Robust Surface States Crossing Fermi Energy In a Correlated \( d \)-electron Insulator \( \text{FeSb}_2 \)

Ke-Jun Xu,\(^1\) Su-Di Chen,\(^1,2\) Yu He,\(^1,2\) Jun-Feng He,\(^1,2\) Shujie Tang,\(^1,2,3\) Chunjing Jia,\(^2\)
Eric Yue Ma,\(^1,2\) Makoto Hashimoto,\(^4\) Dong-Hui Lu,\(^4\) Sung-Kwan Mo,\(^3\) and Zhi-Xun Shen\(^1,2,\ast\)

\(^1\)Geballe Laboratory for Advanced Materials, Department of Physics and Applied Physics, Stanford University, Stanford, California 94305, USA
\(^2\)Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA
\(^3\)Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
\(^4\)Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA

(Dated: November 7, 2018)

\( \text{FeSb}_2 \) is a narrow gap \( d \)-electron insulator that exhibits many similar properties to the prototypical \( f \)-electron Kondo insulator \( \text{SmB}_6 \), including a low temperature resistivity plateau. Using angle-resolved photoemission spectroscopy to probe its low energy electronic structure, we find three Fermi surfaces despite \( \text{FeSb}_2 \) being a bulk insulator. By varying photon energy and temperature, we show that these Fermi surfaces are 2-dimensional in nature and at least one of them appears concomitantly with the resistivity upturn associated with Kondo coherence. We also observe flat-band-like spectral intensity along certain high symmetry directions, which reflects the correlated nature of \( 3d \) electrons. Together with the ubiquitous low temperature resistivity saturation, our findings suggest the presence of robust surface state in a correlated material system.

Topological physics in strongly correlated electron systems has attracted substantial research interest \(^{11-4}\). Currently many efforts are focused on the \( 4f \)-based Kondo insulators \( \text{SmB}_6 \) and \( \text{YbB}_12 \), where the hybridization between \( 4f \) and \( 5d \) bands creates a gap that can host topological surface states. On the experimental side, evidence for surface transport has been found in \( \text{SmB}_6 \) using non-local measurement geometries \(^{5} \) and thickness dependence \(^{6,7} \). Surface states in \( \text{SmB}_6 \) have been revealed by Angle-Resolved Photoemission Spectroscopy (ARPES) \(^{8-10} \), with the spin textures confirmed by spin-resolved ARPES \(^{11} \), although their origin is still under debate \(^{12} \). Furthermore, quantum oscillations have also been observed, yet it is not clear whether they originate from the surface or the bulk states \(^{13-15} \). To better understand these topological Kondo insulator candidates, it is imperative to look for similar physics in related but distinct material systems, for example the \( Fe \)-based \( d \) electron Kondo insulators \( \text{FeSb}_2, \text{FeSi}, \) and \( \text{FeGa}_3 \).

\( \text{FeSb}_2 \) is a narrow gap insulator that had been studied mainly due to its large thermopower at low temperatures \(^{19-21} \). The ground state has been strongly evidenced to contain significant correlation effects and Kondo interactions \(^{22-24} \), with metallicity induced with even \( 0.1\% \) Te doping \(^{24} \). The properties of \( \text{FeSb}_2 \) present many similarities to the prototypical \( 4f \) electron Kondo insulator \( \text{SmB}_6 \). Firstly, electrical transport shows insulating behavior with an activation gap about \( 25 \text{ meV} \), but below about \( 10 \text{ K} \) a resistivity plateau develops, ubiquitous to all samples regardless of synthesis method \(^{25,26} \). Secondly, the magnetic moment vanishes at low temperatures, suggesting the formation of a Kondo singlet. Thirdly, the Fe atom has a mixed valence state between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \), as seen in x-ray absorp-

