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Deep Insight Into the Electronic Structure of Ternary Topological Insulators: A Comparative Study of PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$

*D. Pacilè, S. V. Ereemeev, M. Caputo, M. Pisarra, O. De Luca, I. Grimaldi, J. Fujii, Z. S. Aliev, M. B. Babanly, I. Vobornik, R. G. Agostino, A. Goldoni, E. V. Chulkov, and M. Papagno**

By means of angle-resolved photoemission spectroscopy measurements, the electronic band structure of the three-dimensional PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ topological insulators is compared. The measurements clearly reveal coexisting topological and multiple Rashba-like split states close to the Fermi level for both systems. The observed topological states derive from different surface terminations, as confirmed by scanning tunneling microscopy measurements, and are well-described by the density functional theory simulations. Both the topological and the Rashba-like states reveal a prevalent two-dimensional character barely affected by air exposure. X-ray and valence band photoemission measurements suggest Rashba-like states stem from the van der Waals gap expansion, consistently with density functional theory calculations.

Topological insulators (TIs) have recently emerged as a new state of quantum matter, distinguished from conventional insulators by having a surface state with a massless Dirac dispersion in the bulk energy gap.^[1,2] At odd with graphene, the spin orientation of the Dirac surface state (topological surface state: TSS) is locked with its crystal momentum, and protected from backscattering owing to time-reversal symmetry. These unique properties make TIs a hopeful material to realize new electronic phenomena, among them, Bi_2Se_3 and Bi_2Te_3 have been the most studied.^[3–15] The crystal structure of both Bi_2Se_3 and Bi_2Te_3 can be represented as a stack of five atomic planes (Te(Se)-Bi-Te(Se)-Bi-Te(Se)) to form quintuple layers (QLs). The

Dr. D. Pacilè, Dr. M. Pisarra, Dr. O. De Luca, I. Grimaldi,
Prof. R. G. Agostino, Dr. M. Papagno
Dipartimento di Fisica
Università della Calabria
87036 Arcavacata di Rende (Cs), Italy
E-mail: marco.papagno@fis.unical.it

Dr. S. V. Ereemeev
Institute of Strength Physics and Materials Science
634021 Tomsk, Russia

Dr. S. V. Ereemeev
Tomsk State University
634050 Tomsk, Russia

Dr. S. V. Ereemeev
Saint Petersburg State University
Saint Petersburg 198504, Russia

Dr. M. Caputo, A. Goldoni
Sincrotrone Trieste SCpA
SS14 Km 163.5, 34149 Trieste, Italy

Dr. M. Pisarra
Departamento de Química
Módulo 13
Universidad Autónoma de Madrid
28049 Madrid, Spain

Dr. J. Fujii, Dr. I. Vobornik
CNR-IOM
TASC Laboratory
AREA Science Park Basovizza, 34149 Trieste, Italy

Dr. Z. S. Aliev
Azerbaijan State Oil and Industry University
AZ1010 Baku, Azerbaijan

Dr. Z. S. Aliev
Materials Science and Nanotechnology Department
Near East University
North Cyprus, Mersin 10, 99138 Nicosia, Turkey

Prof. M. B. Babanly
Institute Catalysis and Inorganic Chemistry
Azerbaijan National Academy of Science
AZ1143 Baku, Azerbaijan

Prof. E. V. Chulkov
Donostia International Physics Center (DIPC)
20018 San Sebastián/Donostia, 20080 Basque Country, Spain

Prof. E. V. Chulkov
Departamento de Física de Materiales UPV/EHU
Centro de Física de Materiales CFM – MPC and Centro Mixto CSIC-UPV/EHU
20080 San Sebastián/Donostia, 20080 Basque Country, Spain

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/pssr.201800341>.

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interlayer bonds between adjacent QLs are of van der Waals (vdW) type which infer a strong layered structure to the systems. The resulting band structure of both compounds is rather simple with a single Dirac cone state in a relatively large band gap.^[9,10,16,17]

For the realization of many of the predicted phenomena, one main issue that one has to face is a fine tailoring of the electronic properties. So far, this has been attempted mainly by doping or intercalation, but in both cases the surface states are strongly modified.^[18–29] One other critical point is that future topological-based devices will most likely involve surfaces that are exposed to ambient environment; TIs electronic properties need thus to be robust against air exposure.

