Possible pairing mechanism switching driven by structural symmetry breaking in BiS$_2$-based layered superconductors

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Investigation of isotope effects on superconducting transition temperature ($T_c$) is one of the useful methods to examine whether electron–phonon interaction is essential for pairing mechanisms. The layered BiCh$_2$-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 Bi$_4$O$_4$S$_3$. In this study, we investigated the isotope effects of $^{32}$S and $^{34}$S in the high-pressure phase of (Sr,La)FBiS$_2$, which has a monoclinic crystal structure and a higher $T_c$ of ~10 K under high pressures, and observed conventional-type isotope shifts in $T_c$. The conventional-type isotope effects in the monoclinic phase of (Sr,La)FBiS$_2$ are different from the unconventional isotope effects observed in La(O,F)BiSSe and Bi$_4$O$_4$S$_3$, which have a tetragonal structure. The obtained results suggest that the pairing mechanisms of BiCh$_2$-based superconductors could be switched by a structural-symmetry change in the superconducting layers induced by pressure effects.

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 $\alpha \sim 0.5$ is expected according to BCS theory$^1$. For instance, $\alpha$ values close to 0.5 have been detected in (Ba,K)BiO$_3$ ($\alpha_O \sim 0.5$)$^2$, MgB$_2$ ($\alpha_B \sim 0.3$)$^3$, and borocarbides ($\alpha_B \sim 0.3$)$^4$. In addition, the hydrides (H$_3$S and LaH$_{10}$) high-$T_c$ superconductors also showed a conventional shift in $T_c$ with $\alpha_H = 0.3$–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 (Ch: S, Se) superconductors, has been extensively studied since its discovery in 2012$^9$–$^{11}$. 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$^{11}$. 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$_2$ (RE: rare earth)$^{9,10}$. In addition, the superconducting properties of BiCh$_2$-based systems are very sensitive to the effects of external (physical) and/or chemical pressures$^{14,15}$. 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 ($T_c > 10$ 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$^{17}$. 

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Regarding the mechanisms of superconductivity in the BiCh₂-based family, the pairing mechanisms of the BiCh₂-based superconductor family are still controversial⁰⁹, 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 states²¹–²³, recent theoretical calculations of $T_c$ indicated that a $T_c$ of an order of several K to 10 K in BiS₂-based superconductors with a tetragonal structure cannot be explained within phonon-mediated models²⁴. Furthermore, angle-resolved photoemission spectroscopy (ARPES) proposed unconventional pairing mechanisms owing to the observation of a highly anisotropic superconducting gap in NdO₀.₇₁F₀.₂₉BiS₂²⁵. In addition, a study on the Se isotope effect with ⁷⁶Se and ⁸⁰Se in LaO₀.₆F₀.₄BiSSe (Fig. 1f) indicated the possibility of unconventional (non-phonon) mechanisms with $\alpha_{Se}$ close to 0 (−0.04 < $\alpha_{Se}$ < 0.04)²⁶. In addition, we have recently reported on an unconventional isotope effect with ³²S and ³⁴S in Bi₄O₄S₃ (−0.1 < $\alpha_{S}$ < 0.1) (Fig. 1g)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 BiCh₂-based superconductors.

Figure 1. Structural and compositional data for Sr₁−$x$LaₓFBiS₂ 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 and LaF₃ impurities were 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)FBiS₂, and the tetragonal phase of La(O,F)BiSSe and Bi₄O₄S₃. To emphasise the presence of quasi-one-dimensional network in the monoclinic phase (e), only the shorter Bi-S bonds were depicted. For comparison of the isotope effect exponent (α) and the crystal structure, $\alpha_S$ for (Sr,La)FBiS₂, $\alpha_{Se}$ for La(O,F)BiSSe²⁶, and $\alpha_S$ for Bi₄O₄S₃²⁷ (a half unit cell) are shown.

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Results

Characterisation of isotope samples. In general, the shift in $T_c$ due to isotope effects is very small, even with $\alpha \approx 0.5$ 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 $^{32}$S and $^{34}$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 (Fig. 1a,b). Detailed Rietveld analysis results are summarised in the Supplementary file.

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 Fig. 1d,e, which is similar to the structural evolution of LaO$_{0.5}$F$_{0.5}$BiS$_2$ under pressures.$^{16,30}$ Figure 2a–d 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 change by an increase in applied pressure below 1.4 GPa. A similar behaviour was reported for EuFBiS$_2$; the pressure dependence of $T_c$ of EuFBiS$_2$ showed a plateau under pressures above the critical pressure.$^{31}$ The appearance of the $T_c$ plateau would be related to the structural characteristics of BiS$_2$-based superconductors composed of fluoride-type blocking layers. 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 (d$M$/dT) was calculated and plotted as a function of temperature (Fig. 3c–f). $T_c$ was estimated to be the temperature at which linear fitting lines for just below the transition temperature within a range of 0.5 K, as indicated by the red lines in those figures. The estimated $T_c$ are 10.42, 10.16, 9.94, and 9.73 K for the high-$P$ phases of #32-1, #32-2, #34-1, and #34-2, respectively (see Table 1 for the error). 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

Figure 2. External pressure effects on the temperature dependence of magnetisation for isotope samples of Sr$_{1-x}$La$_x$FBiS$_2$. (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 $T_c$. The inset shows the enlarged plot for the data of high-$P$ phases. 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. See Supplementary file for the estimation of the $T_c$ for the low-$P$ phase.
Figure 3. Estimation of $T_c^{\text{onset}}$ from data of the temperature dependences of magnetisation for isotope samples of $\text{Sr}_x\text{La}_{1-x}\text{FBiS}_2$. (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.

