Selenium isotope effect in the layered bismuth chalcogenide superconductor $LaO_{0.6}F_{0.4}Bi(S,Se)_2$

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We have investigated the Se isotope effect in the layered bismuth chalcogenide ($BiCh_2$-based) superconductor $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ with ^{76}Se and ^{80}Se. For all examined samples, the Se concentration, which is linked to the superconducting properties, is successfully controlled within $x = 1.09$–1.14 in $LaO_{0.6}F_{0.4}BiS_{2-x}Se_x$. From the magnetization and electrical resistivity measurements, changes in T_c are not observed for the $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ samples with ^{76}Se and ^{80}Se isotopes. Our result may indicate that the pairing in $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ is not mediated by phonons, which is consistent with recent theoretical and experimental studies suggesting unconventional superconductivity in the $BiCh_2$-based superconductors.

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I. INTRODUCTION

In most superconductors, electron-phonon interactions are responsible for the emergence of superconductivity [1]. According to the Bardeen-Cooper-Schrieffer (BCS) theory [1], the transition temperature (T_c) of a conventional superconductor is proportional to its phonon energy $\hbar\omega$, where $\hbar$ and ω are the Planck constant and phonon frequency, respectively. Therefore, the T_c of conventional electron-phonon superconductors is sensitive to the isotope effect of the constituent elements. The isotope exponent α is defined by $T_c \sim M^{-\alpha}$, where M is the isotope mass and $\alpha \sim 0.5$ is expected from the BCS theory [1]. Therefore, the isotope effect has been used to investigate whether the mechanisms of superconductors are conventional or unconventional. Indeed, α close to 0.5 has been reported in $(Ba,K)BiO_3$ ($\alpha_O \sim 0.5$) [2], doped fullerene ($\alpha_C \sim 0.4$) [3], MgB_2 ($\alpha_B \sim 0.3$) [4], and Ni- and Pd-based borocarbides ($\alpha_B \sim 0.3$) [5]. In superconductors with unconventional mechanisms, the isotope effect is not consistent with the expectation from the BCS theory. In the cuprate superconductor system, α deviates from 0.5 and shows anomalous dependence on carrier concentration [6,7]. In the Fe-based superconductor, one research group reported $\alpha_{Fe} \sim 0.4$ in SmFeAs(O,F) and $(Ba,K)Fe_2As_2$ [8], but another group reported an inverse isotope effect, negative α_{Fe} for the same composition [9].

In 2012, a new layered superconductor system with a BiS_2 superconducting layer was discovered [10,11]. Since the crystal structure of BiS_2-based superconductors resembled those of cuprate- and Fe-based superconductors, researchers have explored new BiS_2-based superconductors with higher T_c. Six typical superconductor systems with $BiCh_2$-type (Ch:S,Se) superconducting layers and various kinds of blocking layers have been discovered, and the highest record of T_c is 11 K [12,13]. The pairing mechanisms of superconductivity in the $BiCh_2$-based system have been unexplained [14]. In early theoretical calculations, conventional phonon-mediated pairing mechanisms were proposed [15]. In addition, Raman scattering, muon-spin spectroscopy measurements, and thermal conductivity experiments suggested conventional mechanisms with a fully gapped s wave [16–18]. However, recent theoretical calculations indicated that T_c with the order of several to 10 K in the BiS_2-based superconductor cannot be explained within existing conventions [19]. Furthermore, angle-resolved photoemission spectroscopy (ARPES) proposed unconventional pairing mechanisms owing to the observation of the highly anisotropic superconducting gap in $NdO_{0.71}F_{0.29}BiS_2$ [20]. Therefore, we have demonstrated the isotope effect in a $BiCh_2$-based system $La(O,F)Bi(S,Se)_2$.