An innovative approach that allows to design TIs with tunable electronic states, *unaffected* by ambient conditions, relies on Pb-based ternary chalcogenides.^[15,30–33] In contrast to the binary layered compounds, whose structure is formed by QLs only, ternary chalcogenides can include QL and septuple (SL) building blocks.^[15,31] The simplest Pb-based is PbBi_2Te_4 made of seven-layer blocks only (atomic layer sequence Te-Bi-Te-Pb-Te-Bi-Te), displaying an energy gap of 230 meV and a single Dirac cone at the Gamma point.^[31] More complex structure can be realized by stacking QL- and SL-blocks. Importantly, by varying the sequence of the blocks it is possible to design specific topological insulators with peculiar electronic properties. In particular, PbBi_4Te_7 compound is composed by alternating QL and SL blocks, while another compound of the Pb-Bi-Te series, $\text{PbBi}_6\text{Te}_{10}$, is built of SL and two QL blocks. Earlier these compounds were studied separately and multiple Dirac states related to different surface terminations were observed.^[15,32,33] On the other hand, Rashba surface states, which usually reside at the surface of layered TIs, have not been studied in detail and origin of these states has not been clarified.

In this work, we compare the electronic band structure of co-grown PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ compounds by means of angle-resolved photoemission spectroscopy (ARPES) measurements. Scanning tunneling microscopy (STM) investigations confirm that PbBi_4Te_7 is composed by alternating QL and SL units, whereas $\text{PbBi}_6\text{Te}_{10}$ comprises of SL and two QL building blocks. ARPES measurements display multiple $\bar{\Gamma}$ surface Dirac states, and Rashba-type split bands for both compounds. Both the topological and the Rashba-like states exhibit a two-dimensional character and are robust against air exposure. Combined X-ray photoemission spectroscopy (XPS) and valence band measurements before and after air exposure suggest that expansion of the vdW gap induces the Rashba-type states, consistently with density functional theory (DFT) calculations.

Experimental Details: Single crystalline ingot of PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ were grown from non-stoichiometric composition by the vertical Bridgman-Stockbarger method. The synthesis was performed in two steps. First, the polycrystalline composition was synthesized from high-purity (5N) elements in evacuated quartz ampoule at about 1000 K for 8 h mixing incessantly, followed by air cooling. Afterwards, the polycrystalline sample was placed in a conical-bottom quartz ampoule, which was sealed under a vacuum better than 10^{-4} Pa. At the beginning of the growing process, the ampoule was held in the “hot” zone (≈ 920 K) of a two-zone tube furnace for 24 h for a complete melting of the composition. The charged ampoule moves from

the “hot” zone to the “cold” zone with the required rate 1.0 mm h^{-1} . In this way, bulk ingot with average dimensions of ≈ 4 cm in length and 0.8 cm in diameter was obtained. The as-grown ingot was checked by accurately X-ray diffraction (XRD) measurements and found that it consists of single crystalline blocks of PbBi_4Te_7 , $\text{PbBi}_6\text{Te}_{10}$, $\text{PbBi}_8\text{Te}_{13}$ at bottom, middle, and top part, respectively, according to crystallization sequence. Since the $\text{PbBi}_8\text{Te}_{13}$ single crystalline blocks were very small and always mixed with the $\text{PbBi}_6\text{Te}_{10}$ phase at the top part of the ingot, we were not able to isolate high-quality and large single crystalline pieces of $\text{PbBi}_8\text{Te}_{13}$. However, the high-quality single crystalline blocks of the other two PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ phases were properly isolated from the bottom and middle part of the as-grown ingot, and checked accurately by XRD and STM measurements.

