Comparative ARPES studies of LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.23$ and $0.46$)

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Abstract. BiS$_2$-based layered superconductors are new superconductors, having been paid special attention due to the layered crystal structure and the characteristic electronic structure that can lead to exotic mechanism of superconductivity as well as cooperation of superconductivity and ordered phases. In this article, we report valence band dispersions and Fermi surface topology of LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.23$, $T_c < 2$ K) studied by angle-resolved photoemission spectroscopy, and compared them with those of LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.46$, $T_c = 3.1$ K). We discuss experimental $x$ dependent electronic structures and its relation to $T_c$. We also point to anomalous spectroscopic features in LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.46$) that can be explained by band structure calculations considering distorted lattice, suggesting role of dynamical or static lattice distortion to the physical properties.

1. Introduction
The new family of layered superconductors possessing double BiS$_2$ layers has provoked much attention since the discovery of Bi$_2$O$_2$S$_3$ [1]. So far mostly studied compounds are LnO$_{1-x}$F$_x$BiS$_2$ (Ln: Lanthanides), where the highest superconducting critical temperature ($T_c$) of 10.6 K has been reported for LaO$_{1-x}$F$_x$BiS$_2$ [2,3]. The crystal structure consists of alternating stack of double BiS$_2$ layers and La$_2$(O,F)$_2$ spacer layers along the $c$ axis. Some of the compounds exhibit magnetism (Ln = Ce) [4] or charge density of waves (Ln = Eu) above $T_c$ [5], suggesting interplay between the superconductivity and ordered phases.
In LaO$_{1-x}$F$_x$BiS$_2$, the parent compound shows semiconducting temperature dependence on resistivity. As the fluorine concentration ($x$) increases, superconductivity appears at $x = 0.2$, and $T_c$ increases till $x = 0.5$ and decreases with further increase of $x$ [3]. Theoretically, band structure calculations have predicted interesting electronic structure and its relation to the mechanism of the superconductivity. In LaO$_{1-x}$F$_x$BiS$_2$, band structure calculations predicted that LaOBiS$_2$ is a band insulator having a band gap of $\sim$ 0.8 eV [6-9]. While the valence band consists of S 3p (in plane and out of plane) and O 2p orbitals, the conduction band is derived from Bi 6p$_{x,y}$ and in-plane S 3p. Since the O substitution of F introduces electron carriers, the chemical potential of LaO$_{0.5}$F$_{0.5}$BiS$_2$ is expected to locate within the Bi 6p$_{x,y}$ and in-plane S 3p hybridized band. This makes the system metallic. Importantly, calculated Fermi surface has a topological change around $x \sim 0.5$ from isolated electron pockets centered around X(R) in the Brillouin zone for smaller $x$ to connected hole-like sheets around $\Gamma(Z)$ and M(A) for higher $x$ with a strong nesting with a vector ($\pi, \pi$) [along the $\Gamma(Z)$-M(A) direction]. The nested Fermi surface is originated from quasi-one-dimensional nature of the electronic structure [10] and leads to CDW instability [6,7], which can explain the pressure dependence of $T_c$ in LaO$_{0.5}$F$_{0.5}$BiS$_2$ [11]. Possibilities of exotic pairing mechanisms due to electron-electron correlation originating from the nested Fermi surface have also been examined [10,12-14,15]. Therefore, to understand the mechanism of superconductivity, it is highly desirable to experimentally investigate the normal state electronic structure.

Experimentally, photoemission spectroscopy (PES) has played an important role to elucidate the electronic structure of LnO$_{1-x}$F$_x$BiS$_2$. From valence band soft x-ray PES of polycrystalline LaO$_{1-x}$F$_x$BiS$_2$, experimental electronic structure and its $x$ dependence, namely higher binding energy shift of the valence band as well as appearance of new states near the Fermi level ($E_F$) having dominant Bi 6p character, were found to be consistent with the predictions of band structure calculations in general [16].

