

# Discovery of a Three-Dimensional Topological Dirac Semimetal, Na<sub>3</sub>Bi

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**Three-dimensional (3D) topological Dirac semimetals (TDSs) represent a novel state of quantum matter that can be viewed as “3D graphene”. In contrast to two-dimensional (2D) Dirac fermions in graphene or on the surface of 3D topological insulators, TDSs possess 3D Dirac fermions in the bulk. By investigating the electronic structure of Na<sub>3</sub>Bi with angle resolved photoemission spectroscopy, we discovered 3D Dirac fermions with linear dispersions along all momentum directions. Furthermore, we demonstrated the robustness of 3D Dirac fermions in Na<sub>3</sub>Bi against in situ surface doping. Our results establish Na<sub>3</sub>Bi as a model system of 3D TDSs, which can serve as an ideal platform for the systematic study of quantum phase transitions between rich topological quantum states.**

The discoveries of graphene and topological insulators (TIs) have inspired enormous efforts in the search for materials with similar electronic and topological properties (1–4). Graphene, a single sheet of carbon atoms, hosts 2D Dirac fermions in its electronic structure (1, 2, 5); TIs are materials with bulk energy gap but gapless surface states formed by an odd number of Dirac fermions with helical spin texture (3, 4, 6–8). In the course of this search, the following questions arose: Does a 3D counterpart of graphene exist? Can materials other than insulators possess unusual topology in their electronic structures?

In a class of materials called the topological Dirac semimetals both of these questions are answered in the affirmative. There, the bulk conduction and valence bands touch only at discrete (Dirac) points and disperse linearly along all (three) momentum directions, forming bulk (3D) Dirac fermions – a natural 3D counterpart of graphene. Interestingly, although similar electronic structure was discussed more than seven decades ago (9), its topological classification was only appreciated recently (10–15), leading to the theoretical proposal of topological Dirac semimetals (12–16).

The distinct electronic structure of a topological Dirac semimetal not only makes it possible to realize some exciting phenomena and applications of graphene (17) in 3D materials, but also gives rise to many unique properties, such as the giant diamagnetism that diverges logarithmically when the Fermi-energy ( $E_F$ ) is approaching the 3D Dirac point (16, 18, 19), quantum magnetoresistance showing linear field dependence in the bulk (20, 21), unique Landau level structures under strong magnetic field, and oscillating quantum spin Hall effect in quantum well structures (15, 22). Interestingly, the 3D Dirac fermion in a topological Dirac semimetal is composed of two overlapping Weyl fermions (which are chiral massless particles previously studied extensively in high-energy physics, e.g., as a description of neutrinos) (23) that can be separated in the momentum space if time reversal or inversion symmetry is broken. This would result in a topological Weyl semimetal,

another novel topological quantum state showing unique Fermi-arcs geometry (12, 24), exhibiting pressure induced anomalous Hall effect (25) and quantized anomalous Hall effect in quantum well structures (24).

Besides these unusual properties, the topological Dirac semimetal is the neighbor state to various states (Fig. 1A, B) (12–16, 26) ranging from regular band insulators to topological superconductors. This versatility makes the topological Dirac semimetal an ideal mother compound for the realization of other novel states as well as a platform for the systematic study of topological quantum phase transitions.

The physical realization of the topological Dirac semimetal is, however, challenging. In principle, it may be realized through topological phase transitions, such as tuning chemical composition or spin-orbital coupling strength to the quantum critical point through a normal insulator - topological insulator transition (Fig. 1B). Recently, it was realized that the crystal symmetry can protect and stabilize 3D Dirac points in several stoichiometric compounds such as  $\beta$ -cristobalite BiO<sub>2</sub> (14) and A<sub>3</sub>Bi (A=Na, K, Rb) family of compounds

(15). Because of the metastable nature of  $\beta$ -cristobalite BiO<sub>2</sub>, we chose to study Na<sub>3</sub>Bi.

