Inhomogeneous charge distribution in a self-doped EuFBiS₂ superconductor

T. Sugimoto,^{1,2,3} E. Paris,^{3,4} K. Terashima,⁵ A. Barinov,⁶ A. Giampietri,⁶ T. Wakita,⁵ T. Yokoya,⁵ J. Kajitani,⁷ R. Higashinaka,⁷ T. D. Matsuda,⁷ Y. Aoki,⁷ T. Mizokawa,⁸ and N. L. Saini³

¹*Department of Complexity Science and Engineering, University of Tokyo, 5-1-5 Kashiwanoha 277-8561, Japan*

²*Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha 277-8561, Japan*

³*Dipartimento di Fisica, Università di Roma "La Sapienza," Piazzale Aldo Moro 2, 00185 Roma, Italy*

⁴*Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*

⁵*Research Institute for Interdisciplinary Science(RIIS), Okayama University, Okayama 700-8530, Japan*

⁶*Elettra, Sincrotrone Trieste, Strada Statale 14, Km 163.5, Basovizza, 34149 Trieste, Italy*

⁷*Department of Physics, Tokyo Metropolitan University, Hachioji 192-0397, Japan*

⁸*Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan*

(Received 30 May 2018; revised manuscript received 31 July 2019; published 22 August 2019)

Stoichiometric EuFBiS₂ with mixed valent Eu shows self-doped superconductivity at low temperatures due to the Eu-to-Bi charge transfer. The metallic/nonmetallic bistability of the BiS₂ layer can couple with the valence fluctuation of Eu and provide a highly susceptible electronic state. Here, we report space-resolved photoemission measurements on EuFBiS₂ revealing an inhomogeneous charge distribution with the coexistence of metallic and nonmetallic phases at mesoscopic length scales. Angle-resolved photoemission measurements using a submicron beam size have confirmed a clear Fermi surface around the zone boundaries in the metallic region, typically observed in a doped system, while it can be hardly seen in the nonmetallic region. Density functional theory calculations suggest that the out-of-plane S atom position in the structure is one of the important factors for the self-doping in this material.

DOI: [10.1103/PhysRevB.100.064520](https://doi.org/10.1103/PhysRevB.100.064520)

I. INTRODUCTION

Since the discovery of superconductivity in layered BiS₂-based materials [1,2], various systems have been synthesized, with the majority of them having the chemical formula of R(O, F)BiS₂ (R = rare-earth element). ROBiS₂ is semiconducting in which superconductivity is generally introduced by the substitution of F for O in the RO block layer that injects electrons in the BiS₂ layers, resulting in an electronlike Fermi surface of Bi 6p_{x,y} character at the X point of the Brillouin zone [3,4]. Incidentally, these materials possess a peculiar structural instability in which the BiS₂ square lattice [5] is characterized by the coexistence of different low-symmetry local configurations [6,7]. This leads the BiS₂-based systems to be highly susceptible to external stimuli, e.g., chemical or physical pressures [8,9]. Indeed, experimental tools sensitive to the local structure have revealed a large atomic disorder [10–13], likely to be associated with the Bi defect chemistry.

Recently, an isostructural EuFBiS₂ system [the crystal structure is shown in Fig. 1(a)] has been found to be superconducting [14], in which a small physical pressure is able to raise the T_c more than 30 times [15] from the reported T_c of ~0.3 K at ambient pressure. It has been concluded that EuFBiS₂ is a self-doped system due to Eu mixed valence (Eu²⁺/Eu³⁺) in which electrons in the conducting BiS₂ layer are doped by Eu³⁺. In addition, it has been argued that EuFBiS₂ is characterized by a charge-density-wave (CDW)-like instability below ~280 K, indicating an inhomogeneous charge injection, however, direct evidence of such a density-wave-like instability is still missing. All these results on

polycrystalline samples were later confirmed by follow-up studies [16,17]. Filamentary superconductivity with higher T_c (T_c ~ 1.4 K) was found in La-substituted Eu_{1-x}La_xFBiS₂ [16,17], that turns to bulk superconductivity if S is partially substituted by Se in the La-doped EuFBiS₂. Recently, single-crystal samples of EuFBiS₂ have been grown and it is found that a mixed valence of Eu [18] is intrinsic to this system. The fact that T_c increases sharply with pressure [15] makes it likely that charge doping alone (due to the mixed valence of Eu) may not be sufficient for the superconductivity and the structural instability should have some key role in the properties of EuFBiS₂.