On the target phase of this paper, our recent studies on $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ revealed that the emerging superconducting states in this Se-substituted system are quite homogeneous owing to the enhanced in-plane chemical pressure effect and the suppressed local in-plane disorder [21–23]; local in-plane disorder can intrinsically exist in the $BiCh_2$-based system owing to Bi lone pair electrons [24]. In addition, T_c in the $LaO_{1-x}F_xBiSSe$ does not change for $x = 0.2$–0.5, indicating that T_c is insensitive to the electron doping amount in this region. Among those, the sample with $x = 0.4$ shows the sharpest superconducting transition [23]. Based on these facts, we choose the nominal composition of $LaO_{0.6}F_{0.4}BiSSe$ to use in the isotope experiments. Since there is no stable isotope of Bi other than ^{209}Bi and Bi is too heavy for the precise investigation of the isotope effect, we used ^{76}Se and ^{80}Se isotopes. The superconductivity in $BiCh_2$-based systems emerges on the BiCh plane, and the conduction band is composed of Bi-6p orbitals hybridized with Ch-p orbitals [14,25]. In the present system, Se selectively occupies the in-plane site [23]. Therefore, the lattice vibration of Bi and Se should be responsible for the superconductivity if the conventional phonon-mediated mechanisms are working. The Se isotope effect should then be observed in $LaO_{0.6}F_{0.4}BiSSe$ if phonon mediated. Assuming $\alpha_{Se} = 0.5$ (α expected from BCS theory) and $T_c \sim 3.8$ K [23], the difference in T_c (ΔT_c) is expected to be 0.098 K between the samples with ^{76}Se and ^{80}Se. When $\alpha_{Se} = 0.2$ and 0.3, which are close to the values observed in MgB_2 and borocarbide, ΔT_c is expected to be 0.039 and 0.059 K, respectively. Therefore, before synthesizing isotope samples,

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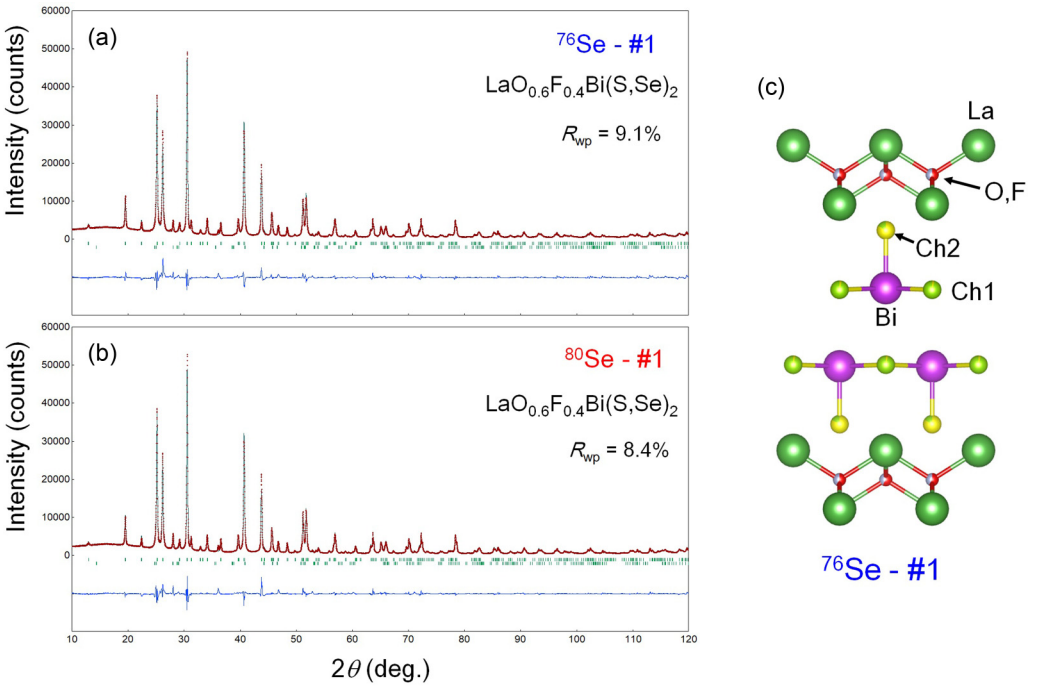

FIG. 1. (a) and (b) X-ray-diffraction patterns and Rietveld refinement results for the ^{76}Se-No. 1 and ^{80}Se-No. 1 samples. The refinements were performed by two-phase analysis with the secondary phase of BiF_3 (3%). The blue profiles plotted at the bottom are the differences between observed and calculated patterns. (c) Schematic of the refined crystal structure for the ^{76}Se-No.1 sample. The Ch1 site is the in-plane chalcogen site.

we optimized the synthesis procedure of the polycrystalline $LaO_{0.6}F_{0.4}BiSSe$ samples using conventional Se powders to investigate very small ΔT_c between ^{76}Se and ^{80}Se.