We performed angle resolved photoemission spectroscopy (ARPES) measurements to investigate the electronic structures of Na<sub>3</sub>Bi (001) single crystals. Further details of the sample preparation and ARPES experiments are available in (27). The crystal structure of Na<sub>3</sub>Bi (Fig. 1C) is comprised of stacked ...Na - (Na/Bi) - Na... triple-layer groups, with the adjacent triple-layers rotated by 60 degrees with respect to each other. The 3D Brillouin zone (BZ) of Na<sub>3</sub>Bi is illustrated in Fig. 1D with high symmetry points indicated. According to recent ab initio calculations (15), a pair of 3D Dirac fermions are located near the  $\Gamma$  point in each BZ (labeled as “D” in Fig. 1D), with linear dispersion along  $k_x$ ,  $k_y$ , and  $k_z$  directions. Because a 3D Dirac fermion is a surface in four-dimensional space ( $E = V_x \cdot k_x^D + V_y \cdot k_y^D + V_z \cdot k_z^D$ , where  $V_x$ ,  $V_y$ , and  $V_z$  are the Fermi-velocities along x, y, and z directions, respectively; and  $k_x^D$ ,  $k_y^D$ , and  $k_z^D$  represent the momentum measured from the Dirac point), in Fig. 1E, we visualize it by using  $k_x^D$ ,  $k_y^D$ , and  $k_z^D$  as variables and colors as representation of  $E$  (the 4<sup>th</sup> dimension). The projections of the 3D Dirac fermion onto two 2D momentum planes are shown in Fig. 1F, G. The figures reflect the calculated small in-plane and large out-of-plane anisotropy ( $V_x \approx V_y = 3.74 \times 10^5$  m/s,  $V_z = 2.89 \times 10^4$  m/s).

The overall electronic structure from ARPES measurements is summarized in Fig. 2. The characteristic peaks of Na and Bi elements are evident in the core-level spectra (Fig. 2A); the band dispersions (Fig. 2B) agree well with our ab initio calculations, represented by solid lines [details of the calculations can be found in (27)]. The electronic structure at the Dirac point is illustrated in Fig. 2C, showing a cone-shape with linear dispersions [details on selecting  $k_z$  positions and identifying Dirac

points in momentum space can be found in (27)]. This Dirac cone dispersion results in a point-like Fermi-surface (FS) at  $\bar{\Gamma}$  in the projected 2D BZ (Fig. 2D). Moreover, the constant energy contours of the Dirac cone at different binding energies (Fig. 2E) demonstrate the small in-plane anisotropy.

To demonstrate the 3D nature of the Dirac cone in  $\text{Na}_3\text{Bi}$ , we need to illustrate that the band dispersion is also linear along  $k_z$  (as well as  $k_x$  and  $k_y$ ), which was achieved by performing photon-energy dependent ARPES measurements (27, 28). By assembling the measurements under broad range of photon energies (27), we obtained the band structures of  $\text{Na}_3\text{Bi}$  throughout the 3D BZ. Figure 3A illustrates the complete FS of  $\text{Na}_3\text{Bi}$  in a 3D BZ, showing a pair of point-like FSs in the vicinity of  $\bar{\Gamma}$  at  $k_x = k_y = 0$  and  $k_{\pm} = \pm 0.095/\text{\AA}$  or  $\pm 0.29\pi/c$ , where  $c$  is the  $z$ -direction lattice constant, which agrees well with our ab initio calculations that predict two Dirac points at  $k_{\pm} = \pm 0.26\pi/c$  (15). Note that in Fig. 3A(ii), which shows the data for a Na-deficient sample surface, an additional cylindrical FS appears and vertically crosses the whole 3D BZ (and thus is dispersionless along  $k_z$ ). This feature originates from the surface states (27, 28) that emerge due to the loss of the surface Na atoms, which easily migrate away during the experiment (27).

Besides the 3D FS, we can investigate the band dispersion along all three  $k$ -directions. Similar to Fig. 2C, the 3D electronic structure along  $k_y$ - $k_z$  direction is illustrated in Fig. 3B, showing a clearly elongated (along  $k_z$  direction) Dirac cone (corresponding to a much smaller  $V_z$  - see Fig. 3B, C). Furthermore, we can study the detailed dispersions along each momentum direction (see schematics in Fig. 3D-F): for a 3D Dirac fermion, ARPES measurements along any  $k$ -direction should yield either linear or hyperbolic dispersions depending on whether the measurement cuts through the Dirac point - this is different from the usual parabolic dispersions of massive electrons.