![Image](image_url)
FIG. 2. Low energy electronic structure in FeSb$_2$. (a) Fermi surface mapping showing intensity within ±10 meV of the Fermi energy ($E_F$) taken using 70 eV photons in the 2nd BZ. Surface BZ is marked with magenta rectangles and high symmetry points in black. Three bands are observed: α in red, β in blue, and γ in green. The dashed lines are guides to the eye. (b) Cuts in the c direction, as illustrated in the inset. Bottom are the momentum distribution curves (MDCs) integrated between +5 meV and -10 meV of $E_F$, showing peaks corresponding to various surface bands. Dashed lines are guides to the eye. (c) False-color spectra (left) and second-derivative plot (right) along the Y–S–Y in the bulk BZ and Γ–X–Γ in the surface BZ. The flat-band-like spectral intensity can be seen at ~100 meV binding energy (yellow dashed line). It is clear from the second derivative plot that the alpha band disperses down across this flat intensity. (d) MDCs of the brown box region shown in (c), showing the α, γ surface bands and the δ band. Dashed lines track the MDC peaks for each band. (e) Energy distribution curves (EDCs) of the same region, showing the flat feature clearly. Bolded lines are $k_F$ of the γ band.

tion spectroscopy \[27\]. Given these intriguing properties, high quality ARPES data are necessary to elucidate the electronic structure and possible topological effects, but are currently lacking due to the 3-dimensional (3D) nature of the crystal and the difficulty in cleaving samples. Recent thickness-dependent transport measurements on a related compound FeSi has indicated surface conduction \[28\]. However, the ARPES measurements on FeSi failed to observe surface bands near the Fermi energy thus far ($E_F$) \[29–36\]. Here we show that, with a combination of small beam spot ($25 \mu$m × $50 \mu$m) and high resolution, surface states crossing $E_F$ can be observed in the closely related FeSb$_2$.

To address the aforementioned questions, we have carried out ARPES measurements on single crystal FeSb$_2$, grown with a Sb self-flux method. The electrical transport and magnetic properties were characterized in a Quantum Design Physical Property Measurement System. The ARPES measurements at SSRL beamline 5-2 were performed with a Scienta D80 analyzer at energy resolutions better than 20 meV and a vacuum pressure better than $5 \times 10^{-11}$ Torr, and those at ALS beamline 10.0.1 with a Scienta R4000 analyzer at energy resolutions better than 25 meV and pressure better than $7 \times 10^{-11}$ Torr. The highest quality data are obtained on the (010) surface, where three sets of Fermi surface features are clearly seen, despite the crystal exhibiting bulk insulating behavior. We also find flat spectral intensities along the Fe–Fe bond directions at 100 meV binding energy, further supporting the presence of strong corre-
FIG. 3. Photon energy and temperature dependence of the electronic structure. (a) $k_\parallel$ dispersion of the $\gamma$ band taken using photon energies from 40 eV to 90 eV, covering about one and half BZs. Green dashed lines are guides to the eye that tracks the $\gamma$ band. (b) Cuts through the BZ in the b-axis for various photon energies. 70 eV photon energy used in this study cuts near the Y–S–Y line. (c) Temperature dependence of EDCs for integrated momentum near $k_\parallel$ of the $\beta$ band taken with 70 eV photons. The surface band intensity is labeled with the black triangles, showing disappearance between 100 K and 150 K. EDCs are divided by the Fermi-Dirac distribution.

