

Two-Fold-Symmetric Magnetoresistance in Single Crystals of Tetragonal BiCh₂-Based Superconductor LaO_{0.5}F_{0.5}BiSSe

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Abstract

We have investigated the in-plane anisotropy of the *c*-axis magnetoresistance for single crystals of a BiCh₂-based superconductor LaO_{0.5}F_{0.5}BiSSe under in-plane magnetic fields. We observed two-fold symmetry in the *c*-axis magnetoresistance in the *ab*-plane of LaO_{0.5}F_{0.5}BiSSe while the crystal possessed a tetragonal square plane with four-fold symmetry. The observed symmetry lowering in magnetoresistance from the structural symmetry may be related to the nematic states, which have been observed in the superconducting states of several unconventional superconductors.

Keywords: BiCh₂-based superconductor, anisotropy of superconducting properties, structural symmetry breaking in magnetoresistance

The BiCh₂-based (Ch: S, Se) superconductor family was discovered in 2012 [1–3], and it has been extensively studied because of the layered crystal structure similar to those of the cuprate and iron-based high-transition-temperature (high- T_c) superconductors: all those layered superconductors have a square network of conduction planes [4,5]. The typical REOBiCh₂ (RE: La, Ce, Pr, Nd) system has a layered structure composed of alternate stacks of REO insulating layers and BiCh₂ conducting layers [2,3]. F substitutions at the O site generate electron carriers in the BiCh₂ layers, which results in the emergence of metallicity and superconductivity. The highest T_c among the BiCh₂-based superconductors is 11 K for LaO_{0.5}F_{0.5}BiS₂ prepared under high pressure [6,7]. Although the material variation has been widely developed, the pairing mechanisms of the superconductivity of BiCh₂-based superconductors have not been completely clarified. Recent theoretical calculations and angle-resolved photoemission spectroscopy (ARPES), however, have suggested that unconventional mechanisms are essential for the superconductivity of BiCh₂-based superconductors [8,9]. In the ARPES study, an anisotropic superconducting gap with nodes was observed in Nd(O,F)BiS₂ [9]. In addition, from a study of the selenium isotope effect on a BiCh₂-based superconductor LaO_{0.6}F_{0.4}BiSSe, the isotope effect exponent α was found to be close to zero (-0.04 < α < +0.04) [10]. This is inconsistent with the conventional electron-phonon mechanism, which generally gives $\alpha \sim 0.5$.

Recently, for layered superconductors, *nematicity* (or *nematic state*) has been a hot topic owing to its possible relation to the unconventional superconductivity states. Nematicity has been originally used for liquid crystals, and nematicity in a layered compound can be described as the spontaneous unidirectional state in which rotational symmetry breaking (lowering) is observed. Electronical nematicity has been observed in various unconventional superconductors such as cuprate and iron-based superconductors. Those superconductors show a rotational symmetry breaking of the electronic structure while the original (four-fold) lattice symmetry is maintained [11,12]. Furthermore, nematic superconductivity has been observed in Cu_xBi₂Se₃ [13–15]. The Cu_xBi₂Se₃ superconductor is known as an odd-parity superconductor, and the odd-parity states can be regarded as topological superconductivity states [14]. In the superconducting states of Cu_xBi₂Se₃, two-fold symmetry of a superconducting gap was observed while the conducting layer possessed a hexagonal network. In addition, similar symmetry breaking in the superconducting state was observed in Sr_xBi₂Se₃ as well [16]. Moreover, the superconductivity in Sr₂RuO₄, which is widely considered to be a chiral *p* wave, has been proposed as the nematic superconductivity state [17].

Since recent studies on BiCh₂-based compounds have proposed unconventional pairing mechanisms, we expected the observation of nematic or related exotic phenomena in the superconducting states of BiCh₂-based compounds. In this study, we investigated the in-plane anisotropy of the *c*-axis magnetoresistance of LaO_{0.5}F_{0.5}BiSSe single crystals under in-plane

magnetic fields. From in-plane anisotropy measurements on the *c*-axis magnetoresistance, we observed the appearance of two-fold symmetry with in-plane azimuth field angles while the crystal structure (the conducting plane) possessed a tetragonal square plane with four-fold symmetry.