In Fig. 3D-F (i-iv), we use four examples along each  $k$ -direction to show typical ARPES dispersions on  $\text{Na}_3\text{Bi}$  [for more measurements and analysis see (27)]. Along each  $k$ -direction, the dispersion evolves from linear [Fig. 3D-F (i)] to hyperbolic [Fig. 3D-F (ii-iv)] shape, as expected. Notably, to fit all of the ARPES measurements [including those in (27)], we only need one set of 3D Dirac cone parameters ( $V_x = 2.75\text{ eV}\cdot\text{\AA}$  or  $4.17\times 10^5\text{ m/s}$ ,  $V_y = 2.39\text{ eV}\cdot\text{\AA}$  or  $3.63\times 10^5\text{ m/s}$ , and  $V_z = 0.6\text{ eV}\cdot\text{\AA}$  or  $0.95\times 10^5\text{ m/s}$ ). This excellent agreement proves that the bulk band structure of  $\text{Na}_3\text{Bi}$  forms 3D Dirac cones, with a large anisotropy along the  $k_z$  direction ( $V_z \approx 0.25V_x$ , see Fig. 3C).

To test the robustness of 3D Dirac fermion in  $\text{Na}_3\text{Bi}$ , we deliberately modified the sample surface (by in situ evaporating K-atoms, see Fig. 4A, B) and monitored the band dispersions' evolution with the increase of surface impurities. In addition, the K-doping can compensate the charge loss caused by the surface Na-atom loss discussed above [and in (27)]. In fact, we were even able to over-compensate the charge loss with sufficient doping and observed the upper part of Dirac cone beyond the Dirac point (Fig. 4C). With the increase of K-doping, the  $E_F$  shifts upward (Fig. 4D-F), whereas the surface state band disappears (Fig. 4E, F) owing to the deterioration of the sample surface by randomly deposited K-atoms. On the other hand, the bulk Dirac cone (both the linear dispersion and the Dirac point) persists despite such surface deterioration (Fig. 4E, F), supporting the notion that the Dirac fermion is protected by the bulk crystal symmetry (which is preserved during surface K-doping).

The topological Dirac semimetal  $\text{Na}_3\text{Bi}$  realizes a 3D counterpart of graphene, opening the door for the exploration of other 3D TDSs, some of which may realize various exciting applications of graphene in 3D materials. Furthermore, the extremely long Fermi-wavelength (which diverges at the Dirac points) of the bulk conducting electrons in a topological Dirac semimetal can greatly enhance the Ruderman-Kittel-

Kasuya-Yosida interaction, making it possible to realize ferromagnetic states by unusually dilute magnetic doping [similar to the Dirac surface states in a topological insulator (29)] - which could make the topological Dirac semimetal an ideal platform for spintronics applications.

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**Acknowledgements:** We thank X. L. Qi and Z. Wang for insightful discussions, and P. Han and R. Yang for the help in data analysis. Y. L. C and B. Z acknowledge the support from the EPSRC (UK) grant EP/K04074X/1 and a DARPA (US) MESO project (no. N66001-11-1-4105). Z. K. L and Z. X. S acknowledge the support from the Department of Energy under contract DE-AC02-76SF00515. Z.F, X.D and H.M.W acknowledge the supports by the NSF of China, the National Basic Research Program of China, and the International Science and Technology Cooperation Program of China. The experiments were performed, and data were collected at Beamline 10.0.1 of the Advanced Light Source, Lawrence Berkeley National Lab, USA.

#### Supplementary Materials

[www.sciencemag.org/cgi/content/full/science.1245085/DC1](http://www.sciencemag.org/cgi/content/full/science.1245085/DC1)