As a result of the isotope-effect study, we found that the changes in T_c between the ^{76}Se and the ^{80}Se samples, estimated from magnetization and electrical resistivity measurements, are apparently smaller than that expected from phonon-mediated mechanisms. Our results may indicate that the pairing in $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ is not mediated by phonons, which is consistent with recent theoretical and experimental studies suggesting unconventional superconductivity in the $BiCh_2$-based superconductors [19,20].

II. EXPERIMENTAL DETAILS

Polycrystalline samples with a starting nominal composition of $LaO_{0.6}F_{0.4}BiSSe$ were prepared by a solid-state-reaction method. Powders of La_2S_3 (99.9%), La_2O_3 (99.9%),

TABLE I. Information about used isotope, refined crystal structure parameters, and superconducting transition temperatures of the $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ samples examined in this paper. The atomic coordinates used in the refinements are La(0,0.5,z), O/F(0,0,0), Bi(0,0.5,z), Ch1(0,0.5,z), and Ch2(0,0.5,z).

Label	^{76}Se-No. 1	^{76}Se-No. 2	^{80}Se-No. 1	^{80}Se-No. 2
Isotope	^{76}Se (99.80%)	^{76}Se (99.80%)	^{80}Se (99.91%)	^{80}Se (99.91%)
Space group	*P*4/*nmm*	*P*4/*nmm*	*P*4/*nmm*	*P*4/*nmm*
a (Å)	4.13711(5)	4.13887(5)	4.13567(4)	4.13917(4)
c (Å)	13.6022(2)	13.6031(2)	13.6014(2)	13.6333(2)
V (Å^3)	232.811(6)	233.024(6)	232.638(4)	233.576(4)
z (La)	0.09603(9)	0.09639(8)	0.09638(8)	0.09629(7)
z (Bi)	0.62834(9)	0.62853(10)	0.62862(8)	0.62865(8)
z (Ch1)	0.3770(2)	0.3755(2)	0.3767(2)	0.3774(2)
z (Ch2)	0.8180(3)	0.8187(3)	0.8180(3)	0.8179(3)
Se occupancy at Ch1	0.980(7)	0.958(7)	0.973(6)	0.988(5)
Se occupancy at Ch2	0.121(6)	0.136(6)	0.155(6)	0.149(7)
x in $LaO_{0.6}F_{0.4}BiS_{2-x}Se_x$	1.101(13)	1.094(13)	1.128(12)	1.137(12)
R_{wp} (%)	9.1	9.3	8.4	7.2
T_c (K)_magnetization	3.77	3.76	3.76	3.77
T_{irr} (K)_magnetization	3.74	3.74	3.74	3.74
T_c (K)_resistivity	3.73		3.73	3.72

