high-$P$ phase have not been experimentally obtained for (Sr,La)FBiS$_2$, and the structural relaxation was not successful for the high-$P$ phase in this work. One can determine that the shape of the Fermi surface is similar between (Sr,La)FBiS$_2$ and La(O,F)BiSSe, because the expected carrier doping amount is comparable. Therefore, we consider that the different isotope effects were due to the modifications of electronic and/or phonon characteristics induced by structural symmetry breaking in the
monoclinic phase. According to previous theoretical calculations for the tetragonal and monoclinic phases of La(O,F)BiS$_2$, band splitting results from a structural transition from tetragonal (low-$P$ phase) to monoclinic (high-$P$ phase)$^{31}$. In addition, the impact of interlayer coupling between two BiS$_2$ layers, caused by the structural symmetry breaking, on the electronic states was suggested as a possibility. The switching of isotope effects between the tetragonal and monoclinic phases may be linked to the formation of the Bi–Bi bonding in the high-$P$ phase in the present system. Although high-resolution structural analyses of the high-$P$ phase of (Sr,La)FBiS$_2$ are needed to further discuss the origin of the different isotope effects, we consider that the results presented and discussed here will encourage extensive studies on the mechanisms of superconductivity in BiCh$_2$-based compounds. The BiCh$_2$-based superconductor family will be useful as a new platform for the investigation into the physics in the crossover regime between phonon-mediated and unconventional superconducting states.

In conclusion, we synthesised (Sr,La)FBiS$_2$ polycrystalline samples with $^{32}$S and $^{34}$S isotope chemicals. With magnetisation measurements under high pressure, we investigated the sulphur isotope effects on $T_c$ for a high-$P$ phase of (Sr,La)FBiS$_2$. As a conventional shift in $T_c$ was observed, we suggested the importance of phonons for the pairing mechanisms for the high-$P$ phase. Based on comparisons with isotope effects in La(O,F)BiSSe and Bi$_4$O$_3$S$_3$, in which unconventional isotope effects have been observed, we suggest that structural symmetry breaking from tetragonal to monoclinic is a key factor for the switch of the isotope effects in the BiCh$_2$-based superconductor family.

Methods

Polycrystalline samples of (Sr,La)FBiS$_2$ were prepared by a solid-state reaction method in an evacuated quartz tube. Powders of La (99.9%), SrF$_2$ (99%), and Bi (99.999%) were mixed with powders of $^{32}$S (ISOFLEX: 99.99%) or $^{34}$S (ISOFLEX: 99.26%) with a nominal composition of Sr$_{0.5}$La$_{0.5}$FBiS$_2$ in an Ar-filled glove box. The mixed powder was pelletised, and sintered in an evacuated quartz tube at 700 °C for 20 h, followed by furnace cooling to room temperature. The obtained compounds were thoroughly mixed, ground, and sintered under the same conditions as the first sintering.

The phase purity and crystal structure of the (Sr,La)FBiS$_2$ samples were examined by laboratory X-ray diffraction (XRD) by the $\theta$-2$\theta$ method with Cu-K$\alpha$1 radiation on a SmartLab (RIGAKU) diffractometer. The schematic images of crystal structures were drawn by VESTA$^{32}$ using structural data refined by Rietveld refinement using RIETAN-FP$^{33}$. The actual compositions of the examined samples were analysed using energy dispersive X-ray spectroscopy (EDX) on a TM-3030 instrument (Hitachi).
The temperature dependence of the magnetisation at ambient pressure and under high pressures was measured using a superconducting quantum interference device (SQUID) on MPMS-3 (Quantum Design) after zero-field cooling (ZFC). Hydrostatic pressures were generated by the MPMS high-pressure capsule cell. The sample was immersed in a pressure transmitting medium (Daphene 7373) and covered with a Teflon cell. The pressure at low temperature was calibrated based on the superconducting transition temperature of the Pb manometer.

Data availability
All relevant data are available from the corresponding authors upon reasonable request.

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Author contributions
A.Y. and Y.M. led the project. A.Y., K. H., Y.G., and Y.M. explored a phase suitable for the investigation of the sulphur isotope effects. A.Y. synthesised the samples. A.Y. and Y.M. characterised the samples using XRD and EDX. A.Y. and Y.G. performed the magnetisation measurements under pressure. Theoretical calculations were carried out by H.U. and K.K. The manuscript was written by A.Y., H.U., and Y.M. with input from all co-authors.

Competing Interests
The authors declare no competing interests.

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Table I. Sample label, $x_{\text{EDX}}$, and $T_c$ for the isotope samples of Sr$_{1-x}$La$_x$FBi$_2$.