The Fermi surface mapping in the a-c plane is presented in Fig. 2a. The data is collected at 15 K, where the insulating phase is well-developed. We find that 70 eV photon energy gave sufficiently good data while cutting across a high symmetry plane (Y–S–R–T) in the $k_\parallel$ direction, perpendicular to the measurement plane. The determination of the inner potential and the geometry of the cuts in the $k_\parallel$ direction is shown in supplement Fig. S2. We show the data from the 2nd zone, where the Fermi surface is more clear. The BZ boundary is labeled with the magenta rectangle, along with several high symmetry points. Several features can be readily visually identified: there is an open Fermi surface $\alpha$ along the $a$ direction, a closed pocket $\beta$ centered on the $Z$ point, and a closed pocket $\gamma$ centered around the $\Gamma$ point. There is a small patch of intensity at $\bar{X}$, however this is from the leaked intensity of a part of the $\alpha$ band just below $E_F$. This is clearly seen in the energy-momentum cut along the $k_\parallel$ direction shown in Fig. 2b. The cut along $\bar{Y} - \bar{X} - \bar{U}$ shows that the intensity near $\bar{X}$ is connected to the $\alpha$ band. As the cut moves to the zone center $\bar{Z} - \bar{\Gamma} - \bar{Z}$, the $\beta$ and $\gamma$ bands form. At the same time, the $\alpha$ band develops a steep dispersion, and has the band bottom at $\sim$300 meV binding energy. The band features near $E_F$ are more clearly seen in the momentum distribution curves (MDCs) at the bottom of the panel, constructed from intensity between +5 meV and -10 meV of $E_F$. Both the $\beta$ and $\gamma$ bands are electron-like, while the $\alpha$ is electron-like only along the $c$ direction and undefined along the $a$ direction. The area enclosed by the $\alpha$, $\beta$, and $\gamma$ bands is about 44%, 10%, and 21% of the full BZ, respectively. We show the $\gamma$ and $\alpha$ band in more detail in Fig. 2c and 2d, where the cut is taken along Y–S–Y. The $\gamma$ band disperses across the flat intensity towards the band bottom at 300 meV binding energy. The flat intensity is shown with a yellow dashed line. Our data lay the framework for comparisons with future spin-resolved ARPES and quantum oscillation experiments.

We first present physical property characterizations of the crystals used in this study. Fig. 1a shows the resistivity and magnetic moment as a function of temperature. At around 5 K a saturation in resistivity is seen, consistent with previous studies. FeSb$_2$ crystalizes in an orthorhombic structure with lattice constants $a = 5.81\AA$, $b = 6.52\AA$, and $c = 3.19\AA$. The Fe atoms form a body centered structure, each with 6 Sb atoms forming a rotated corner-sharing octahedron around it (Fig. 1b). The bulk Brillouin zone (BZ) and the associated (010) surface BZ is shown in Fig. 1c. Throughout this Letter, surface high symmetry points will be denoted with a bar above the corresponding bulk symmetry point notation.

The Fermi surface mapping in the a-c plane is presented in Fig. 2a. The data is collected at 15 K, where the insulating phase is well-developed. We find that 70 eV photon energy gave sufficiently good data while cutting across a high symmetry plane (Y–S–R–T) in the $k_\parallel$ direction, perpendicular to the measurement plane. The determination of the inner potential and the geometry of the cuts in the $k_\parallel$ direction is shown in supplement Fig. S2. We show the data from the 2nd zone, where the Fermi surface is more clear. The BZ boundary is labeled with the magenta rectangle, along with several high symmetry points. Several features can be readily visually identified: there is an open Fermi surface $\alpha$ along the $a$ direction, a closed pocket $\beta$ centered on the $Z$ point, and a closed pocket $\gamma$ centered around the $\Gamma$ point. There is a small patch of intensity at $\bar{X}$, however this is from the leaked intensity of a part of the $\alpha$ band just below $E_F$. This is clearly seen in the energy-momentum cut along the $k_\parallel$ direction shown in Fig. 2b. The cut along $\bar{Y} - \bar{X} - \bar{U}$ shows that the intensity near $\bar{X}$ is connected to the $\alpha$ band. As the cut moves to the zone center $\bar{Z} - \bar{\Gamma} - \bar{Z}$, the $\beta$ and $\gamma$ bands form. At the same time, the $\alpha$ band develops a steep dispersion, and has the band bottom at $\sim$300 meV binding energy. The band features near $E_F$ are more clearly seen in the momentum distribution curves (MDCs) at the bottom of the panel, constructed from intensity between +5 meV and -10 meV of $E_F$. Both the $\beta$ and $\gamma$ bands are electron-like, while the $\alpha$ is electron-like only along the $c$ direction and undefined along the $a$ direction. The area enclosed by the $\alpha$, $\beta$, and $\gamma$ bands is about 44%, 10%, and 21% of the full BZ, respectively. We show the $\gamma$ and $\alpha$ band in more detail in Fig. 2c and 2d, where the cut is taken along Y–S–Y. The $\gamma$ band disperses across the flat intensity towards the band bottom at 300 meV binding energy. The flat intensity is shown with a yellow dashed line.