$\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ single crystals were grown by using a high-temperature flux method in an evacuated quartz tube. First, polycrystalline samples of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ were prepared by the solid-state-reaction method using powders of La_2O_3 (99.9%), La_2S_3 (99.9%), Bi_2O_3 (99.999%), and BiF_3 (99.9%) and grains of Bi (99.999%) and Se (99.999%), as described in Ref. 18. A mixture of the starting materials with a nominal ratio of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ was mixed, pressed into a pellet, and annealed at 700 °C for 20 h in an evacuated quartz tube. The polycrystalline powder of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ (0.62 g) was mixed with CsCl flux (2.2 g), and the mixture was sealed into an evacuated quartz tube. The tube was heated at 900 °C for 12 h and slowly cooled to 645 °C at a rate of -1.0 °C /h, followed by furnace cooling to room temperature. At room temperature, the quartz tube was opened under air atmosphere, and the product was filtered and washed with pure water. The single crystals were analyzed by scanning electron microscopy (SEM). As shown in the inset of Fig. 1(a), plate-like crystals were obtained. The plate surface with a square shape corresponds to the *ab*-plane of tetragonal $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$. The chemical composition of the obtained crystal was investigated by energy-dispersive X-ray spectroscopy (EDX). The average ratio of the constituent elements (except for O and F) was estimated to be $\text{La} : \text{Bi} : \text{S} : \text{Se} = 1 : 0.98 : 1 : 0.98$, which was normalized by the La value. The analyzed atomic ratio is almost consistent with the nominal composition of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$. Considering the error in the EDX analysis, we regard the S : Se composition of the examined crystal as 1 : 1.

Powder X-ray diffraction (XRD) experiment was performed at room temperature by using RIGAKU Miniflex600 equipped with a D/teX-Ultra detector with a Cu-K α radiation. Figure 1(a) shows the powder XRD pattern of the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ single crystals. Only $00l$ peaks were observed, which confirms that the *ab*-plane is well developed. The *c*-axis lattice constant is roughly estimated as 13.565(7) Å. Figure 1(b) shows the F concentration dependences of the *c*-axis lattice constant for the polycrystalline and single-crystal samples of $\text{LaO}_{1-x}\text{F}_x\text{BiSSe}$. Figure 1 (b) shows the F concentration dependences of the *c*-axis lattice constant for the polycrystalline (open rectangles [18]) and single-crystal (black diamond [23], blue triangle[24], and red circles (this work)) samples of $\text{LaO}_{1-x}\text{F}_x\text{BiSSe}$. The estimated *c* for the present crystal is close to that for the polycrystalline sample with $x = 0.5$ [18]. Therefore, in this study, we call the examined crystal $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ using the nominal composition. In addition, we performed single-crystal X-ray structure analysis at room temperature on a $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ single crystal taken from the same batch of crystals used in this study. The structural parameters were refined with the tetragonal

($P4/nmm$) structural model using the refinement program of SHELXL [19]. The analysis results are summarized in Tables S1 and S2 (Supplemental Materials [20]).

The magnetoresistance measurement was performed using a superconducting magnet and the 25 T cryogen-free superconducting magnet [21] at the high field laboratory of the Institute for Materials Research (IMR), Tohoku University. Figure S1 (Supplemental Materials [20]) shows the field dependence of the electrical resistance and the temperature dependence of the H_{c2} for our single crystal of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$. The H_{c2} ($H//ab$) obtained from the Werthamer-Helfand-Hohenberg (WHH) model fitting [22] was 29.5 T for our single crystal. The large in-plane H_{c2} is consistent with the results of previous reports [23,24]. The extremely high H_{c2} could be originating from the breaking of local inversion symmetry at the conducting layers in the BiCh_2 -based superconductors [25]. Hence, we used a high field for investigating the in-plane anisotropy of H_{c2} . To control the magnetic field direction precisely, a two-axis rotational probe was used. Figure 2(a) shows a schematic image of the terminal configuration (made using Au wires and Ag pastes) for the c -axis resistivity measurements. The angles θ and ϕ are defined as shown in Fig. 3 (a). The angle θ is measured from the c -axis, and ϕ is the azimuth angle measured from the a -axis to the b -axis, although the a -axis and the b -axis are equivalent in a tetragonal crystal. Note that the charge current is always perpendicular to the magnetic field when the magnetic field is in the conducting plane, since the c -axis resistivity was measured. Figure 2(b) shows the temperature dependence of the c -axis electrical resistivity for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ single crystal. The T_c^{onset} is 4.3 K, and T_c^{zero} is 3.7 K.