In order to understand the possible relationship between the mixed valence of Eu and the structural instability of BiS₂, it is essential to study the distribution of the electronic structure of EuFBiS₂ in real space. As a matter of fact, an explicit work on the electronic structure of EuFBiS₂ is lacking and all the arguments are based on studies of the electronic structure on an isostructural R(O, F)BiS₂ system. To study the basic electronic structure of EuFBiS₂ under ambient pressure and to see the possible effects of the known structural instability, we have performed space-resolved photoemission on a single crystal of EuFBiS₂. The space-resolved measurements reveal an inhomogeneous charge distribution with a coexistence of metallic and nonmetallic domains at the mesoscopic length scale in EuFBiS₂. Angle-resolved photoemission spectroscopy (ARPES) using a submicron beam shows that the two phases are characterized by the presence and absence of a well-defined Fermi-surface pocket around the X point of the square Brillouin zone. Density functional theory (DFT)

FIG. 1. Space-resolved photoemission spectra of EuFBiS_2 . (a) Crystal structure and definition of S1 and S2 atoms in EuFBiS_2 . (b) Selected area real-space photoemission intensity maps integrated within $-3.45 \text{ eV} \leq E \leq 0.15 \text{ eV}$ and (c) $-0.50 \text{ eV} \leq E \leq 0.15 \text{ eV}$ with a space resolution of $3 \times 3 \mu\text{m}^2$ per pixel. (d) Space-resolved photoemission spectra take at A–F denoted in (b) or (c) with finite offset. The expanded view near E_F without offset is shown in the right. Fermi surfaces obtained by integrating in the energy range of $E_F \pm 50 \text{ meV}$ and band dispersions along high-symmetry lines at the metallic A region (e) and insulating F region (f). The solid lines are to guide $\text{Bi } 6p_x$, Eu^{2+} , and $\text{S } 3p$ bands. (g) Integrated valence band photoemission spectra of metallic A and insulating F regions. (h), (i) Local structure models used for the DFT calculations.

model calculations are used to identify the possible correlation between the local structure and the inhomogeneous charge distribution. The results suggest that the observed inhomogeneous self-doping may be driven by modulation of the out-of-plane S position in the BiS_2 lattice.

II. EXPERIMENTAL AND CALCULATION DETAILS

High-quality single crystals of EuFBiS_2 were grown by the flux (CsCl) method using EuS (99.9%) and BiF_3 (99.99%) powders and Bi_2S_3 (99.999%) grains as starting materials. They were vacuum sealed in a quartz tube and annealed at 900°C for 12 h, followed by slow cooling to 645°C at a rate of 1.5°C/h . The flux was removed by H_2O to extract the single crystals. A single-crystal x-ray analysis, using a Rigaku Mercury diffractometer, revealed the average crystal structure to have the space group $P4/nmm$ (No. 129) and the lattice parameters $a = 4.0508(5) \text{ \AA}$ and $c = 13.530(7) \text{ \AA}$, consistent with a previous report [$a = 4.0508(1) \text{ \AA}$ and $c = 13.5338(3) \text{ \AA}$] [14]. More information on the sample

is provided in the Supplemental Material [19] (see also Refs. [14,20] therein).

Space-resolved ARPES measurements were performed at the spectromicroscopy beamline, Elettra synchrotron facility, Trieste [21]. An incident photon beam of 27 eV was focused using Schwarzschild optics down to a $500 \times 500 \text{ nm}^2$ spot size. Fermi-surface mapping was carried out by changing the position of the electron energy analyzer with the beam and sample fixed. The single-crystal sample was cleaved at 50 K in ultrahigh vacuum ($< 10^{-10} \text{ mbar}$) in order to obtain a clean surface. The total energy resolution, including both the monochromator and electron energy analyzer, was measured to be $\sim 100 \text{ meV}$ while the angular resolution was $\leq 0.5^\circ$ ($\sim 0.021 \text{ \AA}^{-1}$ in k space). All the measurements were carried out within 12 h after the cleavage and the sample temperature was kept constant at 50 K .

First-principles calculations are based on the density functional theory (DFT) as implemented in QUANTUM ESPRESSO [22]. The projector augmented-wave method was adopted, and the energy cutoff for the plane-wave basis was set to

70 Ry. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) type function was used to describe the exchange-correlation term. The crystal structure parameters were taken from Ref. [14].