| Band | Luttinger volume ($A^{-2}$) | % of BZ | $v_F$ (m/s) |
|------|-----------------------------|--------|-------------|
| $\alpha$ | 0.94 | 44% | $6.1 \times 10^6 @ \bar{U}-\bar{X}$ |
|       |     |       | $3.0 \times 10^4 @ \bar{\Gamma}-\bar{Z}$ |
| $\beta$ | 0.22 | 10% | $7.5 \times 10^3 @ \bar{Z}-\bar{\Gamma}$ |
| $\gamma$ | 0.46 | 21% | $3.1 \times 10^4 @ \bar{\Gamma}-\bar{X}$ |

TABLE I. Information of the surface bands. The area for the $\alpha$ band is taken as the electron-like part around the center of the zone.
FIG. 4. Bulk bands in the Y–S–R–T plane. (a) Cut along S–R–S. Red dashed line is calculation using LDA, red solid line is with GW approximation, both taken from [37]. Band near $E_F$ is the $\alpha$ surface band. Black dashed line is a band that is severely underestimated in the calculation. (b) Cut along R–T–R, showing the $\beta$ band and the flat intensity. (c) constant energy mapping at 100 meV binding energy, showing 1D flat intensity (yellow dashed lines) along the $a$ and $c$ directions. BZ is labeled by the magenta lines. (d) cuts near S point. Along R–T there is strong intensity at 100 meV binding energy (see also Fig. 2e). The flat spectral intensity does not extend away from R–T. The dashed lines are guides to the eye. Inset shows the location of the cuts.

line and has a bandwidth of less than 20 meV. There is another band $\delta$ labeled by the grey dashed line at lower binding energy. The Fermi velocity for each surface band is extracted at the specified location and summarized in table 1, along with the other parameters. We note that the Fermi velocity for the $\gamma$ and $\alpha$ bands are comparable to the surface states in SmB$_6$ [38].

The observed bands at $E_F$ are likely to be surface bands due to the fact that the bulk crystal is insulating and bulk bands are not expected to cross $E_F$. We further demonstrate the 2D nature of these bands by varying the photon energy and probing the $k_0$ dispersion, which is perpendicular to the measurement plane. In Fig. 3a we show the spectral intensity integrated between $\pm$ 10 meV of $E_F$ from 40 eV to 90 eV photon energy, with the BZ in the a-b plane overlaid on top. The green dashed lines mark the intensities from the $\gamma$ band. The photon energy range used covers about 1.5 BZs in the $b$ direction (also shown in Fig. 3b). We also show a Fermi surface mapping taken with 57 eV photons (supplementary Fig. S3), demonstrating exactly the same three Fermi surfaces as those in Fig. 2a even though this photon energy cuts through a different part of the BZ. Thus we conclude that the Fermi surfaces observed here are 2D, which reassures their surface origin.