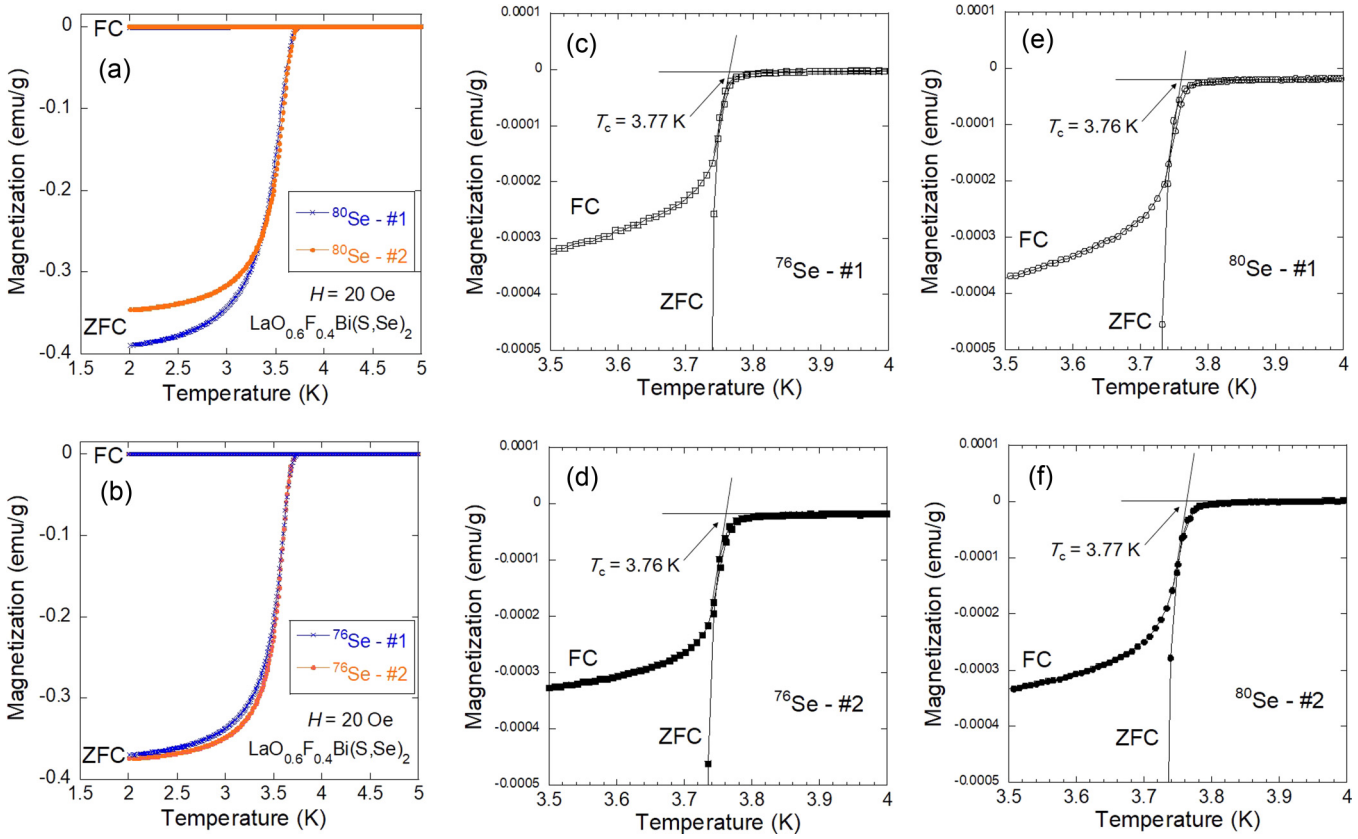

FIG. 2. (a) Temperature dependences of magnetization from 2 to 5 K for the ^{76}Se-No. 1 and ^{76}Se-No. 2 samples. (b) Temperature dependences of magnetization from 2 to 5 K for the ^{80}Se-No. 1 and ^{80}Se-No. 2 samples. ZFC and FC denote data measured after zero-field cooling and field cooling, respectively. (c)–(f) Enlarged temperature dependences of magnetization around the superconducting transition. The onset T_c is estimated as 3.77, 3.76, 3.76, and 3.77 K for ^{76}Se-No. 1, ^{76}Se-No. 2, ^{80}Se-No. 1, and ^{80}Se-No. 2, respectively. Irreversible temperature T_{irr}, defined as the temperature at which the difference between ZFC and FC curves emerges, is also estimated from these plots and listed in Table I.