III. RESULTS AND DISCUSSION

Figures 1(b) and 1(c) show space-resolved photoemission intensity maps integrated within the energy interval of $-3.5 \text{ eV} \leq E \leq 0.15 \text{ eV}$ and $-0.5 \text{ eV} \leq E \leq 0.15 \text{ eV}$, respectively. The latter energy interval is a zoom over the electronlike band near the Fermi level (E_F) characterized by Bi $6p_{x/y}$ orbitals [3]. The spectromicroscopy image of the complete sample is shown in the Supplemental Material [19]. Figures 1(b) and 1(c) represent the images measured on a selected area of the well-cleaved EuFBiS₂ single crystal using a spatial resolution of $3 \times 3 \mu\text{m}^2$ per pixel. The area was chosen considering the flatness of the sample surface. A clear contrast can be seen in the image showing integrated photoelectron intensity in the vicinity of E_F [Fig. 1(c)] while it is weak in the wide energy integrated image [Fig. 1(b)]. The contrast comes from the intense and weak Bi $6p_{x/y}$ states near E_F . This observation suggests that EuFBiS₂ is electronically inhomogeneous with coexisting domains characterized by a differing density of states (DOS) near E_F . The domain dimensions are in the range of $\sim 30\text{--}100 \mu\text{m}$ depending on the scan areas [the scan area displayed in Figs. 1(b) and 1(c) is $135 \times 225 \mu\text{m}^2$], thus the length scale of the observed domains in EuFBiS₂ appears to be mesoscopic. We have found similar spectral variations all over the cleaved sample area with some parts having a relatively large surface roughness. The spectral variation between the metallic and nonmetallic regions is very robust and does not depend on the degree of roughness. Therefore it is not a characteristic of the vicinity of any defects or sample edges and hence may be different from what has been found in the stoichiometric CeOBiS₂ by spectromicroscopy [23].

In order to see the spatial evolution of Bi $6p_{x/y}$ states and other near E_F features, we have measured a sequence of photoemission spectra moving across the boundary between different domains, denoted by A–F in Figs. 1(b) and 1(c). The sequentially scanned space-dependent photoemission spectra are shown in Fig. 1(d). The energy positions of both Bi $6p_{x/y}$ and S1 $3p_{x/y}$ change continuously from the bright to dark region. This indicates that the Bi $6p_{x/y}$ and S1 $3p_{x/y}$ have some correlation and/or hybridization, and the local atomic configuration may be evolving continuously from the A to F region without any sharp boundary between the metallic and nonmetallic regions. Besides the energy position, the spectral weight of Bi $6p_{x/y}$ also changes gradually (decreases) from A to F as shown in Fig. 1(d), much clearer in the zoomed view near E_F displayed without any offset.

In order to determine the detailed electronic band structure, we have performed angle-resolved photoemission (ARPES) and valence band photoemission spectroscopy at A (bright) and F (dark) locations representing the metallic and nonmetallic regions. The ARPES experiments were performed using a focused beam of size $500 \times 500 \text{ nm}^2$. The integrated spectral intensity in the vicinity of $E_F \pm 50 \text{ meV}$ is shown in Figs. 1(e) and 1(f) for the bright and dark regions. The corresponding

band dispersions are shown in the lower panels of Figs. 1(e) and 1(f). A reference sample was not measured together with the sample, however, the energy calibration was performed before starting the measurement run. A typical electronlike Fermi-surface pocket at the X point of the Brillouin zone can be seen in Fig. 1(e) while it is hardly seen in Fig. 1(f), therefore denoted as metallic and insulating in the figure. The band dispersions of the metallic phase around Γ , along Γ -X (cut m1), and around X, along X-M (cut m2), are shown. A clear dispersing Bi $6p_{x/y}$ band crossing E_F can be seen in cut m2. On the other hand, the same cuts for the insulating phase (denoted by cut i1 and cut i2) result in a highly depleted intensity of the Bi $6p_{x/y}$ band. These observations confirm that the bright region in the spectromicroscopy image indeed corresponds to a metallic phase while the dark region should be nonmetallic (insulating). The basic band structures in the two regions appear to be similar, except for the presence and absence of Fermi surfaces in the two phases. The similarity and differences can be further seen in Fig. 1(g) showing the valence band photoemission spectra measured at the A and F points. The spectra are angle integrated covering the shown Brillouin zone and can be considered a larger area average of Fig. 1(d). The apparent differences include intensities of Bi $6p_{x/y}$ and Eu^{3+} , the binding energies of S1 $3p$, and the binding energy of F $2p$. The intensity differences of Bi $6p_{x/y}$ and Eu^{3+} are likely to be related to the different amounts of self-doped electrons. The intensity of Eu^{3+} increases in going from the nonmetallic to the metallic regions. On the other hand, the Eu^{2+} component, expected to decrease in going from the nonmetallic to the metallic regions, is mixed with the S1 $3p$ in the metallic case. Since there is a continuous spatial spectral evolution of the metallic region without any clear boundary with the nonmetallic region, it is rather difficult to check if the total area of the Eu^{2+} and Eu^{3+} components is conserved.