The presented measurements were performed on fresh surfaces obtained by cleavage at room temperature (RT) in ultrahigh-vacuum (UHV) conditions. The high quality of the achieved (111) surfaces was verified by the sharp features in the low-energy electron diffraction (LEED) pattern and STM measurements (**Figure 1**). Experiments were carried out at the APE-IOM beamline of the Elettra synchrotron radiation facility. This beamline has distinct UHV-chambers connected in situ, so to perform complementary characterization (ARPES, XPS, and STM) of the same surface. All experiments were performed under UHV conditions with a base pressure below 1×10^{-10} Torr.

ARPES investigations have been carried out with a Scienta DA30 hemispherical electron energy and momentum analyzer in the photon energy region 15–60 eV at 77 K. XPS measurements have been recorded at RT with an electron energy analyzer Omicron EA125 by using different photon energy in the range 830–350 eV. STM measurements were carried out with a home-built room-temperature scanning tunneling microscope.

The electronic structure calculations were performed within the density functional theory implemented in VASP code.^[34,35] We used the all-electron projector augmented wave basis sets^[36,37] with the generalized gradient approximation^[38] to the exchange correlation (XC) potential. Spin-orbit interaction was included in the calculations. To take into account the effect of dispersion interactions we use DFT-D3 method by Grimme et al.^[39] as implemented in the VASP code.

Results and Discussion: The crystal structure of both PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ is rhombohedral (**Figure 1**) and consist of alternate stacking of five-layer (Te-Bi-Te-Bi-Te) and seven-layer blocks (Te-Bi-Te-Pb-Te-Bi-Te) bonded one to another by vdW interactions. Each layer has only one, hexagonally arranged, type of atom (Te, Bi, or Pb).

Figure 1a,b are representative topographic images of fresh cleaved PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ surfaces, respectively. Due to weak interactions between the blocks, the crystals can be easily cleaved resulting in different terminations of the topmost surface. The line profile along the line showed in panel (a) and presented in **Figure 1c**, confirms that, in the case of PbBi_4Te_7 , the topmost surface consists of QL or SL layer blocks having different step heights of about 1.2 and 1.7 nm, respectively. These two blocks always alternate themselves in a QL-SL-QL-SL... sequence. We note that the apparent heights are somewhat larger than the previously reported values.^[15,32] However, since STM probes the sample local density of states convoluted with

Figure 1. a,b) Constant-current STM image on fresh cleaved PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ ($V_B = 1.0$ V; $I_t = 0.2$ nA; $T = 300$ K; size 400 nm $\times$ 200 nm) surfaces. c,d) Apparent height profiles along the gray line in (a) and (b), respectively, revealing the presence of terraces with different step height due to different surface terminations. In the left- and right-hand side of panels (a) and (b) the atomic structure of PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ are depicted, respectively. QL and SL mark quintuple and septuple blocks. Inset of panels (a) and (b) show the low-energy electron diffraction patterns on PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$, respectively, collected with an electron beam of 55 eV.

that of the STM tip, the apparent height values can be different if the STM data are collected with different tips.

The crystal structure of $\text{PbBi}_6\text{Te}_{10}$ is slightly more complex having three possible surface terminations, as evidenced by the line profile displayed in Figure 1d. In particular, there are two quintuple-layers (QL_1 and QL_2) and one septuple layer block with step height of 1.2 , 1.2 , and 1.7 nm, respectively.^[33] The three blocks are always found in the $\text{QL}_1\text{-QL}_2\text{-SL-QL}_1\text{-QL}_2\text{-SL}$...stacking.

Figure 2a,b are the measured electronic band structure along the $\bar{\text{M}}\text{-}\bar{\Gamma}\text{-}\bar{\text{K}}$ direction of PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$, respectively. Since the average size of the surface terraces ($\approx 10^4$ nm²) is much smaller than the beam spot ($\approx 10^8$ nm²), all surface blocks are illuminated during ARPES experiments, and thus the band structure of different surface terminations is captured at the same time. Furthermore, the high-quality of the crystal structure allows the electronic band structure to be unambiguously resolved. In particular, two sharp and distinct topological surface states, labeled 5 and 7 L, are observed for PbBi_4Te_7 . These two features are due to different surface terminations, QL- and SL-blocks, respectively.^[15] In $\text{PbBi}_6\text{Te}_{10}$, since there are three different surface terminations, each one supporting Dirac surface states, three distinctive Dirac states, labeled 5 L₁, 5 L₂, and 7 L, are observed. The rigid band shift of about 500 meV in our experimental data as compared with *ab-initio* calculations^[15] is likely due to *n*-type intrinsic defects or impurities, or induced by photons during ARPES experiments.^[40]