Figure 3(c) shows the θ angle dependence of the c -axis resistivity at the conditions of $\phi = 90^\circ$, $\mu_0 H = 15$ T, and $T = 2.5$ K. ρ_{\min} is defined as the minimum c -axis resistivity at which the magnetic field is exactly parallel to the conducting plane. Figure 3(d) shows the ϕ dependences of ρ_{\min} at several temperatures in the range 2.0–5.0 K for Sample A shown in Fig. 3 (b). Below 3.0 K, the ϕ dependence of ρ_{\min} shows dips at $\phi = \pm 90^\circ$, indicating two-fold symmetry of ρ_{\min} . With decreasing temperature, the amplitude of the two-fold-symmetric $\rho_{\min}(\phi)$ becomes apparent. At 2.0 K, the two-fold symmetry of $\rho_{\min}(\phi)$ is still observed while ρ_{\min} approaches zero resistivity; the noisy data is due to the low resistivity close to our measurement limit. The observation of the two-fold symmetry of $\rho_{\min}(\phi)$ in the superconducting states was unexpected because the crystal structure (the conducting plane) possesses a tetragonal (four-fold) symmetry. Furthermore, the two-fold symmetry was observed in the ϕ dependence of ρ_{\min} for another sample (Sample B in Fig. 3 (b)) obtained from a different batch (See Fig. S2 of Supplemental Materials [20]). We confirmed that the two-fold symmetric behavior in ρ_{\min} is similarly observed when the electrode configuration is changed (rotated by 90°) in the distinct sample. Therefore, the two-fold symmetry in $\rho_{\min}(\phi)$ is not originating from the possible inhomogeneous current flow (See Fig. 3(b)). At 5.0 K, ρ_{\min} is almost independent of ϕ , which suggests that the observed two-fold symmetry appears in superconducting states but not in normal states.

Now, we discuss the possible origins of the observed two-fold symmetry of $\rho_{\min}(\phi)$ in the superconducting states of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$. First, it should be noted that there is a possibility of symmetry lowering of the conducting plane structure because some of the parent compounds of BiCh_2 -based superconductors show structural instability and a structural transition from tetragonal ($P4/nmm$) to monoclinic ($P2_1/m$). However, the structural transition is typical for parent (non-doped) phases and is suppressed by carrier doping. In fact, our single-crystal structural analysis showed that the space group of our $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ crystal at room temperature was tetragonal, which is consistent with the results of previous studies [18,23]. In addition, as shown in Fig. S4 of Supplemental Materials [20], the temperature scan of the synchrotron powder X-ray diffraction pattern for the polycrystalline sample of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ (not single crystal) confirmed no structural transition down to 100 K. The split of the 200 peak was observed when the transition from tetragonal to monoclinic (or orthorhombic) occurred. Furthermore, no anomaly was observed in the temperature dependence of resistivity from 300 to 5 K (See Fig. S3 of Supplemental Materials [20]). Therefore, we consider that the observed two-fold symmetry is due to electronic (or orbital) origins and not due to structural origins. Then, the possible scenario is the appearance of nematic states as observed in other unconventional layered superconductors such as the cuprate, Fe-based, and doped Bi_2Se_3 superconductors [13–16]. Although there has been no theoretical prediction about nematicity in the superconducting states of BiCh_2 -based compounds, we can expect that unconventional mechanisms of superconductivity are emerging in the examined crystal, on the basis of recent theoretical and experimental studies on the BiCh_2 -based system [8–10]. Hence, the observed two-fold symmetry of the c -axis magnetoresistance may be related to the unconventional superconductivity linked with fluctuations of electronic states. To obtain further knowledge on the superconductivity mechanisms and the anisotropic (possibly nematic) states, studies of anisotropy on thermodynamic parameters for BiCh_2 -based superconductors are desired.

In conclusion, we have investigated the in-plane anisotropy of the c -axis magnetoresistance of single crystals of a BiCh_2 -based superconductor $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ under in-plane field configuration. We observed two-fold symmetry of the c -axis magnetoresistance in the ab plane of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ while the conducting plane possessed a tetragonal square plane with four-fold symmetry. We consider that the observed in-plane anisotropy of the c -axis magnetoresistance would be due to electronic (or orbital) origins and not due to structural origins. The observed two-fold symmetry is possibly related to the nematic states, which have been observed in the superconducting states of several unconventional superconductors with a layered structure.