Materials and Methods

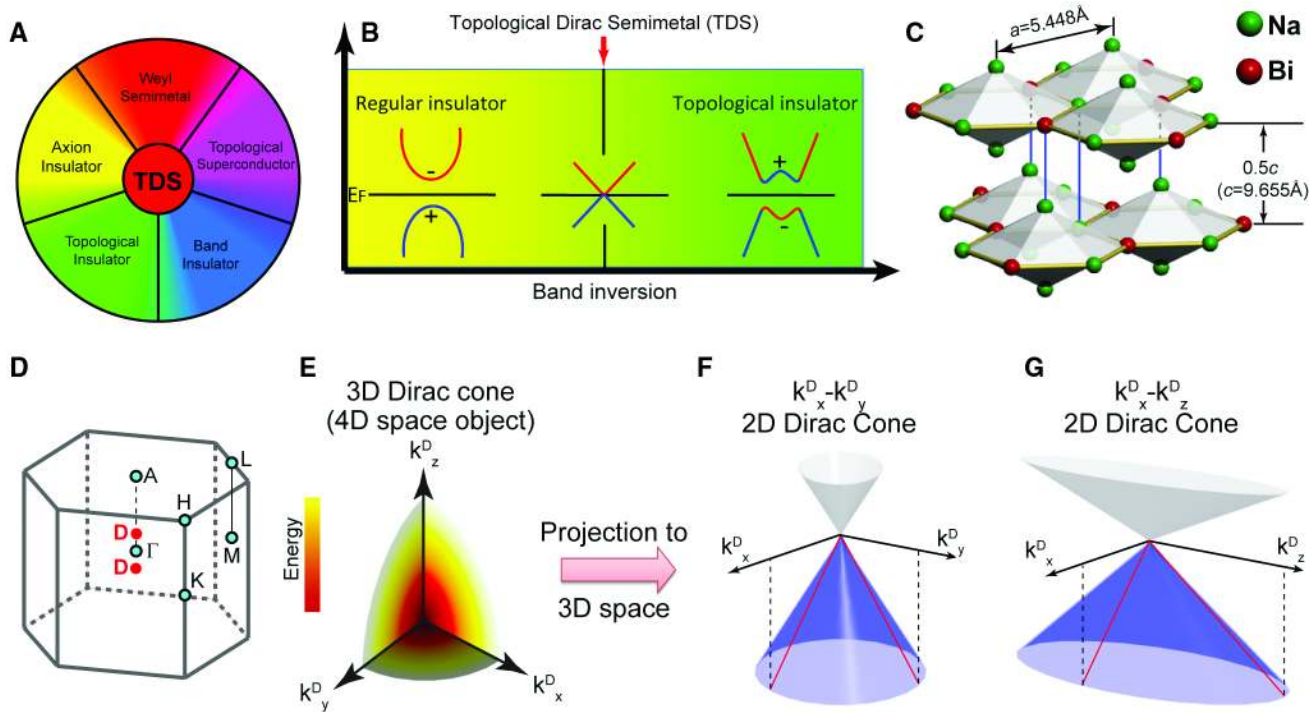
Figs. S1 to S8

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23 August 2013; accepted 02 January 2014