The hallmark of the observed topological states (band dispersion, Dirac point energy, group velocity, and kink like structure) are in perfect agreement with earlier studies.^[15,32,33]

In addition to the topological states, ARPES measurements reveal Rashba-like states at the zone center in the energy region -0.17 ± 0.05 eV (Figure 2) for both samples. Constant energies ARPES maps in panels (c–e) prove that these states display an almost circular contour at all the investigated energies. Interestingly, the main Rashba-like states of both compounds display similar features, having a nearly parabolic dispersion with a minimum at 0.17 eV and momentum offset $k_0 = \pm 0.035$ Å⁻¹. Also, the estimated Rashba energy and coupling constant have approximately the same values (≈ 0.03 eV and ≈ 1.7 eV Å, respectively), in agreement with earlier measurements.^[15,33]

Figure 3a–c present the measured electronic states of PbBi_4Te_7 along the $\bar{\Gamma}\text{-}\bar{\text{M}}$ direction for different photon energy. To better visualize the band dispersion and to enhance the contrast, we show in Figure 3d–f the same data differentiated along the energy axis. These measurements prove that, similarly to $\text{PbBi}_6\text{Te}_{10}$, the Rashba-like state in PbBi_4Te_7 display a poor k_z dispersion. In fact, apart from matrix-element effects,^[41] neither the Rashba-like, nor the topological states dispersion vary when measured with different photon energies. In addition, at odd with earlier measurements,^[32] we were able to clearly resolve the 5 L-derived topological state by performing surface sensitive ARPES measurements (Figure 3c,f). This finding reveals that the charge density of the 5 L state is not mainly confined in the bulk^[32] but has relevant contribution close to the surface as well.

If the observed multiple topological states are due to different terminations that make up the surface of both compounds, the origin of the Rashba-like states is less straightforward. Rashba-like

Figure 2. Experimental band structure of (a) PbBi_4Te_7 and (b) $\text{PbBi}_6\text{Te}_{10}$ along $\bar{M}-\bar{\Gamma}-\bar{K}$ direction. Unsymmetrized constant energy ARPES maps (c,d) at the Fermi level and (e,f) at $E-E_F = -0.17$ eV, for PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$, respectively. The inset of panel (a) shows the bulk Brillouin zone (black lines) and the corresponding (111) surface Brillouin zone (cyan thick lines) for both compounds. In panels (a) and (b), the horizontal red and green dashed lines mark the energy of the ARPES maps displayed in (c,d) and (e,f).

states can arise because of “aging” effect or expansion of van der Waals gaps.

The aging effect is concerned with donor-type contaminants adsorbed on *n*-doped topological insulators. The adsorbed species result in donor-type surface states inducing spatial regions of screening charges (space charge regions) which may extend tens of Angstrom in the interior of the crystal. If the redistribution of screening charges is strong enough, the conduction band minimum might cross the Fermi level producing a downward band bending (eV_{bb}) and a plasma of electrons within the space charge region. This free-electron gas is, however, trapped by the band bending potential V_{bb} resulting in quantized electronic states and spin-split bands.^[18–26,42]

To unveil possible contaminants, we have performed detailed X-ray photoemission measurements on the same sample surfaces of Figure 2. Both PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ (Figure 4a red and blue curve, respectively) are contaminants free within the detection limit of the measurements (parts per thousand). We do observe O and C related photoemission structures after exposure the PbBi_4Te_7 surface to air (green curve in Figure 4b). In this case, Bi and Te atoms undergo to a chemical shift as evidenced by Te 3*d* (inset of Figure 4b) and Bi 4*f* lines (Figure 4c); importantly, the valence band remains *protected*: no remarkable energy shifts of the electronic states nor additional electronic (Rashba-like) bands are observed in the valence band (Figure 4d). To our knowledge, this is the first example of spin-

Figure 3. Band structure for PbBi_4Te_7 along the $\bar{M}-\bar{\Gamma}-\bar{M}$ direction measured with (a) 15 eV, (b) 25 eV, and (c) 50 eV photons, and same data differentiated along the energy axis in (d), (e), and (f), respectively.

split electronic states unaffected by prolonged air exposure. These experimental findings suggest that the investigated systems do not undergo to the aging effect, and that foreign atoms adsorbed at surface cannot be responsible of the observed Rashba-like bands.