To reveal the relationship between these surface states and the bulk properties, we also measure their temperature evolution. Fig. 3c shows the energy distribution curves (EDC) integrated from momentum near $k_F$ of the $\beta$ band. The surface state, shown as the shoulder feature marked by the black triangle at $\sim$ 25 meV binding energy, disappears between 100 K and 150 K during warming, consistent with the resistivity upturn. This suggests that the surface state is intimately tied with the Kondo energy scale. Temperature cycling rules out a purely trivial surface degradation effect; while there is weak surface degradation, as demonstrated by the weaker peak at $\sim$130 meV binding energy, the surface state shoulder
Next we show the bands at higher binding energy measured near the Y-S-R-T high symmetry plane and compare them to band structure calculations. Fig. 4a and 4b shows the cut along S-R-S and R-T-R respectively. The slight asymmetry comes from the fact that the cut is slightly curved at this high photon energy and cuts through different $k_x$ across the BZ. Comparing to the band structure calculated using the GW approximation [37], we find a reasonable agreement when the surface bands are excluded. Similar to Fig. 2b, there is also a flat spectral feature along the R-T-R direction, shown in Fig. 4b. This flat feature can be tracked in momentum space and is shown in the constant energy cuts through different $k$ points. Strikingly, the flat features only exist along the Y-T and Y-S directions which coincide with the Fe-Fe bond direction. In Fig. 4d we show the cuts near one of the 1D flat features. The flat intensity at 100 meV binding energy is partially contributed from the $\gamma$ and $\delta$ bands. In the cuts away from the Y-S direction, there is a clear gap between the $\gamma$ and $\delta$ bands, however on the Y-S-Y cut there is strong intensity everywhere, even between the bands. The flat intensity measured here is very different from the 4f Kondo insulators, where the 4f levels are flat throughout the whole BZ. The character of this intensity seems to go beyond the band picture, which suggests the strong correlation effect between 3d electrons and requires further investigations.

We now compare the FeSb$_2$ system with the f-electron topological Kondo insulator candidates SmB$_6$ and YbB$_{12}$. Both SmB$_6$ and YbB$_{12}$ are thought to be so-called “true Kondo insulators” [39], in the sense that the gap is opened at $E_F$ purely due to Kondo interactions. However, this also complicates the interpretation of quantum oscillation results, since the gap may collapse under high magnetic field. Indeed, SmB$_6$ and YbB$_{12}$ have negative magnetoresistance, with their gaps closing at $\sim$85 T [40] and $\sim$50 T [41] respectively. On the other hand, how the Kondo interaction influences the gap in FeSb$_2$ and whether the gap is intrinsic to the bandstructure is unclear. However, experimentally FeSb$_2$ shows a positive magnetoresistance up to at least 18 T (see supplementary Fig. S1) at 4 K, suggesting it is less prone to magnetic-field induced gap-closing. Thus, FeSb$_2$ would be a cleaner test case for understanding the quantum oscillations in Kondo systems.

In conclusion, we have used ARPES to reveal several salient features in the electronic structure of a strongly correlated d-electron insulator FeSb$_2$. We find 3 features that disperse across the Fermi level, despite an insulating bulk. These states are 2D-like and at least one of them disappears around a temperature scale where resistivity displays a rapid upturn. These observations, together with the ubiquitous resistivity saturation at low temperature, suggest the possible presence of robust surface states. In addition, the measured flat-band-like features suggest the presence of a unique case of strong correlations and presents guidelines for theory to model this system. Future experiments, for example spin-resolved ARPES and surface transport, are needed to further characterize the surface states. Combined with theory, we may then be able to answer the question of whether these surface states are topological.

Note added: during the preparation of this manuscript, we noticed a recent ARPES work on FeSb$_2$ [42]. The authors observe a surface band crossing $E_F$ at the same location in the BZ as the $\gamma$ band in our work. However, no clear evidence for $\alpha$ or $\beta$ bands are reported at those high photon energies.

We thank B. Moritz and E. W. Huang for useful discussions. The work at SLAC and Stanford is supported by the U.S. DOE, Office of Basic Energy Science, Division of Materials Science and Engineering. ALS and SSRL are operated by the Office of Basic Energy Sciences, U.S. DOE, under Contracts No. DE-AC02-05CH11231 and No. DE-AC02-76SF00515, respectively. K. X. acknowledge support from the Betty and Gordon Moore Foundation.