The amount of self-doping is different in different regions, and is apparent from the presence and absence of the Fermi surface, therefore, the Eu-Bi charge transfer is expected to couple to the local lattice distortions [6,7] providing bistability of the metallic and nonmetallic phases. Indeed, the highly disordered nature of these materials has been revealed by the local structure measurements [10,11,13]. Here, we first assume that the observed inhomogeneous charge distribution is related to the local structure of S2 that changes the self-doping exchange pathway of Eu-S2-Bi to inject charge in the Bi $6p_{x/y}$ orbitals. This assumption is partially based on our earlier findings on the Ce(O,F)BiS₂ system [24] and also on the fact that the Bi-S2 distance changes substantially with doping [10]. In other words, we assume that the S2 position with respect to the BiS₂ plane changes continuously from A to F. In order to examine this possibility, we have performed first-principles calculations by changing the local structure of S2 in two ways: (i) change the position of S2 itself as shown in Fig. 1(h), i.e., as a function of $\Delta d_{(\text{S}2)}$ and (ii) change the buckling amount (change the position of the Bi-S2 “dumbbell”) as shown in Fig. 1(i), i.e., as a function of $\Delta d_{(\text{Bi})}$.

Here, it is worth recalling that, in addition to a doping-induced change in the Bi-S2 distance, the actual structural distortions in BiS₂-based materials are very complex with the coexistence of low-symmetry local configurations [6,7]

FIG. 2. DFT calculations for EuFBiS₂ as a function of $\Delta d_{(S2)}$. (a) Band structures using $\Delta d_{(S2)} = 0, +0.0676, +0.136, +0.203$, and $+0.278$ Å. The zoom-overs near E_F are shown in the bottom. (b) Bi 6 $p_{x/y}$ band bottom around the X point is shown as a function of Bi-S2 bond length. (c) Total energy of the system as a function of Bi-S2 bond length. (d) $\Delta d_{(S2)}$ -dependent total DOS. (e) Possible local structures in the insulating and metallic phases. All the band structures and DOS were calculated within the σ GGA + U scheme using the on-site Coulomb interaction among Eu 4 f electrons to be 8 eV.

characterized by different in-plane Bi-S1 distances. Since it is difficult to include such a complex distortion pattern (with multiple Bi-S1 distances and a variable Bi-S2 distance) in the calculations, here we have limited it to a minimal local structure model to perform DFT calculations for the two cases described with a focus on the out-of-plane S atom location. A combined analysis of space-resolved x-ray diffraction and space-resolved x-ray absorption measurements will be required to establish a quantitative correlation between the inhomogeneous charge distribution and the structural distortions in the self-doped EuFBiS₂.

For the calculations, first, the band structure was examined as a function of the on-site Coulomb interaction U . We found that the result for $U = 8$ eV agrees with the ARPES results the most and hence this value was adopted for further calculations. We have applied this to the two local structure configurations described above as (i) and (ii), i.e., to change the S2 position with respect to the BiS₂ layer by keeping the Bi atom within the layer (change in the Bi-S2 distance) and changing the S2 position by lifting also the Bi atom out of the BiS₂ layer (keeping the Bi-S2 distance fixed). As for the latter case (ii), it turned out that the parameter $\Delta d_{(Bi)}$ hardly affects the band structure. The results of these calculations along with the U dependence are included in the Supplemental Material [19]. On the other hand, case (i), in which the Bi-S2 distance is changing, appears more instructive, showing a systematic

variation in the band structure that may explain in part the space-resolved photoemission results.