A different mechanism which induces Rashba-states is an expansion of van der Waals gaps induced by imperfections/defects trapped between neighboring blocks during the growth process. Such expansion affects the band structure inducing new spin-split electronic states.^[29,43,44]

To explore this scenario, we have performed DFT calculations for the PbBi_4Te_4 asymmetric slab with SL and QL terminations on the opposite surfaces. The spectrum of this slab reported in **Figure 5a** nicely reproduces the earlier calculation results obtained for symmetric slabs^[15,31] and ARPES measurements in the part related to dispersion of the Dirac states. However, this spectrum does not predict the Rashba-like state resided on the surface of the real crystal. To simulate the latter we performed calculations of the slab with expanded outermost vdW gaps on its both sides. At odd with Bi_2Se_3 and related compounds,^[29] where detailed investigation for a wide range of expansions was done, in the present simulation we use a moderate value of vdW expansion that amounts of 20% for both SL and QL terminations of the slab. **Figure 5b** evidences that such an expansion leads to

emergence of two Rashba states. The first Rashba state located at the SL-terminated surface arises due to the splitting off from the bottom of the 1st (pink) conduction band and reside in the bulk band gap. The second Rashba band located on the QL-terminated surface splits off from the bottom of the 2nd (green) conduction band but lies in the bulk continuum region and therefore is hardly detectable experimentally. To get more insight on the nature of the Rashba states we considered the orbital composition of the two lowest conduction bands in the vicinity of the Γ point. Since the Rashba states have basically p_z character, we summed the weights of p_z orbitals of atoms constituting the SL and QL blocks. As can be seen in **Figure 5c**, the 1st, lowest band in the vicinity of Γ is predominantly SL band while the 2nd one is mainly contributed by the atomic orbitals of QL block.

The case of $\text{PbBi}_6\text{Te}_{10}$ is more complicated. For the pristine surface the spectrum, combined from three different calculations for symmetric 7 L, 5 L₁, and 5 L₂ terminated slabs, shows three Dirac states and three different bulk bands (pink, green, and cyan) forming the lower part of the bulk conduction band continuum (**Figure 6a**). However, in contrast to the previous case we cannot simply designate them to proper terminations. Considering the orbital weights in the bulk band structure we again sum up the atomic contributions from SL block (**Figure 6b**) but for two equivalent QLs by symmetry reasons we combine

Figure 4. a) XPS measurements on PbBi₄Te₇ (red curve) and PbBi₆Te₁₀ (blue curve) measured with 700 eV photons just after cleavage. b) XPS measurements on PbBi₄Te₇ before (red curve) and after exposure to air for 15 min (green curve) measured with 830 eV photons. The inset shows the Te 3d-states for the clean surface (red curve) split by spin-orbit interaction into the doublet 3d_{3/2} and 3d_{5/2} at 582.07 and 571.65 eV binding energy. After air exposure (green curve) new components shifted by 3.62 eV toward higher binding energy are observed. c) Bi and Pb 4f-states for the clean PbBi₄Te₇ surface (red curve) collected at 370 eV split by spin-orbit interaction into Bi 4f_{5/2} (162.30 eV), Bi 4f_{7/2} (157.00 eV), and Pb 4f_{5/2} (141.50 eV), Pb 4f_{7/2} (136.65 eV). After air exposure (green curve) Bi 4f-states present new resonances shifted by 1.2 eV toward lower energy. d) ARPES spectrum of PbBi₄Te₇ measured with photons of 50 eV after exposure to air.