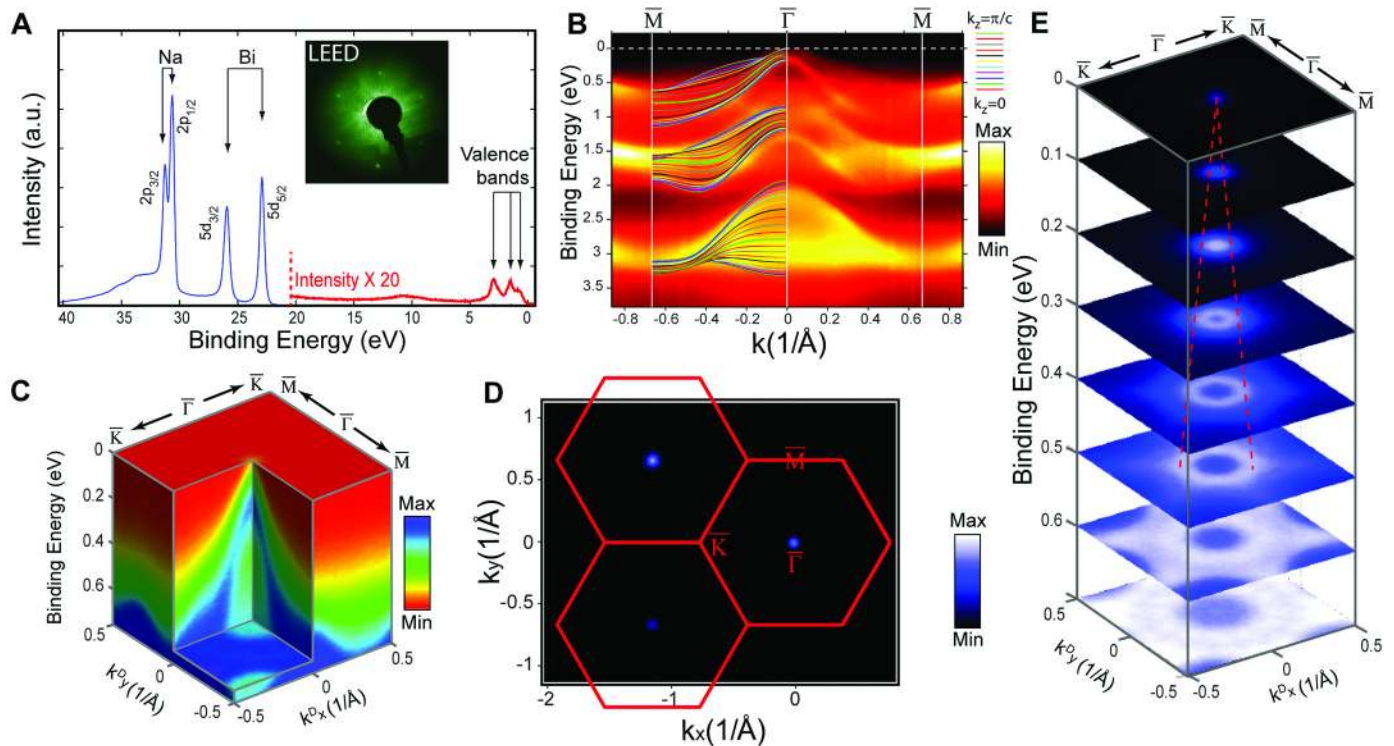
Published online 16 January 2014

10.1126/science.1245085

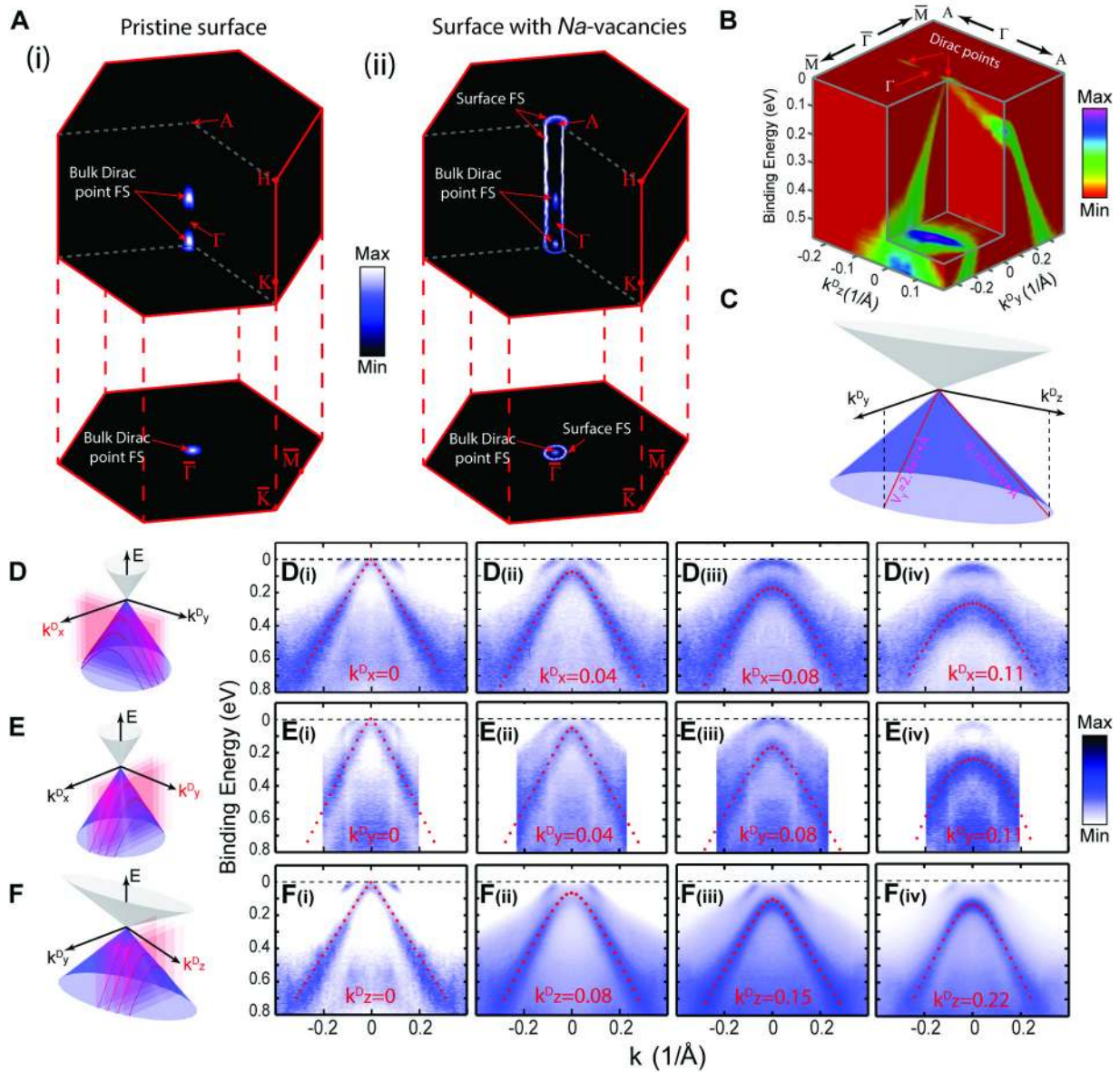


**Fig. 1. Basic characteristics of the TDS.** (A) The TDS state neighbors various novel states. (B) The TDS state may be realized at the quantum critical point in the topological quantum phase transition from a normal insulator to a topological insulator. The “+” and “-” signs denote the even and odd parity of the bands at the time reversal invariant point, respectively. (C) Crystal structure and (D) the BZ of Na<sub>3</sub>Bi. Cyan dots indicate the high symmetry points of the BZ; and the red dots highlight the 3D Dirac point positions. (E) Visualization of a 3D Dirac fermion dispersion ( $E = V_x \cdot k^D_x + V_y \cdot k^D_y + V_z \cdot k^D_z$ ), color scale is used to represent energy. (F, G) Projection of the 3D Dirac fermion onto  $(k^D_x, k^D_y, E)$  and  $(k^D_x, k^D_z, E)$  spaces (see text). Red lines outline the linear dispersions along  $k^D_x$ ,  $k^D_y$  and  $k^D_z$  directions.