Table 1. Sample label, $x_{\text{EDX}}$, and $T_c$ for the isotope samples of $\text{Sr}_x\text{La}_{1-x}\text{FBiS}_2$.
slightly higher than $x$ for #34-2, while the difference is within the error bars shown in Fig. 1c. The difference in $T_c$ can be seen in Fig. 3e,f. The trend that a higher $T_c$ is observed for a sample with higher $x$ is consistent with the trend seen for #32-1 and #32-2. Although the $T_c$ is sensitive to the La concentration, we can reach a conclusion by comparing the $T_c$ based on the analysed La concentrations. 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.

As La concentrations for #32-2 and #34-2 are very close, estimation of their $\alpha_C$ may be essential, which gives $\alpha_C \sim 0.7$. This value is slightly larger than the conventional $\alpha = 0.5$ expected from BCS theory, but it suggests the importance of phonon-mediated pairing in the high-$P$ phase of (Sr,La)FBiS$_2$. There are uncertainties in the determination of the essential $\alpha_C$ 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 $^{32}$S and $^{34}$S is not large. However, with the results shown here and the systematic analyses of $\alpha_C$, 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$_2$ and Bi$_4$O$_4$S$_3$. We discuss the possible differences in the structural and electronic characteristics of (Sr,La)FBiS$_2$ ($\alpha_C \sim 0.7$) and La(O,F)BiSSe ($-0.04 < \alpha_C < 0.04$) in the following section.

**Discussion**

As summarised in Fig. 1, isotope effect suggesting the importance of phonon 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$_3$ [30]. Although there are some possible factors, which could affect isotope effect, other than pairing states [31,32], we consider that the observed difference in isotope effect is essentially caused by the different pairing states between those systems. The reason for proposing the scenario is the recent observation of nematic superconductivity in La(O,F)BiSSe [33,34]; nematic superconductivity has been observed in unconventional superconductors like Fe-based and Bi$_2$Se$_3$-based superconductors [35,36]. Since nematic superconductivity emerges in both LaO$_{0.5}$F$_{0.5}$BiSSe (tetragonal) and LaO$_{0.5}$F$_{0.5}$BiSSe (tetragonal) and Bi$_4$O$_4$S$_3$ (tetragonal) with different carrier concentrations but with comparable structures of the BiSSe conducting layer, unconventional pairing states would commonly present in tetragonal BiCh$_2$-based superconductors with a tetragonal symmetry without structural distortion or local disorder. In contrast, nematic superconductivity was not observed in Nd(O,F)BiSSe [27], which is also tetragonal but has larger local structural disorder than La(O,F)BiSSe [11,17,19]. These facts suggest the importance of structural symmetry in the conducting layers and would support our scenario suggested in this article. Here, we discuss the possible differences in electronic states and pairing states between tetragonal and monoclinic phases.

The high-$P$ phase of (Sr,La)FBiS$_2$ has a monoclinic structure and a distorted in-plane structure in the BiS$_2$ layers [38]. 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 there are two possible superconducting transitions of the manometer (Pb) and the 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)BiSSe, band splitting results from a structural transition from tetragonal (low-$P$ phase) to monoclinic (high-$P$ phase) [38]. 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. Let us remind that the theoretical study on the calculation of $T_c$ for LaO$_{0.5}$F$_{0.5}$BiS$_2$ by Morice et al. [24] was performed on a tetragonal unit cell. Their conclusion is consistent with the unconventional isotope effects observed in tetragonal La(O,F)BiSSe and Bi$_4$O$_4$S$_3$. If the same calculation of $T_c$ could be performed on a monoclinic unit cell, a $T_c$ of 10 K may be reproducible. For that, high-resolution structural analyses of the high-$P$ phase of (Sr,La)FBiS$_2$ are needed.

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$_4$S$_3$, 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 $^{125}$S (ISOFLEX: 99.99%) or $^{35}$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. Except for the starting materials, the synthesis method was the same as our recent study on (Sr,La)FBiS$_2$.

The phase purity and crystal structure of the (Sr,La)FBiS$_2$ samples were examined by laboratory X-ray diffraction (XRD) by the θ-2θ method with Cu-Kα1 radiation on a SmartLab (RIGAKU) diffractometer. The schematic images of crystal structures were drawn by VESTA using structural data refined by Rietveld refinement using RIETAN-FP. Through the XRD analyses, Bi and LaF$_3$ impurity phases were detected. The actual compositions of the examined samples were analysed using energy dispersive X-ray spectroscopy (EDX) on a TM-3030 instrument (Hitachi). The average value of x$_{Bi}$ was calculated using the data obtained for five points on the sample surface. Standard deviation was estimated and shown in Table 1. Through the XRD analyses, small spots with La-rich compositions were found. The impurity phase will be LaF$_3$, since a LaF$_3$ phase was found in XRD.

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 made of nonmagnetic Cu-Be, as described in our recent high pressure study on (Sr,RE)FBiS$_2$. 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. The magnetisation data shown in this paper contains background magnetisation. For sample #32-1, the maximum pressure was lower than that for other samples, which is due to the setup of high-pressure cell with a shorter piston stroke.

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.

**Additional information**

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