Figure 5. a) Calculated surface electronic structure of PbBi₄Te₇ slab with SL and QL surface terminations on the opposite side of the slab. b) The electronic structure of the PbBi₄Te₇ slab with outer SL(QL) detached by 20%. c) Close view of the bulk conduction band near the Γ point with indication of weights of p_z orbitals of the atoms forming SL and QL.

Figure 6. a) Surface electronic structure of $\text{PbBi}_6\text{Te}_{10}$. b–d) The bulk conduction band near the Γ point with indication of weights of p_z orbitals of the atoms forming SL and QL.

separately the weights of the p_z orbitals of Te and Bi atomic layers from the sides of QLs that are near QL/SL vdW spacing (Figure 6c) and those from atomic layers near QL/QL one (Figure 6d).

As can be seen in Figure 6b–d, the lowest conduction band is equally contributed by SL and QL/SL orbitals while those from QL/QL is absent in the first band and dominate in the second band. The third conduction band is contributed equally by all orbitals. Despite the mixed orbital composition of the lowest bulk bands the 1st and 2nd bands lie very close to each other while the third one is distant from them. Such a bulk band structure dictates that, irrespective of the surface termination, the emergent Rashba states originating from the two lowest bands will appear in the gap, and they do show up in the ARPES spectrum (see Figure 2b). Instead, the third Rashba state originated from third, distant bulk band, should appear in the continuum region, like the state on QL-terminated surface of PbBi_4Te_7 .

In conclusion, we have performed a comparative study of PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ ternary topological insulators prepared within a single ingot as high quality crystalline blocks. The presented ARPES measurements highlight coexisting and *protected* two-dimensional topological states. These states stem from distinct surface terminations that compose the stepped surface of both PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$, as revealed by STM measurements. We also observe two-dimensional Rashba-like states for both compounds. The Rashba bands are rather intrinsic states induced by the atoms trapped in the van der Waals gaps rather than by the band-bending effect, as deduced by our XPS and ARPES measurements, and further supported by DFT calculations.

At odd with earlier observed topological and Rashba-like states on the Bi_2Se_3 surface, which are very sensitive to air or CO exposure owing to a surface band-bending effect, in the case of PbBi_4Te_7 and $\text{PbBi}_6\text{Te}_{10}$ the TSS and the Rashba states are almost insensitive to air exposure. In addition, by varying the sequence of the building blocks of the crystal, and the amount of defects within in the vdW gap, it is in principle possible to design topological insulators with specific electronic character.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

density functional theory, electronic structure, photoemission, scanning tunneling microscopy, topological insulators

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- [1] M. Z. Hasan, C. L. Kane, *Rev. Mod. Phys.* **2010**, *82*, 3045.
- [2] X.-L. Qi, S.-C. Zhang, *Rev. Mod. Phys.* **2011**, *83*, 1057.
- [3] Q. K. Xue, *Nat. Nanotechnol.* **2011**, *6*, 197.
- [4] F. Xiu, L. He, Y. Wang, L. Cheng, L. T. Chang, M. Lang, G. Huang, X. Kou, Y. Zhou, X. Jiang, Z. Chen, J. Zou, A. Shailos, K. L. Wang, *Nat. Nanotechnol.* **2011**, *6*, 216.
- [5] H. Peng, K. Lai, D. Kong, S. Meister, Y. Chen, X.-L. Qi, S.-C. Zhang, Z.-X. Shen, Y. Cui, *Nat. Mater.* **2010**, *9*, 225.
- [6] X.-L. Qi, R. Li, J. Zang, S.-C. Zhang, *Science* **2009**, *323*, 1184.
- [7] L. Fu, C. L. Kane, *Phys. Rev. Lett.* **2008**, *100*, 096407.
- [8] L. A. Wray, S.-Y. Xu, Y. Xia, Y. S. Hor, D. Qian, A. V. Fedorov, H. Lin, A. Bansil, R. J. Cava, M. Z. Hasan, *Nat. Phys.* **2010**, *6*, 855.
- [9] K. Kuroda, M. Arita, K. Miyamoto, M. Ye, J. Jiang, A. Kimura, E. E. Krasovskii, E. V. Chulkov, H. Iwasawa, T. Okuda, K. Shimada, Y. Ueda, H. Namatame, M. Taniguchi, *Phys. Rev. Lett.* **2010**, *105*, 076802.
- [10] S.V. Ereemeev, Y. M. Koroteev, E. V. Chulkov, *JETP Lett.* **2010**, *91*, 387.
- [11] X. Wan, A. M. Turner, A. Vishwanath, S. Y. Savrasov, *Phys. Rev. B* **2011**, *83*, 205101.