Bi_2O_3 (99.99%), BiF_3 (99.9%), and Bi (99.999%) grains were used. Powders of Se isotopes ^{76}Se (99.80%) and ^{80}Se (99.91%) were purchased from ISOFLEX. The powders with the starting nominal composition of $LaO_{0.6}F_{0.4}BiSSe$ were mixed using a mortar, pressed into pellets, sealed into an evacuated quartz tube, and heated at 700 °C for 20 h. The product was ground, mixed for homogenization, pressed into pellets, and annealed in an evacuated quartz tube at 700 °C for 20 h. X-ray-diffraction (XRD) patterns were collected by a Rigaku x-ray diffractometer with Cu $K\alpha$ radiation using the 2θ-θ method with a range of $2\theta = 10°$–$120°$. The obtained x-ray patterns were refined using the Rietveld method [26]. To obtain better refinement, a secondary phase of BiF_3, typically a 3% mass fraction, was included in the refinements. In addition, very small impurity peaks, possibly LaS, were observed in the diffraction patterns. In the Rietveld refinements, occupancy at the O/F site was fixed at $O_{0.6}F_{0.4}$ because O and F cannot be reliably refined using x-ray-diffraction data. Isotropic displacement parameters were fixed as the values obtained from the refinement of the synchrotron XRD data [23]. A schematic of the crystal structure was captured using VESTA [27]. The temperature dependence of magnetization was measured after both zero-field cooling (ZFC) and field cooling (FC) using a superconducting quantum interference devise magnetometer with an applied field of 20 Oe by a magnetic property measurement system 3. The onset T_c in the magnetization measurements was defined using a cross point of two linear fitting lines as shown in Figs. 2(b)–2(e). The irreversible temperature T_{irr} was defined as the temperature at which the difference between ZFC and FC curves emerged. The temperature dependence of electrical resistivity was measured using a four-terminal method with a current of 1 mA by a physical property measurement system (Quantum Design). The T_c's in the electrical resistivity measurements were defined as the temperature where the zero-resistivity state was observed. To precisely discuss the isotope effect, we have compared the resistivity transitions for three samples measured together on the same sample pack.

III. RESULTS AND DISCUSSION

As seen in Fig. 1, using Rietveld refinement of the x-ray diffraction pattern, we confirmed that the obtained samples were structurally comparable with regard to impurity amount, lattice constant, and chalcogen (S/Se) concentration as listed in Table I. After Rietveld refinements, we found that the actual Se concentration was slightly larger than that of S in the obtained samples. Particularly, Se concentration (x) affects the superconducting properties in $LaO_{0.6}F_{0.4}BiS_{2-x}Se_x$; hence, we compare the superconducting properties of $x = 1.09$–1.14 only to precisely discuss the isotope effects. The detailed information about crystal structure parameters is summarized in Table I. Here, we show the superconducting properties of

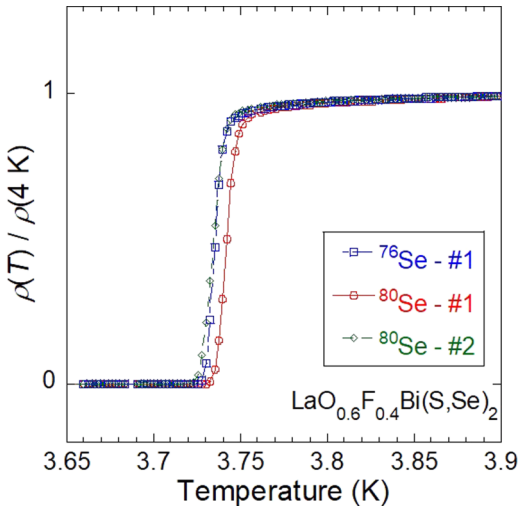

FIG. 3. Temperature dependences of normalized electrical resistivity $[\rho(T)/\rho(4\mathrm{K})]$ for the ^{76}Se-No. 1 and ^{80}Se-No. 1 samples around the superconducting transition. The onset T_c is estimated as 3.74 and 3.75 K for ^{76}Se-No. 1 and ^{80}Se-No. 1, respectively. For both samples, zero resistivity is observed at $T_c^{zero} = 3.73$ K.

two samples with ^{76}Se, labeled as ^{76}Se-No. 1 and ^{76}Se-No. 2 and two samples with ^{80}Se, labeled as ^{80}Se-No. 1 and ^{80}Se-No. 2.