Angle-resolved photoemission spectroscopy (ARPES) of NdO$_{1-x}$F$_x$BiS$_2$ observed small electron-like pocket around the X(R) point in the Brillouin zone [17,18]. Large difference between the carrier concentrations determined from the observed area of the electron pocket and those estimated from nominal concentration were noticed [17,18]. ARPES studies of CeO$_{1-x}$F$_x$BiS$_2$ [19] and LaO$_{1-x}$F$_x$BiSe$_2$ ($x = 0.18$) [20] have also reported Fermi surface topology for smaller carrier concentrations. In contrast to the other ARPES studies, our vacuum ultraviolet and soft x-ray ARPES of LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.46$) showed Fermi surface topology for higher carrier concentration [21]. The observed ARPES intensity map showed electron like Fermi surface sheets and square-like intensity distribution, latter of which suggests that in the compound $E_F$ lies close to the position where topological change occurs. This means that $E_F$ is close to van Hove singularity leading to high density of states, different from ARPES of NdO$_{1-x}$F$_x$Bi$_2$. ARPES of LaO$_{1-x}$F$_x$BiS$_2$ observes the Fermi surface topology consistent with that expected from the nominal concentration determined from EDX. This indicates that LaO$_{1-x}$F$_x$BiS$_2$ is a suitable system for studying $x$ dependent changes in band structures and Fermi surface topology.

Previous PES studies have also reported anomalous features that cannot be explained by band structure calculations. Soft x-ray PES reported reduced intensity for the new states at $E_F$ [16]. Anomalous dispersive features of the electron pocket, which exhibit marked temperature dependence, was observed for ARPES data of NdO$_{1-x}$F$_x$BiS$_2$ and ascribed to strong electron-phonon coupling effects [17]. From the ARPES studies of LaO$_{1-x}$F$_x$BiS$_2$, we reported anomalous features around 0.4 eV binding energy in momentum regions away from the electron pocket [21]. Further investigation of the anomalous features can give some hint to understand the underlying physics.

In this paper, we report ARPES study of LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.23$) and compared it with our previous ARPES study of LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.46$) [21], in order to reveal $x$-dependent changes in band dispersion and Fermi surface topology. Comparative ARPES studies provide evidence for correlation between carrier concentration and $T_c$ in LaO$_{1-x}$F$_x$BiS$_2$. We also discuss a possible origin of the anomalous spectral features observed in LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.46$), suggesting that strong electron-phonon coupling and CDW instability can give influence on the physical properties.
2. Experimental

LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.23$) single crystals were grown using a CsCl/KCl flux method. The ratio of the components was estimated by electron probe microanalysis. $T_c$s were determined from the temperature where the resistivity became zero [$T_c^{\text{zero}} < 2$ K ($x = 0.23$) and $T_c^{\text{zero}} = 3.1$ K ($x = 0.46$)].

ARPES measurements were performed at BL-28A in Photon Factory with a VG Scienta electron analyzer, and the energy of a circularly polarized light was set at 70 eV. The energy resolution was set to 30 meV for $h\nu = 70$ eV, and the angular resolution of ARPS was set to 0.2°. The binding energies of samples were deduced by referencing $E_F$ of gold electronically contacted with samples. Samples were cleaved and measured in situ under a vacuum better than $3 \times 10^{-8}$ Pa at $T = 10$ K, which was above the transition temperature of the sample. The samples were stable in the vacuum and showed no sign of degradation during the measurement period of 72 h.

3. Results and discussion

3.1. Valence band dispersions

Figures 1 (a) and (b) show experimental band dispersions obtained from LaO$_{1-x}$F$_x$BiS$_2$ single crystals with $x = 0.23$ and 0.46, respectively, measured along Γ(Z)-X(R) in the Brillouin zone. The darker regions correspond to bands. Theoretical band dispersions are superimposed on the plot of $x = 0.46$ with dotted orange lines, for comparison. In both data, many bands are closely located in the region between 2 eV and 6 eV binding energies, which are derived from mainly S 3$p$ and O 2$p$ orbitals. The dispersions of two samples appear to be similar with small differences in detail. The location in energy and width of the band are nearly the same, especially at Γ(Z). In contrast, the energy position of the