| Sample label | $x_{\text{EDX}}$   | $T_c$ (K) | Applied pressure (GPa) |
|--------------|--------------------|-----------|------------------------|
| #32-1        | 0.387(8)           | 10.40     | 1.21                   |
| #32-2        | 0.361(12)          | 10.14     | 1.36                   |
| #34-1        | 0.368(8)           | 9.92      | 1.37                   |
| #34-2        | 0.361(8)           | 9.71      | 1.39                   |
Fig. 1. Structural and compositional data for Sr$_{1-x}$La$_x$FBiS$_2$ samples with different isotope mass for sulphur. (a) Powder XRD patterns for #32-1, #32-2, #34-1, and #34-2. Numbers above the XRD pattern are Miller indices. Small amount of Bi impurity was detected for #34-1 as indicated by arrows. (b) Zoomed XRD patterns near the 102 and 004 peaks. (c) La concentration ($x$) analysed by EDX. (d-g) Schematic images of crystal structure of the low-$P$ (tetragonal) phase and the high-$P$ phase (monoclinic) of (Sr,La)FBiS$_2$ and the tetragonal phase of La(O,F)BiSSe and Bi$_4$O$_4$S$_3$. For comparison of the isotope effect exponent ($\alpha$) and the crystal structure, $\alpha_S$ for (Sr,La)FBiS$_2$, $\alpha_{Se}$ for La(O,F)BiSSe$^{26}$, and $\alpha_S$ for Bi$_4$O$_4$S$_3$$^{27}$ (a half unit cell) are shown.
Fig. 2. External pressure effects on the temperature dependence of magnetisation for isotope samples of Sr$_{1-x}$La$_x$FBi$_2$S$_4$. (a-d) Temperature dependences of magnetisation for 32-1, #32-2, #34-1, and #34-2, respectively. Superconducting transitions at around 7 K are $T_c$ of the Pb manometer. (e) Pressure dependence of $T_c$. Note that the $T_c$ for low-$P$ phases was roughly estimated because of superconducting signals mixed with those of the high-$P$ phase and the Pb manometer.
Fig. 3. Estimation of $T_c$ onset from data of the temperature dependences of magnetisation for isotope samples of Sr$_{1-x}$La$_x$FBiS$_2$. (a) Temperature dependences of magnetisation for the high-$P$ phases of 32-1, #32-2, #34-1, and #34-2. (b) Zoomed figure of (a) near the $T_c$. (c-f) Temperature dependence of the temperature differential of magnetisation for 32-1, #32-2, #34-1, and #34-2. $T_c$ was estimated as the temperature at which linear fitting lines of just above and just below the onset of the transition cross as indicated by the red lines in the figures.
Supplementary file

Conventional isotope effect in BiS\(_2\)-based superconductor (Sr,La)FBiS\(_2\):
possible pairing mechanism switching driven by structural symmetry breaking

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Table S1. Rietveld refinement results for the examined Sr\(_{1-x}\)La\(_x\)FBiS\(_2\) samples with \(^{32}\)S and \(^{34}\)S isotopes. In the refinements, a single-phase analysis mode was used, and the La concentration \(x\) was fixed as the value determined by EDX.

| Label | \#32-1 | \#32-2 | \#34-1 | \#34-2 |
|-------|--------|--------|--------|--------|
| \(x\) (EDX) | 0.387(8) | 0.361(12) | 0.368(8) | 0.361(8) |
| Space group | | Tetragonal \(P4/nmm\) (#194) | | |
| \(a\) (Å) | 4.084 (3) | 4.084(4) | 4.084(3) | 4.083(4) |
| \(c\) (Å) | 13.352(11) | 13.353(13) | 13.366(11) | 13.345(12) |
| \(z\) (Sr,La) | 0.1108(2) | 0.1109(2) | 0.1141(3) | 0.1133(3) |
| \(z\) (Bi) | 0.62368(14) | 0.6226(2) | 0.6256(2) | 0.6245(2) |
| \(z\) (S1) | 0.3703(10) | 0.3780(9) | 0.3638(12) | 0.3692(12) |
| \(z\) (S2) | 0.8165(6) | 0.8112(6) | 0.8192(7) | 0.8156(7) |
| \(R_{wp}\) (%) | 14.1 | 13.0 | 15.9 | 13.1 |

[Atomic coordinates]
(Sr,La): (0, 0.5, \(z\))
F: (0, 0, 0)
Bi: (0, 0.5, \(z\))
S1 (in-plane site): (0, 0.5, \(z\))
S2 (out-of-plane site): (0, 0.5, \(z\))
Fig. S1. Calculated band structure for $\text{Sr}_{0.6}\text{La}_{0.4}\text{FBiS}_2$ (tetragonal) and $\text{LaO}_{0.6}\text{F}_{0.4}\text{BiSSe}$ (tetragonal). (a, c) Calculated electronic band structure and Fermi surface for $\text{Sr}_{0.6}\text{La}_{0.4}\text{FBiS}_2$. The band calculations were performed from a (Ba,La)FBiS$_2$ model with a lattice structure of Sr$_{1-x}$La$_x$FBiS$_2$ with $x = 0.4$. (b, d) Calculated electronic band structure and Fermi surface for LaO$_{1-x}$F$_x$BiSSe with $x = 0.4$. 
Methods for band calculations

First-principles band calculations for Sr$_{1-x}$La$_x$BiS$_2$ and LaO$_{1-x}$F$_x$BiSSe were performed using the WIEN2k package$^{1,2}$. We used a virtual crystal approximation to simulate partial substitution. Because of technical reasons concerning the virtual crystal approximation, we used Ba instead of Sr for (Sr,La)FBiS$_2$. In the WIEN2k package, the virtual crystal approximation can be performed for elements adjacent to each other in the periodic table. We calculated the electronic band structure of (Sr,La)FBiS$_2$ using the VASP package$^{3,4}$, assuming virtual crystal approximation. We have confirmed that the electronic band structure is not strongly affected by the replacement of Sr by Ba in the calculations. The electronic band structures of Br$_{0.6}$La$_{0.4}$FBiS$_2$ and LaO$_{0.6}$F$_{0.4}$BiSSe were obtained by adopting the experimental lattice constants of Sr$_{1-x}$La$_x$FBiS$_2$ (#32-2: parameters shown in Table S1) and LaO$_{0.6}$F$_{0.4}$BiSSe$^5$, respectively. We used $RK_{\text{max}} = 7$ and a 18×18×5 $k$-mesh for self-consistent calculations, and adopted the Perdew-Burke-Ernzerhof exchange-correlation functional$^6$ including the spin-orbit coupling.

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