The $\Delta d_{(S2)}$ (variation of Bi-S2 distance with respect to the nominal value of 2.5 Å)-dependent band structure is shown in Fig. 2(a). A zoom over the near E_F band structure is included in the lower panels. The system is nonmetallic for $\Delta d_{(S2)} = 0$ Å. The Bi 6 $p_{x/y}$ band bottom comes down monotonically towards E_F with increasing $\Delta d_{(S2)}$. The Bi 6 $p_{x/y}$ band appears to cross E_F for $\Delta d_{(S2)} > +0.136$ Å. Energy of the Bi 6 $p_{x/y}$ band bottom is plotted as a function of Bi-S2 bond length in Fig. 2(b). Incidentally, the Eu 4 f holelike bands start to cross E_F almost for the same $\Delta d_{(S2)}$, indicating possible self-doping that may occur from Eu 4 f to Bi 6 p orbitals. In a real system the Eu 4 f bands should locate below E_F because of the coexisting Eu²⁺ and Eu³⁺. Therefore, the total energy of the self-doped region should be lower than the total energy estimated by the DFT calculations. Figure 2(c) shows the total energy as a function of the Bi-S2 bond length in which the precision is about ± 0.01 Ry (error bars). The total energy monotonically increases with the Bi-S2 bond length. When the energy gain by the Eu 4 f electrons in the self-doped region is taken into consideration, the total energy might be very close in the range of the Bi-S2 bond-length variation. The possible energy gain is indicated by arrows in Fig. 2(c). This indicates that polytypism in EuFBiS₂ is highly plausible and the coexisting electronic phases might be related to the local

structural instability. The total DOS as a function of $\Delta d_{(S2)}$ is shown in Fig. 2(d). Apart from others, the F 2*p* tends to shift towards E_F with increasing Bi-S2 bond length. Such a shift can be appreciated in the measured integrated valence band photoemission spectra shown in Fig. 1(g).

We should mention that, while the experimentally observed S1 3*p* states from the metallic phase shift to a higher energy in comparison to the one from the insulating regions, the calculated S1 3*p* states from the metallic phase appear to shift towards lower energy. Therefore, the minimal model including only the Bi-S2 bond length seems insufficient to describe this variation since these states may be affected by the Bi-S1 distortions, not considered in the model calculations. Nevertheless, an overall agreement between the gross features suggests that the position of S2 with respect to the BiS₂ layer plays an important role in the doping mechanism in these materials. Thus, the inhomogeneous charge distribution observed in the space-resolved photoemission is likely to be related to differing local structure configurations with longer (metallic) and shorter (nonmetallic) Bi-S2 bond lengths due to an instable structure characterized by BiS₂ distortions.

IV. CONCLUSIONS

In summary, we have studied the electronic structure of EuFBiS₂ by space-resolved photoemission spectroscopy. We have found an inhomogeneous charge distribution in EuFBiS₂, characterized by the coexistence of metallic and nonmetallic domains at the mesoscopic length scale. ARPES

measurements using a submicron beam size reveal that the metallic phase has a well-defined Fermi-surface pocket, unlike the nonmetallic phase. It has been discussed that the observed inhomogeneous charge distribution could be related to the local structural distortions in EuFBiS₂. First-principles calculations are performed for different local atomic configurations, showing satisfactory agreement between the experimentally observed features and the model calculations. The results suggest that the position of the out-of-plane S atom is important for the inhomogeneous charge doping in the Bi 6*p_{x/y}* band from the EuF layer. Moreover, space-resolved x-ray diffraction and x-ray absorption measurements on EuFBiS₂ are likely to provide further information on the correlation between the inhomogeneous charge distribution and the structural distortions. This is also due to the fact that actual distortions in these materials are very complex and difficult to be included in the model calculations.

ACKNOWLEDGMENTS

The present work is part of the bilateral agreement between the Sapienza University of Rome and the University of Tokyo, including Waseda University, Tokyo Metropolitan University, and Okayama University. T.S. acknowledges the support from a JSPS Research Fellowship for Young Scientists. This work is partially supported by JSPS/MEXT KAKENHI (Grants No. 15H03693, No. 15H05884, No. 16J05692, No. 16K05454, No. H1503691, and No. 19H01839).