Acknowledgement

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Reference

- [1] Y. Mizuguchi, H. Fujihisa, Y. Gotoh, K. Suzuki, H. Usui, K. Kuroki, S. Demura, Y. Takano, H. Izawa, O. Miura, *Phys. Rev. B* **86**, 220510 (2012).
- [2] Y. Mizuguchi, S. Demura, K. Deguchi, Y. Takano, H. Fujihisa, Y. Gotoh, H. Izawa, O. Miura, *J. Phys. Soc. Jpn.* **81**, 114725 (2012).
- [3] Y. Mizuguchi, *J. Phys. Chem. Solids*, **84**, 34 (2015).
- [4] J. G. Bednorz, K. A. Müller, *Z. Phys. B-Condens. Matter* **64**, 189 (1986).
- [5] Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
- [6] K. Deguchi, Y. Mizuguchi, S. Demura, H. Hara, T. Watanabe, S. J. Denholme, M. Fujioka, H. Okazaki, T. Ozaki, H. Takeya, T. Yamaguchi, O. Miura, Y. Takano, *EPL* **101**, 17004 (2013).
- [7] Y. Mizuguchi, T. Hiroi, J. Kajitani, H. Takatsu, H. Kadowaki, O. Miura, *J. Phys. Soc. Jpn.* **83**, 053704 (2014).
- [8] C. Morice, R. Akashi, T. Koretsune, S. S. Saxena, R. Arita, *Phys. Rev. B* **95**, 180505 (2017).
- [9] Y. Ota, K. Okazaki, H. Q. Yamamoto, T. Yamamoto, S. Watanabe, C. Chen, M. Nagao, S. Watauchi, I. Tanaka, Y. Takano, S. Shin, *Phys. Rev. Lett.* **118**, 167002 (2017).
- [10] K. Hoshi, Y. Goto, Y. Mizuguchi, *Phys. Rev. B* **97**, 094509 (2018).
- [11] J. Wu, A. T. Bollinger, X. He, I. Božović, *Nature* **547**, 432 (2017).
- [12] S. Kasahara, H. J. Shi, K. Hashimoto, S. Tonegawa, Y. Mizukami, T. Shibauchi, K. Sugimoto, T. Fukuda, T. Terashima, Andriy H. Nevidomskyy, Y. Matsuda, *Nature* **486**, 382 (2012).
- [13] Y. S. Hor, A. J. Williams, J. G. Checkelsky, P. Roushan, J. Seo, Q. Xu, H. W. Zandbergen, A. Yazdani, N. P. Ong, R. J. Cava, *Phys. Rev. Lett.* **104**, 057001 (2010).
- [14] S. Yonezawa, K. Tajiri, S. Nakata, Y. Nagai, Z. Wang, K. Segawa, Y. Ando, Y. Maeno, *Nature Phys.* **13**, 123 (2017).
- [15] K. Matano, M. Kriener, K. Segawa, Y. Ando, G. Zheng, *Nat. Phys.* **12**, 852 (2016).
- [16] Y. Pan, A. M. Nikitin, G. K. Araizi, Y. K. Huang, Y. Matsushita, T. Naka, A. de Visser, *Sci. Rep.* **6**, 28632 (2016).
- [17] W. Huang and H. Yao, *Phys. Rev. Lett.* **121**, 157002 (2018).
- [18] K. Nagasaka, A. Nishida, R. Jha, J. Kajitani, O. Miura, R. Higashinaka, T. D. Matsuda, Y. Aoki, A. Miura, C. Moriyoshi, Y. Kuroiwa, H. Usui, K. Kuroki, Y. Mizuguchi, *J. Phys. Soc. Jpn.* **86**, 074701 (2017).
- [19] G. M. Sheldrick, *Acta Cryst. C* **71**, 3 (2015).
- [20] (Supplemental Materials) Experimental data obtained with a different crystal grown from a different precursor and the temperature dependence of electrical resistivity and synchrotron X-ray data (200 peak) for LaO_{0.5}F_{0.5}BiSSe are shown. Single crystal structural analysis result and the temperature dependence of the H_{c2} are also displayed.

- [21] S. Awaji, K. Watanabe, H. Oguro, H. Miyazaki, S. Hanai, T. Tosaka, and S. Ioka, *Sci. Technol.* **30**, 065001 (2017).
- [22] N. R. Werthamer, E. Helfand and P. C. Hohenberg, *Phys. Rev.* **147**, 295 (1966).
- [23] M. Tanaka, T. Yamaki, Y. Matsushita, M. Fujioka, S. J. Denholme, T. Yamaguchi, H. Takeya, Y. Takano, *Appl. Phys. Lett.* **106**, 112601 (2015).
- [24] N. Kase, Y. Terui, T. Nakano, N. Takeda, *Phys. Rev. B* **96**, 214506 (2017).
- [25] Y. C. Chan, K. Y. Yip, Y. W. Cheung, Y. T. Chan, Q. Niu, J. Kajitani, R. Higashinaka, T. D. Matsuda, Y. Yanase, Y. Aoki, K. T. Lai, and S. K. Goh, *Phys. Rev. B* **97**, 104509 (2018).