![Figure 1](image_url). The valence band ARPES result of LaO$_{1-x}$F$_x$BiS$_2$ single crystal with $x = 0.23$, compared with that with $x = 0.46$ [21]. The results are made by plotting minus second derivative of near $E_F$ ARPES intensity as functions of binding energy and wave vector. Darker parts correspond to experimentally observed bands. Orange lines are theoretical band dispersions calculated from band structure calculations with SOC. The measured direction is indicated by a line in each schematic Brillouin zone.
bottom of the electron pocket is largely different. This indicates that the change of the electronic structure as a function of \( x \) is not rigid-band like. This is consistent with the band structure calculations, which predicted that the band dispersions of LaO\(_{1-x}\)F\( _x \)Bi\( _2 \)S\(_2 \) are sensitive to both lattice structure and fluorine doping [22]. Nevertheless, the change in the energy position of the bottom of the electron pocket is in line with electron doping with increasing of \( x \) and therefore the change of Fermi surface topology is expected.

Before examining Fermi surface, it is worth noticing the importance of spin-orbit coupling (SOC) of Bi \( 6p \) to explain the band structure of LaO\(_{1-x}\)F\( _x \)Bi\( _2 \)S\(_2 \). The comparison between the experimental and theoretical band dispersions in \( x = 0.46 \) sample shows some correspondence. For example, the experimental band dispersion of the electron pocket is well explained by the calculations. For the valence band, the experimental band dispersions around \( \Gamma(Z) \) at 2, 5, and 6 eV as well as that around X(R) at 1.5 eV well follow the calculated dispersions. The band structure calculations without SOC predicted a larger gap between the top of the valence band and the bottom of the electron pocket and also predicted another smaller electron pocket at X(R), which is not observed in the present data. These findings tell that the electronic structure with SOC better explains the observed band dispersions, indicating the importance of SOC for the electronic structure of LaO\(_{1-x}\)F\( _x \)Bi\( _2 \)S\(_2 \). Role of SOC has been examined from the splitting of the electron pocket [17].

### 3.2. Fermi surface

In order to look at the \( x \) dependent Fermi surface topology, we plotted the near \( E_F \) ARPES intensity map of \( x = 0.23 \) as functions of \( k_x \) and \( k_y \) and compared it with that of \( x = 0.46 \), as shown in Figs. 2(a) and (b). The darker parts correspond to the Fermi surface or the momentum regions where the band is close to \( E_F \). In both the data, Fermi surface around X(R) are clearly observed, whose electron like character are evident from the band dispersions shown in each inset. While the shape of the electron pocket in \( x = 0.23 \) sample appears to be rather circular, that in \( x = 0.46 \) sample is rectangular. The area of the electron pocket in \( x = 0.46 \) sample appears to be approximately two times larger than that in \( x = 0.23 \) sample, indicating \( x \) dependent increase of carrier concentration. Interestingly, in \( x = 0.46 \) sample, square-like intensity distribution is also found centered at the \( \Gamma(Z) \) point. These features in \( x = 0.46 \) are consistently explained by the calculated Fermi surface, which is superimposed in the figure with orange curves. The rather smaller intensity around the mid point of the corner of the square-like

![Figure 2](image-url)
intensity distribution around $\Gamma(Z)$ will be discussed in the next subsection.

In LaO$_{1-x}$F$_x$BiS$_2$, $T_c$ shows $x$ dependence: the larger $x$ concentration is, the higher $T_c$ is. The present ARPES provides direct evidence that $T_c$ is directly related to the carrier concentration, at least for LaO$_{1-x}$F$_x$BiS$_2$. On the other hand, very small carrier concentration estimated from previous ARPES of NdO$_{1-x}$F$_x$BiS$_2$ with $T_c$ of 4.5 K suggests existence of other parameters for determining $T_c$ in LnO$_{1-x}$F$_x$BiS$_2$.