Figures 2(a) and 2(b) show the temperature dependences of magnetization for the ^{76}Se-No. 1, ^{76}Se-No. 2, ^{80}Se-No. 1, and ^{80}Se-No. 2 samples. For all samples, a sharp transition and a large diamagnetic signal are observed. The enlarged figures of the magnetization around the superconducting transition are displayed in Figs. 2(c)–2(f). Surprisingly, the onset T_c does not change within 0.01 K for all samples. The onset T_c is estimated as 3.77, 3.76, 3.76, and 3.77 K for ^{76}Se-No. 1, ^{76}Se-No. 2, ^{80}Se-No. 1, and ^{80}Se-No. 2, respectively. In addition, irreversible temperature T_{irr}, defined as the temperature at which the difference between ZFC and FC curves emerged and corresponding to the emergence of the superconducting current path, is estimated to be the same $T_{irr} = 3.74$ K. Figure 3 shows the temperature dependences of normalized electrical resistivity $[\rho(T)/\rho(4\ \mathrm{K})]$ for ^{76}Se-No. 1, ^{80}Se-No. 1, and ^{80}Se-No. 2, which were measured together on the same sample pack. The resistivity data were normalized using resistivity at 4 K for comparison of T_c. T_c is estimated as 3.73, 3.73, and 3.72 K for ^{76}Se-No. 1, ^{80}Se-No. 1, and ^{80}Se-No. 2, respectively.

Based on the observed ΔT_c in the magnetization and electrical resistivity, we conclude that α_{Se} in $LaO_{0.6}F_{0.4}BiS_{2-x}Se_x$ with $x = 1.09$–1.14 is very close to zero. According to our Rietveld analyses (see Table I), the Ch1 site (the in-plane site) is almost completely occupied with Se: Se occupancy at the Ch1 site is 95–99%. Therefore, the present results indicate that phonons, at least in-plane phonons, may not be responsible for pairing in the superconductivity of $LaO_{0.6}F_{0.4}Bi(S,Se)_2$. This conclusion is consistent with the theoretical calculations by Morice *et al.* [19]. Although the pairing mechanisms for the superconductivity of $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ cannot be completely clarified with the present isotope effect only, we briefly discuss the possibility of unconventional superconductivity in this system. As mentioned above, unconventional mechanisms in the $BiCh_2$-based superconductor family have been proposed by several theoretical and experimental studies [19,20,28–30]. Particularly, the ARPES experiment observed the existence of accidental nodes in nodal s-wave symmetry and proposed several possibilities of unconventional pairing mechanisms with competition or cooperation among multiple pairing interactions, such as phonon, charge, and spin fluctuations [20]. Indeed, from neutron diffraction and pair density function analysis, the importance of charge fluctuation to the superconductivity of $La(O,F)BiS_2$ has been proposed [29]. In addition, pairing mechanisms mediated by orbital fluctuation are also possible. If our present conclusion that phonons may not be essential for superconductivity was correct, the mechanisms that are purely electronic or dominated by electronic contribution would drive the superconductivity in $LaO_{0.6}F_{0.4}Bi(S,Se)_2$. Our present results for the Se isotope effect on T_c of $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ should be an important step to clarify the mechanisms for the superconductivity of $BiCh_2$-based layered superconductors. However, to completely exclude the phonon-mediated mechanisms, we have to examine the S isotope effect for the same composition $[LaO_{0.6}F_{0.4}Bi(S,Se)_2]$ and for a system with a pure BiS_2 layer, such as $Nd(O,F)BiS_2$ with a higher T_c of 5 K.

IV. CONCLUSION

We have investigated the isotope effect on T_c of the $BiCh_2$-based layered superconductor $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ using ^{76}Se and ^{80}Se isotopes. Comparing the transition temperatures investigated from magnetization and electrical resistivity measurements, we have revealed that the exponent α_{Se} is close to zero. Our results may indicate that the pairing in $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ is not mediated by phonons, which is consistent with recent theoretical and experimental studies suggesting unconventional superconductivity in the $BiCh_2$-based superconductors.

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