Bulk sensitive angle-resolved photoelectron spectroscopy on Nd(O,F)BiS$_2$

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Abstract. Bulk electronic structure of novel layered superconductor Nd(O,F)BiS$_2$ was studied by using soft x-ray angle-resolved photoelectron spectroscopy (ARPES). Electron-like Fermi surface centered at the X(R) point was observed, consistent with earlier ARPES reports on surface-sensitive VUV light source. Based on the comparison of the electronic structure between Nd(O,F)BiS$_2$ and La(O,F)BiS$_2$, we discuss possible important factors for the superconductivity in this series of material.

1. Introduction

BiCh$_2$-based superconductors (Ch: Chalcogen) are newly discovered materials [1] which possess similar layered structure with high-transition temperature ($T_c$) cuprates and iron-based superconductors. Their typical chemical formula is REOBiCh$_2$ where RE is rare earth atom, and it consists of alternate stacking layers of RE$_2$O$_2$ and BiCh$_2$. Except for the RE = Eu case [2], the parent compounds with stoichiometry show insulating behavior, and a partial substitution of O with F changes the system from insulator to metal and superconductivity emerges with maximum $T_c$ of 10.6 K [1]. This substitution is regarded as effective carrier doping into Bi-Ch hybridized bands [3]. Such a crystal structure of block layers and conductive layers is suggestive of a possibility that one can design a new BiCh$_2$-based
material with higher $T_c$ using a combination of ingredients, just as in cuprates and iron-based superconductors.

Interestingly, the $T_c$ in this series of superconductor shows RE-atom dependence, that is, the smaller the ion-radius of RE-atom is, the higher $T_c$ tends to be obtained. More specifically, single crystals of La(O,F)BiS$_2$ show maximum $T_c$ of ~3.1 K [4] while that of Nd(O,F)BiS$_2$ is ~5.1 K [5]. It has been pointed out that the evaluated value of the in-plane chemical pressure effect correlates well with $T_c$ [6]. There, the microscopic reason for the observed correlation has been argued in relation with electronic structures. Therefore, a comparative study of the electronic structure in a series of RE(O,F)BiS$_2$ superconductors are highly valuable.

Angle-resolved photoelectron spectroscopy (ARPES) can directly observe the experimental band dispersions thus has been served as a strong tool for studying the electronic structure in solids. In earlier ARPES results on Nd(O,F)BiS$_2$ [7,8], it has been reported that only small electron-like Fermi surface near the X(R) point exists. This is in contrast to the theoretical prediction that the Bi-S hybridized band holds van hove singularity near (π/2, π/2) which is expected to tough Fermi energy ($E_F$) by electron doping [3]. The carrier number estimated from Luttinger volume deviates far from the F content value estimated by electron-probe microanalysis (EPMA) [7,8]. Recent scanning tunneling microscope (STM) [9] reported that the electronic structure of topmost surface of Nd(O,F)BiS$_2$ obtained by cleaving does not match the density of states predicted by first principles calculations [10], suggesting that the surface electronic states can be strongly modulated from that of bulk system. Since previous ARPES studies have been performed at surface-sensitive settings, a re-examination of the electronic structure by bulk-sensitive method has been highly desired.

In this paper, we use soft x-ray ARPES to revisit the bulk electronic structure of Nd(O,F)BiS$_2$. While the surface component was observed in the Bi 4f core level spectra, the obtained Fermi surface as well as the overall electronic structure near $E_F$ well correspond to those reported earlier by surface-sensitive ARPES. We discuss the possible explanation for this phenomena and compare the results with La(O,F)BiS$_2$ [11].

2. Experimental
The single crystal of Nd(O,F)BiS$_2$ was synthesized by flux method [12]. The nominal F composition was 0.3, while EPMA analysis showed that the value was ~0.29. The soft x-ray ARPES was performed at BL25SU of SPring-8 using SES200 analyzer. The used photon energy was 880 eV for both of the core level and the valence band measurements. The energy resolution was set at approximately 0.2 eV. $E_F$ was determined by the Fermi cut-off energy of Au that was electronically contacted with the sample. The clean surface for the measurement was obtained by in-situ cleaving, and ARPES measurement was performed in an ultrahigh vacuum of ~ 10$^{-8}$ Pa.