3.3. Anomalous features observed in ARPES

So far we reported experimental band structure and its consistency with band structure calculations. We have also found strong deviations of the experimental electronic structure from theoretical studies. One of the results is related to the anomalous spectral intensity found in the compounds. In the insets of Fig. 2, the ARPES intensity tends to be smaller for lower binding energy. A related finding for the electron pocket was reported for ARPES of NdO$_{1-x}$F$_x$BiS$_2$ [17], where the feature was discussed in terms of strong coupling of electrons with lattice. Anomalous features in the other momentum regions may give further understanding for the electron-phonon coupling. In the upper row of Fig. 3, we show ARPES intensity maps along cuts a-f. We found that, though the band dispersions along cuts a-c are reasonably well explained by the calculated bands, those along cuts d-f cannot be done very well. In cuts d-f, large intensity is left around 0.4 eV binding energy, though the calculated bands are located close to $E_F$. Actually, the structure around 0.4 eV can be observed every cut, as shown in the second derivative maps in the lower row. One can also notice that the intensity variation of the 0.4 eV structure shows a clear momentum dependence (cuts d-f), which follows existence of the bands near $E_F$. These results seem to suggest that the structure around 0.4 eV is made up of two components: momentum dependent one and momentum independent one.

STS/STM studies reported a broad structure centered around 0.4 eV with an energy gap at $E_F$ [23], indicating insulating nature of the surface states. The momentum independent part of ARPES data, which is a localized state, may be something to do with the insulating surface electronic states observed in STS/STM. For the momentum dependent component, we would like to point out striking similarity with the band structure calculations for a distorted lattice [12,13]. According to the band structure calculations, LaO$_{1-x}$F$_x$BiS$_2$ with $x \sim 0.5$ has instability toward lattice distortion with a wave vector of $(\pi, \pi)$, due to the strong nesting and large electron-phonon coupling. The band structure calculations for the distorted lattice predicted the momentum dependent modification of bands. The band dispersions around the region where the van Hove singularity is located are largely affected by

![Figure 3](image-url)  

**Figure 3.** ARPES intensity (upper row) maps [21] and their minus second derivative (lower row) maps as functions of binding energy and wave vector measured along 6 cuts (a – f) shown in Fig. 2 (b). The white curves in the intensity maps are results of band calculations for LaO$_{0.54}$F$_{0.46}$BiS$_2$ with SOC.
the distortion. The momentum region corresponds to that around the midpoint of the square-like intensity distribution in Fig. 2(b). More specifically, the band forming the van Hove singularity, which is located slightly above $E_F$ in the undistorted lattice, can slip into occupied part in the distorted lattice. Theoretical studies predicted either static or dynamical type of distortion [6, 7]. If it is dynamical, we may be observing the sum of the snapshots of electronic structure affected by the distortion, as the time scale of PES is extremely short, an order of $10^{-15}$ second, compared to the lattice motion. We may be observing electronic structures from both the undistorted and statically distorted regions simultaneously. This may be able to explain the relatively small intensity at $E_F$ around the midpoint of the square-like intensity distribution and existence of the momentum dependent 0.4 eV structure. The similarity between the experimental observation and the theoretical prediction for distorted lattice in LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.46$) suggests that the strong electron-phonon coupling near the instability may be important to understand the physical properties.

4. Summary

The experimental band dispersions and Fermi surface topology of LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.23$) were observed by ARPES and compared with those of $x = 0.46$. The non rigid band like $x$ dependence of LaO$_{1-x}$F$_x$BiS$_2$ was observed from comparative valence band ARPES data. Increase of the area of the electron-like Fermi surface around X(R), which indicates increase of carrier concentration, was observed and found to correlate with $T_c$. This indicates that the carrier concentration is a parameter directly related to $T_c$ in LaO$_{1-x}$F$_x$BiS$_2$. The anomalous features observed around the region at the midpoint of the square-like intensity distribution can be explained by band structure calculations for distorted lattice, which suggests the importance of dynamical or static lattice distortion to consider the physical properties of LaO$_{1-x}$F$_x$BiS$_2$ ($x = 0.46$).

Acknowledgments

We thank Dr. T. Yildirim for valuable discussion. ARPES experiments at Photon Factory were performed under proposal numbers 2013G703. This work was partially supported by JSPS KAKENHI Grant Numbers 25800205 and 15H03691. This work was also partially supported by the Program for Promoting the Enhancement of Research Universities from MEXT.