- [12] B. Singh, A. Sharma, H. Lin, M. Z. Hasan, R. Prasad, A. Bansil, *Phys. Rev. B* **2012**, 86, 115208.
- [13] B. Singh, H. Lin, R. Prasad, A. Bansil, *Phys. Rev. B* **2013**, 88, 195147.
- [14] S.-Y. Xu, Y. Xia, L. A. Wray, S. Jia, F. Meier, J. H. Dil, J. Osterwalder, B. Slomski, A. Bansil, H. Lin, R. J. Cava, M. Z. Hasan, *Science* **2011**, 332, 560.
- [15] S. V. Ereemeev, G. Landolt, T. V. Menshchikova, B. Slomski, Y. M. Koroteev, Z. S. Aliev, M. B. Babanly, J. Henk, A. Ernst, L. Patthey, A. Eich, A. A. Khajetoorians, J. Hagemeister, O. Pietzsch, J. Wiebe, R. Wiesendanger, P. M. Echenique, S. S. Tsirkin, I. R. Amiraslanov, J. H. Dil, E. V. Chulkov, *Nat. Commun.* **2012**, 3, 635.
- [16] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, Z.-X. Shen, *Science* **2009**, 325, 178.
- [17] Y. L. Chen, J.-H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H.-H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, Z.-X. Shen, *Science* **2010**, 329, 659.
- [18] Z.-H. Zhu, G. Levy, B. Ludbrook, C. N. Veenstra, J. A. Rosen, R. Comin, D. Wong, P. Dosanjh, A. Ubaldini, P. Syers, N. P. Butch, J. Paglione, I. S. Elfimov, A. Damascelli, *Phys. Rev. Lett.* **2011**, 107, 186405.
- [19] H. M. Benia, C. Lin, K. Kern, C. R. Ast, *Phys. Rev. Lett.* **2011**, 107, 177602.
- [20] M. Bianchi, D. Guan, S. Bao, J. Mi, B. B. Iversen, P. D. C. King, P. Hofmann, *Nat. Commun.* **2010**, 1, 128.
- [21] M. Bianchi, R. C. Hatch, J. Mi, B. B. Iversen, P. Hofmann, *Phys. Rev. Lett.* **2011**, 107, 086802.
- [22] L. A. Wray, S.-Y. Xu, Y. Xia, D. Hsieh, A. V. Fedorov, Y. S. Hor, R. J. Cava, A. Bansil, H. Lin, M. Z. Hasan, *Nat. Phys.* **2011**, 7, 32.
- [23] P. D. C. King, R. C. Hatch, M. Bianchi, R. Ovsyannikov, C. Lupulescu, G. Landolt, B. Slomski, J. H. Dil, D. Guan, J. L. Mi, E. D. L. Rienks, J. Fink, A. Lindblad, S. Svensson, S. Bao, Balakrishnan, B.B. Iversen, J. Osterwalder, W. Eberhardt, F. Baumberger, Ph. Hofmann, *Phys. Rev. Lett.* **2011**, 107, 096802.
- [24] T. Valla, Z.-H. Pan, D. Gardner, Y. S. Lee, S. Chu, *Phys. Rev. Lett.* **2012**, 108, 117601.
- [25] M. Bianchi, R. C. Hatch, Z. Li, P. Hofmann, F. Song, J. Mi, B. B. Iversen, Z. M. Abd El-Fattah, P. Löptien, L. Zhou, A. A. Khajetoorians, J. Wiebel, R. Wiesendanger, J. W. Wells, *ACS Nano* **2012**, 6, 7009.
- [26] B. Zhou, Z. K. Liu, J. G. Analytis, K. Igarashi, S. K. Mo, D. H. Lu, R. G. Moore, I. R. Fisher, T. Sasagawa, Z. X. Shen, Z. Hussain, Y. L. Chen, *Semicond. Sci. Technol.* **2012**, 27, 124002.
- [27] J. Henk, A. Ernst, S. V. Ereemeev, E. V. Chulkov, I. V. Maznichenko, I. Mertig, *Phys. Rev. Lett.* **2012**, 108, 206801.