3. Results and discussion
3.1. Core level spectra
Figure 1(a) shows the core level spectrum of Nd(O,F)BiS$_2$ in a wide energy range. Multiple peaks are observed such as Nd 4d (~120 eV), O 1s (~543 eV), F 1s (~697 eV), Bi 4f (~160 eV), and S 2s (~230 eV), that are consistent with the constituents of the sample. We did not find C 1s component around 280 eV, suggesting the high quality of the crystal. In figure 1(b), we show Bi 4f and S 2p core level spectra and their detection-angle dependence in an expanded energy range. The spectra are normalized by total intensity integrated from 157 to 167 eV. It is clear from the figure that both of Bi 4f$_{5/2}$ and 4f$_{7/2}$ core levels have several components. Such multiple peaks are unexpected in bulk since Bi atoms occupy only one chemically-equivalent site in the unit cell. The peak intensity at higher binding energy side (~159 and ~164 eV) becomes stronger as the detection-angle (surface-sensitivity) is increased. This indicates the higher binding energy peaks are mainly originating from surface component and the rest would be the bulk component. The observation of surface Bi states is consistent with earlier STM results [9]. Next we discuss the electronic structure in the near-$E_F$ region.
Figure 1. (a) Core level spectrum of Nd(O,F)BiS$_2$ in a wide energy range. (b) Detection-angle ($\theta$) dependence of Bi 4f core level spectrum.

3.2. Near $E_F$ region

We show in Figure 2(a) the ARPES intensity plot near $E_F$ ($E_F \pm 0.05$ eV) as a function of two-dimensional wave vectors to map out the experimental Fermi surface of Nd(O,F)BiS$_2$. We have observed rectangular-like Fermi surface centered at the X(R) point. In upper panel of Fig. 2(b), we show $E$-$k$ plot along X(R) to X(R) direction depicted as a blue line in Fig. 2(a). Near the X(R) point, the observed band shows downward dispersion, which indicates the sign of the carrier is electron. By combining those observations, we can conclude that bulk electronic structure of Nd(O,F)BiS$_2$ holds electron-like Fermi surface topology. Then one might ask that where is the surface component in electronic structure? In order to answer this question, we show in lower panel of Fig. 2(b) the second derivative of $E$-$k$ mapping. In the figure, not only the dispersive feature near the X(R) point but also a nondispersive component at ~ 0.2 eV is seen. Such a nondispersive character and the energy position of the band well correspond to the local density of states observed on the surface of Nd(O,F)BiS$_2$ in STM measurements. Therefore, we attribute this nondispersive structure to be surface state.

Next we compare the electronic structure of Nd(O,F)BiS$_2$ with that of La(O,F)BiS$_2$ [11]. The Bi 4f core level spectrum of La(O,F)BiS$_2$ also shows a surface component. In the near $E_F$ region, a nondispersive component is observed also in La(O,F)BiS$_2$ although its energy is slightly different (~0.4 eV for nearly optimal doped La(O,F)BiS$_2$ case). So it is likely that the electronic structure of BiS$_2$ plane is near to instability toward charge localization. On the other hand, the Fermi surface topology in the superconducting phase may not be the same between LaO$_{0.54}$F$_{0.46}$BiS$_2$ ($T_c = 3.1$ K) and NdO$_{0.71}$F$_{0.29}$BiS$_2$ ($T_c = 5.1$ K). It has been reported that the electronic structure of LaO$_{0.54}$F$_{0.46}$BiS$_2$ is in close proximity to Lifshitz transition [11]. Thus, in RE = La case, the evolution of superconductivity seems to be related to the occupation of van Hove singularity predicted near $(\pi/2, \pi/2)$ [3]. In this study, we have clarified that the bulk Fermi surface of NdO$_{0.71}$F$_{0.29}$BiS$_2$ is electronlike and the Fermi energy is far from the one where the van Hove singularity touches $E_F$. If we assume that the electronic structures of both samples are similar, the present study also indicates that even though the density of states at $E_F$ is lower, $T_c$ of Nd(O,F)BiS$_2$ is higher. In this series of material, there has to be other factors than the carrier density that effectively determine $T_c$. An in-plane chemical pressure effect has been proposed to be the one. If so, its influence should be observed in the electronic structure as discussed in iron-based superconductors. A more comprehensive study with high energy resolution for both of La(O,F)BiS$_2$ and Nd(O,F)BiS$_2$ has to be performed.
4. Summary

We have performed soft x-ray ARPES on Nd(O,F)BiS$_2$ to study its bulk electronic structure. The core level spectrum of Bi 4f shows detection-angle dependence, indicative of the presence of surface electronic states of Bi. In near $E_F$ region, we have observed both of dispersive electron-like band forming Fermi surface centered at the X(R) point and nondispersive structure at ~0.2 eV. Therefore, the bulk electronic structure is essentially consistent with the one reported earlier by surface-sensitive PES regarding the Fermi surface topology, where the lower carrier number in Nd(O,F)BiS$_2$ produces higher $T_c$ than La(O,F)BiS$_2$ that points towards possible unconventional mechanism of superconductivity in this series of material.

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