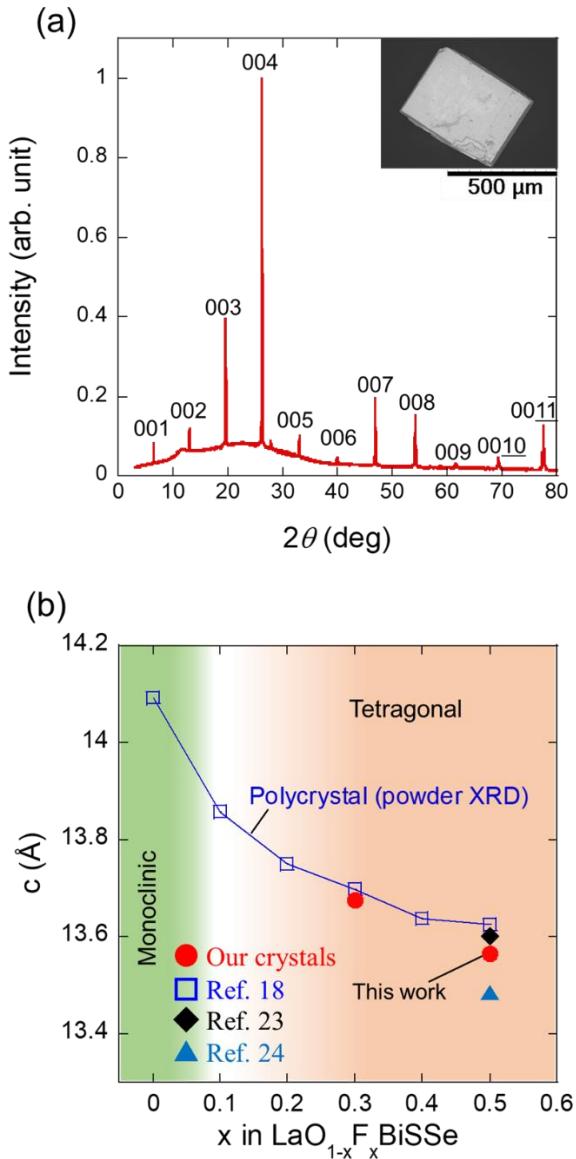


Fig. 1. (color online) (a) XRD pattern of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ single crystals. The inset shows an SEM image of a $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ single crystal. (b) F concentration (x) dependences of the c -axis lattice constant for single crystals and polycrystalline samples of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ [18, 23, 24].