- [28] J. Henk, M. Flieger, I. V. Maznichenko, I. Mertig, A. Ernst, S. V. Ereemeev, E. V. Chulkov, *Phys. Rev. Lett.* **2012**, 109, 076801.
- [29] S. V. Ereemeev, M. G. Vergniory, T. V. Menshchikova, A. A. Shaposhnikov, E. V. Chulkov, *New J. Phys.* **2014**, 14, 113030.
- [30] S. V. Ereemeev, Y. M. Koroteev, E. V. Chulkov, *JETP Lett.* **2010**, 92, 161.
- [31] K. Kuroda, H. Miyahara, M. Ye, S. V. Ereemeev, Yu. M. Koroteev, E. E. Krasovskii, E. V. Chulkov, S. Hiramoto, C. Moriyoshi, Y. Kuroiwa, K. Miyamoto, T. Okuda, M. Arita, K. Shimada, H. Namatame, M. Taniguchi, Y. Ueda, A. Kimura, *Phys. Rev. Lett.* **2012**, 108, 206803.
- [32] T. Okuda, T. Maegawa, M. Ye, K. Shirai, T. Warashina, K. Miyamoto, K. Kuroda, M. Arita, Z. S. Aliev, I. R. Amiraslanov, M. B. Babanly, E. V. Chulkov, S. V. Ereemeev, A. Kimura, H. Namatame, M. Taniguchi, *Phys. Rev. Lett.* **2013**, 111, 206803.
- [33] M. Papagno, S. V. Ereemeev, J. Fujii, Z. S. Aliev, M. B. Babanly, S. K. Mahatha, I. Vobornik, N. T. Mamedov, D. Pacilé, E. V. Chulkov, *ACS Nano* **2016**, 10, 3518.
- [34] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, 48, 13115.
- [35] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, 6, 15.
- [36] P. E. Blöchl, *Phys. Rev. B* **1994**, 50, 17953.
- [37] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, 59, 1758.
- [38] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865.
- [39] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, 132, 154104.
- [40] E. Frantzeskakis, S. V. Ramakutty, N. de Jong, Y. K. Huang, Y.: Pan, A. Tytarenko, M. Radovic, N. C. Plumb, M. Shi, A. Varykhalov, A. de Visser, E. van Heumen, M. S. Golden, *Phys. Rev. X* **2007**, 7, 041041.
- [41] Z.-H. Zhu, C. N. Veenstra, G. Levy, A. Ubaldini, P. Syers, N. P. Butch, J. Paglione, M. W. Haverkort, I. S. Elfimov, A. Damascelli, *Phys. Rev. Lett.* **2013**, 110, 216401.
- [42] M. R. Scholz, J. Sánchez-Barriga, D. Marchenko, A. Varykhalov, A. Volykhov, L. V. Yashina, O. Rader, *Phys. Status Solidi RRL* **2013**, 7, 139.
- [43] L. Plucinski, A. Herdt, S. Fahrenndorf, G. Bihlmayer, G. Mussler, S. Döring, J. Kampmeier, F. Matthes, D. E. Bürgler, D. Grützmacher, S. Blügel, C. M. Schneider, *J. Appl. Phys.* **2013**, 113, 053706.
- [44] C. Chen, S. He, H. Weng, W. Zhang, L. Zhao, H. Liu, X. Jia, D. Mou, S. Liu, J. He, Y. Peng, Y. Feng, Z. Xie, G. Liu, X. Dong, J. Zhang, X. Wang, Q. Peng, Z. Wang, S. Zhang, F. Yang, C. Chen, Z. Xu, X. Dai, Z. Fang, X. J. Zhou, *Proc. Natl. Acad. Sci. USA* **2012**, 109, 3694.