References:

[1] S. Raghu, X.-L. Qi, C. Honerkamp, and S.-C. Zhang, Phys. Rev. Lett. 100, 156401 (2008).
[2] M. Levin and A. Stern, Phys. Rev. Lett. 103, 196803 (2009).
[3] D. Pesin and L. Balents, Nat. Phys. 6, 376381 (2010).
[4] M. Dzero, K. Sun, V. Galitski, and P. Coleman, Phys. Rev. Lett. 104, 106408 (2010).
[5] S. Wolgast, C. Kurdkar, K. Sun, J. W. Allen, D.-J. Kim, and Z. Fisk, Phys. Rev. B 88, 180405 (2013).
[6] D. Kim, S. Thomas, T. Grant, J. Bošmer, Z. Fisk, and J. Xia, Sci. Rep. 3, 3150 (2013).
[7] D. Kim, J. Xia, and Z. Fisk, Nat. Mater. 13, 466470 (2014).
[8] N. Xu, X. Shi, P. K. Biswas, C. E. Matt, R. S. Dhaka, Y. Huang, N. C. Plumb, M. Radović, J. H. Dil, E. Pomjakushina, K. Conder, A. Amato, Z. Salman, D. M. Paul, J. Mesot, H. Ding, and M. Shi, Phys. Rev. B 88, 121102(R) (2013).
[9] J. Jiang, S. Li, T. Zhang, Z. Sun, F. Chen, Z. R. Ye, M. Xu, Q. Q. Ge, S. Y. Tan, X. H. Niu, M. Xia, B. P. Xie, Y. F. Li, X. H. Chen, H. H. Wen, and D. L. Feng, Nat. Commun. 4, 3010 (2013).
[10] M. Neupane, N. Alidoust, S.-Y. Xu, T. Kondo, Y. Ishida, D. J. Kim, C. Liu, I. Belopolski, Y. J. Jo, T.-R. Chang, H.-T. Jeng, T. Durakiewicz, L. Balicas, H. Lin, A. Bansil, S. Shin, Z. Fisk, and M. Z. Hasan, Nat. Commun. 4, 2991 (2013).
[11] N. Xu, P. K. Biswas, J. H. Dil, R. S. Dhaka, G. Landolt, S. Muff, C. E. Matt, X. Shi, N. C. Plumb, M. Radović, E. Pomjakushina, K. Conder, A. Amato, S. V. Borisenko, R. Yu, H.-M. Weng, Z. Fang, X. Dai, J. Mesot, H. Ding, and M. Shi, Nat. Commun. 5, 4566 (2014).
FIG. S1. Magnetoresistance (MR) of FeSb\textsubscript{2} up to 17.5T at 4.2K, showing a positive MR for the whole field range. Data taken in the SCM3 magnet at National High Magnetic Field Laboratory using a 4-point geometry.
The out of plane momentum is conserved in the following manner

\[ k_\perp = \sqrt{\frac{2m_e^*}{\hbar^2} \{E_k + V_0\} - k^2_\parallel} = \sqrt{\frac{2m_e^*}{\hbar^2} \{E_k + V_0\} - \frac{2m_e^*E_k}{\hbar^2} \sin^2 \theta} \]

Where \( E_k \) is the emitted electron kinetic energy, \( m_e^* \) is the final state band effective mass, and \( V_0 \) is the inner potential, a parameter for the energy difference between the final state to the vacuum level. \( V_0 \) is usually determined in ARPES measurements by measuring the photon energy dependence of the electronic structure and using the periodicity of high symmetry points to extrapolate the value.

FIG. S2. Determination of inner potential. Shown here is a \( k_y \) - \( k_x \) mapping at a binding energy of 200 meV taken at ALS beamline 10.0.1, showing periodic features that allows the determination of the inner potential to be 6 eV. The dispersion in \( k_y \) also demonstrates the 3D nature of the bulk bands.
FIG. S3. Fermi surface mapping taken at 57 eV photon energy, and shows the exact same Fermi surface as 70 eV even though it cuts across a different $k_\perp$. BZ boundary is labeled in Magenta. $\alpha$ band labeled in red, $\beta$ band in light blue, $\gamma$ band in green. Data taken at ALS beamline 10.0.1.