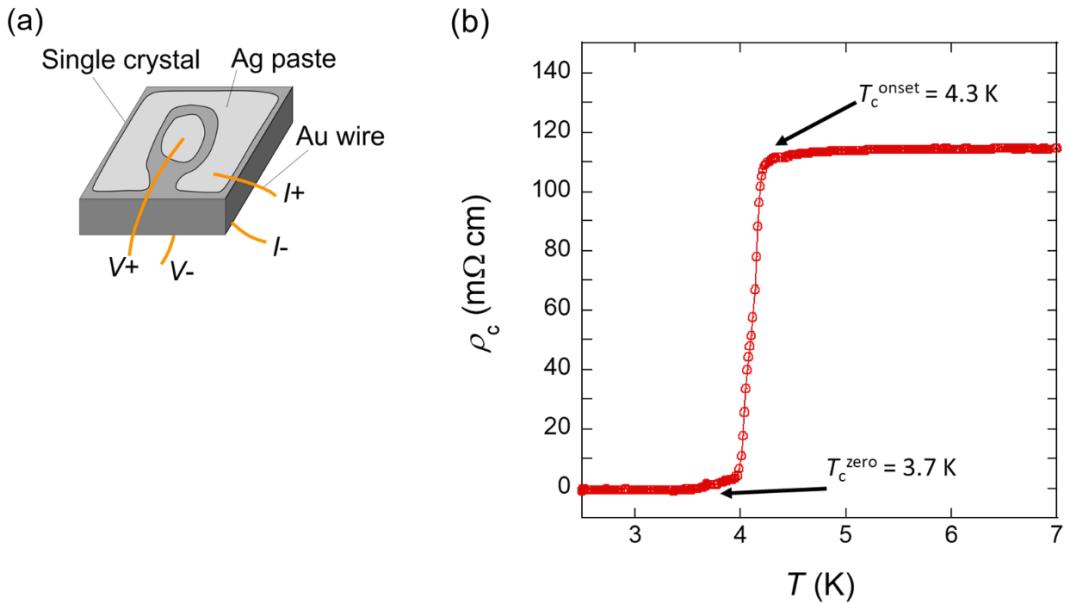


Fig. 2. (color online) (a) Schematic image of the terminal configuration (Au wires and Ag pastes) for the *c*-axis electrical resistivity measurements. (b) Temperature dependence of the *c*-axis electrical resistivity for a $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ single crystal from 2.5 to 7.0 K.

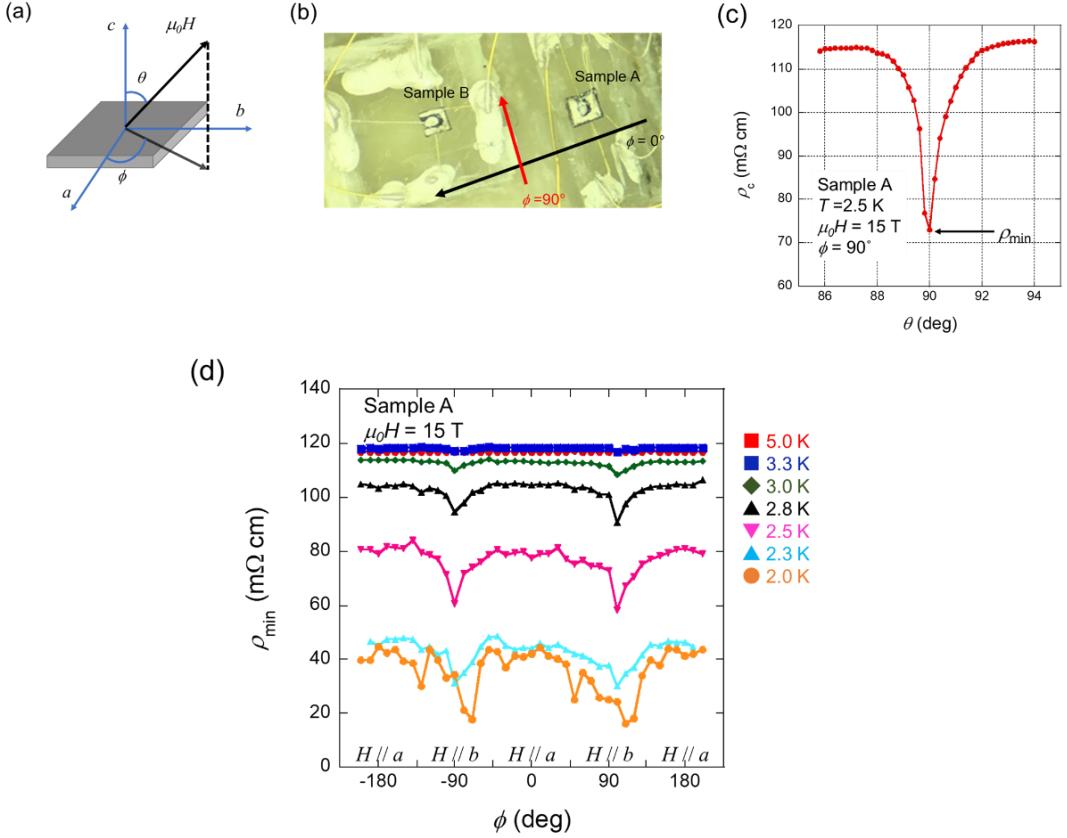


Fig. 3. (color online) (a) Schematic image of the rotation angles for the anisotropy measurement. (b) Photograph of samples and terminals used in the measurements. The in-plane anisotropy measurements of sample A and B are shown in the Fig. 3 (d) and Fig. S2 (Supplemental Materials [20]), respectively. (c) θ angle dependence of the c -axis electrical resistivity at $\phi = 90^\circ$, $\mu_0 H = 15$ T, and $T = 2.5$ K. (d) ϕ dependences of ρ_{\min} at several temperatures in the range 2.0–5.0 K.