References

[1] Mizuguchi Y 2015 J. Phys. Chem. Solid 84 34
[2] Mizuguchi Y, Demura S, Deguchi K, Takano Y, Fujihisa H, Gotoh Y, Izawa H and Miura O 2012 J. Phys. Soc. Jpn. 81 114725
[3] Deguchi K, Mizuguchi Y, Demura S, Hara H, Watanabe T, Denholmie S J and Takano Y 2013 Europhys. Lett. 101 17004
[4] Demura S, Deguchi K, Mizuguchi Y, Sato K, Honjyo R, Yamashita A, Yamaki T, Hara H, Watanabe T, Denholmie S J, Fujioka M, Okazaki H, Ozaki T, Miura O, Yamaguchi T, Takeya H and Takano Y 2015 J. Phys. Soc. Jpn. 84 024709
[5] Zhai H-F, Tang Z-T, Jiang H, Xu K, Zhang K, Zhang P, Bao J-K, Sun Y-L, Jiao W-H, Nowik I, Felner I, Li Y-K, Xu X-F, Tao Q, Feng C-M, Xu Z-A and Cao G-H 2014 Phys. Rev. B 90 064518
[6] Wan X, Ding H-C, Savrasov S Y and Duan C-G 2013 Phys. Rev. B 87 115124
[7] Yildirim T 2013 Phys. Rev. B 87 020506
[8] Li B, Xing Z W and Huang G Q 2013 Europhys. Lett. 101 47002
[9] Shein I R and Ivanovskii A L 2013 JETP Letters 96 769
[10] Usui H, Suzuki K and Kuroki K 2012 Phys. Rev. B 86 220501(R)
[11] Kotegawa H, Tomita Y, Tou H, Izawa H, Mizuguchi Y, Miura O, Deguchi K and Takano Y 2012 J. Phys. Soc. Jpn. 81 103702
[12] Zhou T and Wang Z D 2013 J. Supercond. Nov. Magn. 26 2735
[13] Liang Y, Wu X, Tsai W F and Hu J 2014 Front. Phys. 9 194
[14] Martins G B, Moreo A and Dagotto E 2013 Phys. Rev. B 87 081102
[15] Agatsuma T and Hotta T 2015 To appear in J. Magn. Magn. Mater.
[16] Nagira S, Sonoyama J, Wakita T, Sunagawa M, Izumi Y, Muro T, Kumigashira H, Oshima M, Deguchi K, Okazaki H, Takano Y, Miura O, Mizuguchi Y, Suzuki K, Usui H, Kuroki K, Okada K, Muraoka Y and Yokoya T 2014 J. Phys. Soc. Jpn. 83 033703
[17] Zeng L K, Wang X B, Ma J, Richard P, Nie S M, Weng H M, Wang N L, Wang Z, Qian T, Ding H 2014 Phys. Rev. B 90 054512
[18] Ye Z R, Yang H F, Shen D W, Jiang J, Niu X H, Feng D L, Du Y P, Wan X G, Liu J Z, Zhu X Y, Wen H H and Jiang M H 2014 Phys. Rev. B 90 045116
[19] Saini N L, Ootsuki D, Paris E, Joseph B, Barinov A, Tanaka M, Takano Y, Mizokawa T 2014 Phys. Rev. B 90 214517
[20] Sugimoto T, Ootsuki D, Morice C, Artacho E, Saxena S S, Schwier E F, Zheng M, Kojima Y, Iwasawa H, Shimada K, Arita M, Namatame H, Taniguchi M, Takahashi M, Saini N L, Asano T, Higashinaka R, Matsuda T D, Aoki Y, and Mizokawa T 2015 Phys. Rev. B 92 041113(R)
[21] Terashima K, Sonoyama J, Wakita T, Sunagawa M, Ono K, Kumigashira H, Muro T, Nagao M, Watauchi S, Tanaka I, Okazaki H, Takano Y, Miura O, Mizuguchi Y, Usui H, Suzuki K, Kuroki K, Muraoka Y and Yokoya T 2014 Phys. Rev. B 90 220512(R)
[22] Suzuki K, Usui H and Kuroki K 2013 Physics Procedia 45 21
[23] Machida T, Fujisawa Y, Nagao M, Demura S, Deguchi K, Mizuguchi Y, Takano Y and Sakata H 2014 J. Phys. Soc. Jpn. 83 113701