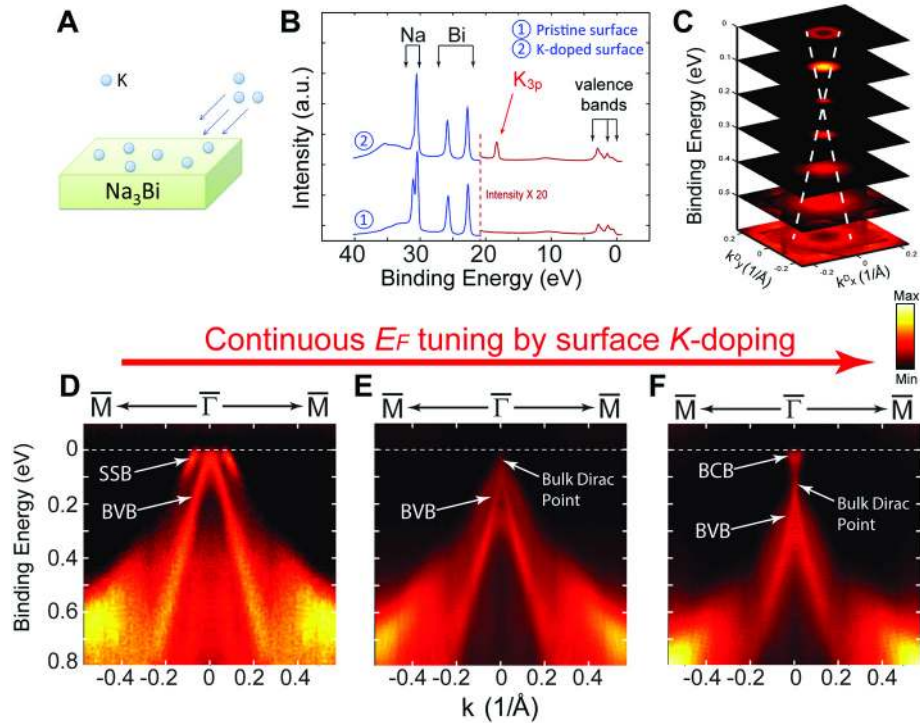




**Fig. 2. Electronic structure of Na<sub>3</sub>Bi.** (A) Core level photoemission spectrum clearly shows strong characteristic Na 2p and Bi 5d doublet peaks (blue curve). Features at low binding energy ( $E_B < 21$  eV) were magnified 20 times to enhance the details (red curve). Inset is the LEED pattern that clearly shows the hexagonal structure of Na<sub>3</sub>Bi (001) surface. (B) Comparison of the valence band spectra between ARPES measurement (background) and ab initio calculations (solid lines) along the  $\bar{M}-\bar{\Gamma}-\bar{M}$  direction. The color of the lines represents different  $k_z$  dispersions in the calculation. (C) 3D intensity plot of the photoemission spectra at the Dirac point, showing cone-shape dispersion. (D) Broad FS map from ARPES measurements that covers three BZs. The red hexagons represent the surface BZ; and the uneven intensity of the FS points of different BZ results from the matrix element effect. (E) Stacking plot of constant energy contours at different binding energy shows Dirac cone band structure. Red dotted lines are the guides to the eye that indicate the dispersions and intersect at the Dirac point.



**Fig. 3. Dispersion of the 3D Dirac fermion along all three momentum directions.** (A) FS map across the whole 3D BZ (top panel) and its projection to the surface BZ (bottom panel) on pristine (i) and Na-deficient (ii) surfaces. An additional FS appears in panel (ii) [see text and (27) for details]. (B) 3D intensity plot of the photoemission spectra (along the  $k_y$ - $k_z$  direction) shows the elongated (along the  $k_z$ -direction) cone-shape dispersion, indicating the large anisotropy between  $k_y$  and  $k_z$  direction. (C) The schematic of the  $k_y$ - $k_z$  Dirac cone reconstructed from the experimental fit parameters:  $V_y = 2.4$  eV·Å, and  $V_z = 0.6$  eV·Å (27). (D-F) Schematics show the dispersions (red curves) that slice through the 3D Dirac cones at different ( $k_x^D$ ,  $k_y^D$  or  $k_z^D$ ) momentum locations, showing either linear or hyperbolic shape. The Dirac velocity parameters obtained from our experiments are:  $V_x = 2.8$  eV·Å,  $V_y = 2.4$  eV·Å, and  $V_z = 0.6$  eV·Å (27). D(i-iv) Measured dispersion at  $k_x^D = 0, 0.04, 0.08$  and  $0.11$  Å<sup>-1</sup>, respectively. Red dotted lines show the fitted dispersions that agree well with the experiments [see text and (27)]. E(i-iv) Experiment and fitted dispersions at  $k_y^D = 0, 0.04, 0.08$  and  $0.11$  Å<sup>-1</sup>, respectively. F(i-iv) Experiment and fitted dispersions at  $k_z^D = 0, 0.08, 0.15$  and  $0.22$  Å<sup>-1</sup>, respectively.



**Fig. 4. Bulk Dirac fermion stability and  $E_F$  tuning by surface doping.** (A) Illustration of the in situ surface K-doping. (B) Core level photoemission spectra before and after the K-doping show the rise of the  $K_{3p}$  core level peak (which can be used to monitor the dosage level). (C) Stacking plot of constant energy contours shows the upper Dirac cone after the in situ K-doping. White dashed lines are the guides to the eye that trace the Dirac dispersions. (D-F) ARPES intensity plots show the rising of the  $E_F$  position with K-dosage. Acronyms: SSB, surface state band; BCB, bulk conduction band; BVB, bulk valence band. (D): Before in situ K-doping; (E) at K-doping needed to bring  $E_F$  to the bulk Dirac point; (F): further K-doping drives the system into n-type. Note that the SSB in (D) is destroyed by the K-doping, and thus does not show in (E) and (F).