[Supplemental Materials]

Two-Fold-Symmetric Magnetoresistance in Single Crystals of Tetragonal BiCh₂-Based Superconductor LaO_{0.5}F_{0.5}BiSSe

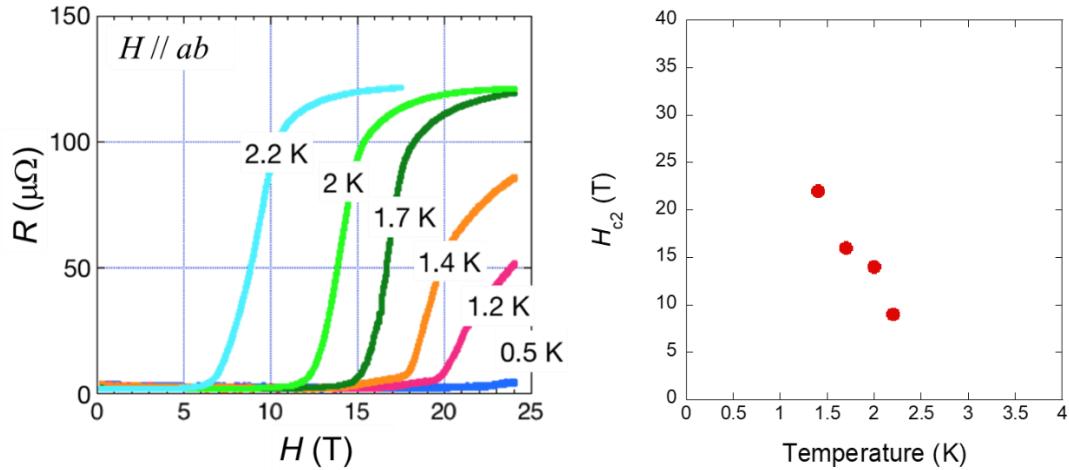


Fig. S1(a). The field dependence of the electrical resistance with various temperature for our single crystal of LaO_{0.5}F_{0.5}BiSSe obtained from the same batch of the investigated crystal. Fig. S1(b). The temperature dependence of the H_{c2} . The H_{c2} is defined as the mid-points at which the resistance drop is half of normal state.

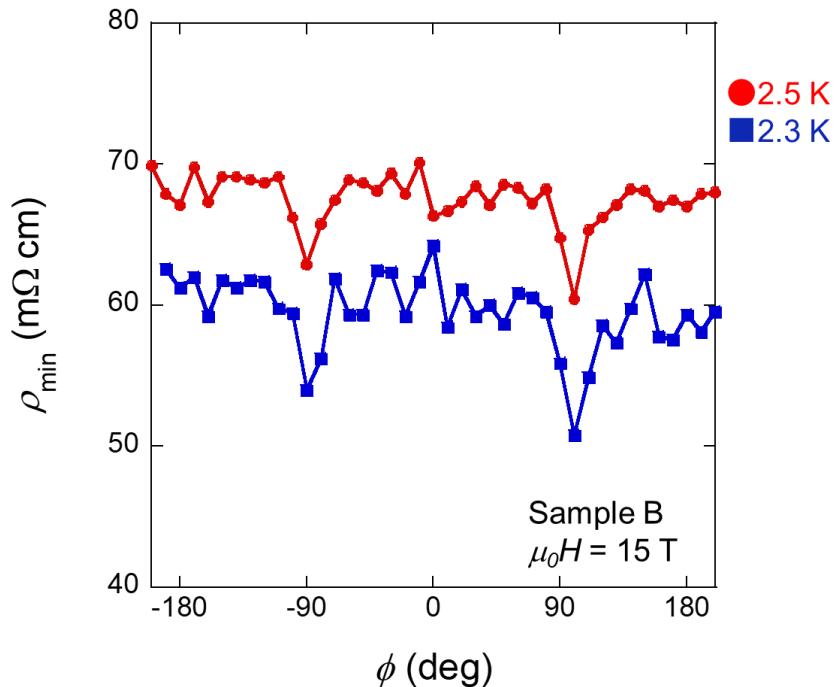


Fig. S2. ϕ angle dependences of the ρ_{\min} at $T = 2.3$ K and 2.5 K for a crystal of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ obtained from a different batch (Sample B in Fig. 3 (b)).