-
- [1] Y. Mizuguchi, H. Fujihisa, Y. Gotoh, K. Suzuki, H. Usui, K. Kuroki, S. Demura, Y. Takano, H. Izawa, and O. Miura, *Phys. Rev. B* **86**, 220510(R) (2012).
 - [2] Y. Mizuguchi, S. Demura, K. Deguchi, Y. Takano, H. Fujihisa, Y. Gotoh, H. Izawa, and O. Miura, *J. Phys. Soc. Jpn.* **81**, 114725 (2012).
 - [3] H. Usui, K. Suzuki, and K. Kuroki, *Phys. Rev. B* **86**, 220501(R) (2012).
 - [4] T. Sugimoto, D. Ootsuki, C. Morice, E. Artacho, S. S. Saxena, E. F. Schwier, M. Zheng, Y. Kojima, H. Iwasawa, K. Shimada, M. Arita, H. Namatame, M. Taniguchi, M. Takahashi, N. L. Saini, T. Asano, R. Higashinaka, T. D. Matsuda, Y. Aoki, and T. Mizokawa, *Phys. Rev. B* **92**, 041113(R) (2015).
 - [5] T. Yildirim, *Phys. Rev. B* **87**, 020506(R) (2013).
 - [6] Q. Liu, X. Zhang, and A. Zunger, *Phys. Rev. B* **93**, 174119 (2016).
 - [7] X. Zhou, Q. Liu, J. A. Waugh, H. Li, T. Nummy, X. Zhang, X. Zhu, G. Cao, A. Zunger, and D. S. Dessau, *Phys. Rev. B* **95**, 075118 (2017).
 - [8] Y. Mizuguchi, *J. Phys. Chem. Solids* **84**, 34 (2015).
 - [9] H. Usui and K. Kuroki, *Novel Supercond. Mater.* **1**, 50 (2015).
 - [10] E. Paris, B. Joseph, A. Iadecola, T. Sugimoto, L. Olivi, S. Demura, Y. Mizuguchi, Y. Takano, T. Mizokawa, and N. L. Saini, *J. Phys.: Condens. Matter* **26**, 435701 (2014).
 - [11] Y. Mizuguchi, E. Paris, T. Sugimoto, A. Iadecola, J. Kajitani, O. Miura, T. Mizokawa, and N. L. Saini, *Phys. Chem. Chem. Phys.* **17**, 22090 (2015).
 - [12] A. Athauda, J. Yang, S. Lee, Y. Mizuguchi, K. Deguchi, Y. Takano, O. Miura, and D. Louca, *Phys. Rev. B* **91**, 144112 (2015).
 - [13] E. Paris, Y. Mizuguchi, T. Wakita, K. Terashima, T. Yokoya, T. Mizokawa, and N. L. Saini, *J. Phys.: Condens. Matter* **30**, 455703 (2018).
 - [14] H. F. Zhai, Z. T. Tang, H. Jiang, K. Xu, K. Zhang, P. Zhang, J. K. Bao, Y. L. Sun, W. H. Jiao, I. Nowik, I. Felner, Y. K. Li, X. F. Xu, Q. Tao, C. M. Feng, Z. A. Xu, and G. H. Cao, *Phys. Rev. B* **90**, 064518 (2014).
 - [15] C. Y. Guo, Y. Chen, M. Smidman, S. A. Chen, W. B. Jiang, H. F. Zhai, Y. F. Wang, G. H. Cao, J. M. Chen, X. Lu, and H. Q. Yuan, *Phys. Rev. B* **91**, 214512 (2015).
 - [16] Y. Mizuguchi, E. Paris, T. Wakita, G. Jinno, A. Puri, K. Terashima, B. Joseph, O. Miura, T. Yokoya, and N. L. Saini, *Phys. Rev. B* **95**, 064515 (2017).
 - [17] G. S. Thakur, R. Jha, Z. Haque, V. P. S. Awana, L. C. Gupta, and A. K. Ganguli, *Supercond. Sci. Technol.* **28**, 115010 (2015).
 - [18] E. Paris *et al.* (unpublished).
 - [19] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.100.064520> for more information on the sample and spectromicroscopy image of the complete sample. *U* dependence of the band structure and model calculations in which the S2 position is changed by lifting the Bi atom out of the BiS₂ layer in EuFBiS₂ is also shown (see text).
 - [20] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **64**, 112 (2008).
 - [21] P. Dudin, P. Lacovig, C. Fava, E. Nicolini, A. Bianco, G. Cautero, and A. Barinov, *J. Synchrotron Radiat.* **17**, 445 (2010).

- [22] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos *et al.*, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [23] T. Sugimoto, E. Paris, T. Wakita, K. Terashima, T. Yokoya, A. Barinov, J. Kajitani, R. Higashinaka, T. D. Matsuda, Y. Aoki, T. Mizokawa, and N. L. Saini, *Sci. Rep.* **8**, 2011 (2018).
- [24] T. Sugimoto, B. Joseph, E. Paris, A. Iadecola, T. Mizokawa, S. Demura, Y. Mizuguchi, Y. Takano, and N. L. Saini, *Phys. Rev. B* **89**, 201117(R) (2014).