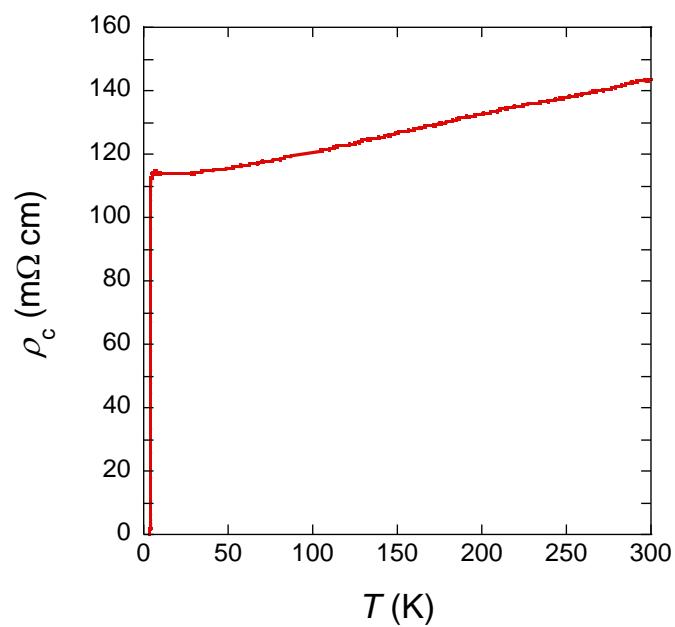


Fig. S3. Temperature dependence of electrical resistivity for the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ crystal.

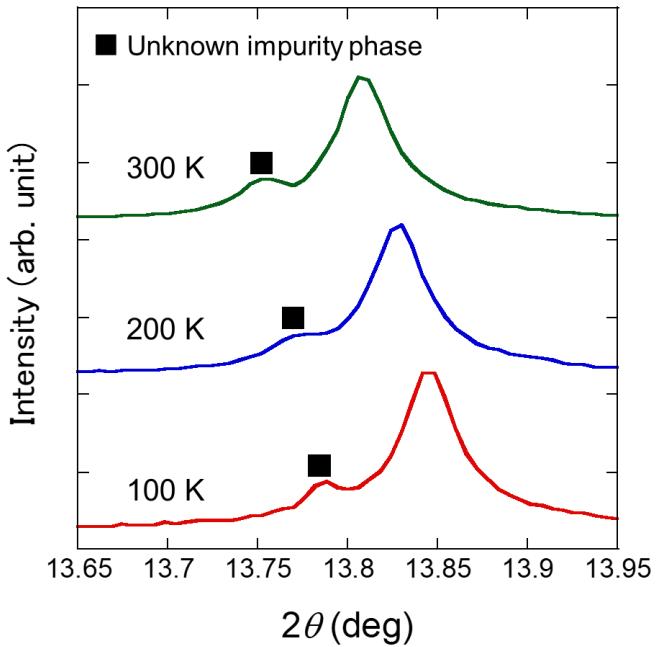


Fig. S4. The temperature dependence of the 200 peak of powder synchrotron X-ray diffraction for the polycrystalline sample of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$. A structural transition from tetragonal to lower-symmetry (monoclinic or orthorhombic) was not observed at $T > 100$ K. The data was corrected with synchrotron X-ray [$\lambda = 0.495586(1)$ Å] at BL02B2, SPring-8 under a proposal of No. 2017B1211.

Table S1. Refined atomic coordinates and B_{eq} .

site	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}} (\text{\AA}^2)$
Bi	0.25000	0.25000	0.87293(6)	1.22(3)
La	- 0.25000	- 0.25000	0.59611(9)	0.77(3)
Ch1 (Se)	- 0.25000	- 0.25000	0.87578(19)	1.50(5)
Ch2 (S)	0.25000	0.25000	0.6861(3)	0.36(7)
O/F	- 0.25000	0.25000	0.50000	0.35(19)

Table S2. Refined structural parameters and analysis condition.

Formula	LaOBiSSe
Formula weight	474.91
Space group	Tetragonal $P4/nmm$ (#129)
Lattice type	Primitive
Z value	2
<i>a</i> (\text{\AA})	4.1348(6)
<i>c</i> (\text{\AA})	13.569(3)
<i>V</i> (\text{\AA}^3)	231.98(7)
<i>R</i>	0.0280
<i>wR</i> ₂	0.0808
Crystal dimensions	0.100 \times 0.080 \times 0.040 mm
Diffractometer	XtaLAB mini (RIGAKU)
Radiation	MoK _{\alpha} ($\lambda = 0.71075 \text{\AA}$) (graphite monochromated)
Temperature (K)	293