Topological nodal line states and a potential catalyst of hydrogen evolution in the TiSi family

Jiangxu Li‡,1 Hui Ma‡,1,2 Shaobo Feng,1 Sami Ullah,1 Ronghan Li,1 Junhua Dong,2 Diannzhong Li,1 Yiyi Li,1 and Xing-Qiu Chen†

1Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Science, School of Materials Science and Engineering, University of Science and Technology of China, 110016 Shenyang, Liaoning, China.
2Environmental Corrosion Center, Institute of Metal Research, Chinese Academy of Sciences, 110016, Shenyang, Liaoning, China

(Dated: April 25, 2017)

Topological nodal line (DNL) semimetals, formed by a closed loop of the inverted bands in the bulk, result in the nearly flat drumhead-like surface states with a high electronic density near the Fermi level. The high catalytic active sites associated with the high electronic densities, the good carrier mobility, and the proper thermodynamic stabilities with \(\Delta G_H\approx0\) are currently the prerequisites to seek the alternative candidates to precious platinum for catalyzing electrochemical hydrogen (HER) production from water. Within this context, it is natural to consider whether or not the DNLs are a good candidate for the HER because its non-trivial surface states provide a robust platform to activate possibly chemical reactions. Here, through first-principles calculations we reported on a new DNL TiSi-type family with a closed Dirac nodal line consisting of the linear band crossings in the \(k_y\) plane. The hydrogen adsorption on the (010) and (110) surfaces yields the \(\Delta G_H\) to be almost zero. The topological charge carries have been revealed to participate in this HER. The results are highlighting that TiSi not only is a promising catalyst for the HER but also paves a new routine to design topological quantum catalyst utilizing the topological DNL-induced surface bands as active sites, rather than edge sites-, vacancy-, dopant-, strain-, or heterostructure-created active sites.

Topological semimetals[1], which have been classified into topological Dirac semimetal (TDs)[2,3], topological Weyl semimetals (TWs)[10–22], and topological nodal line semimetals (DNLs)[23–43] and beyond [35], have currently attracting extensively interest in condensed matter physics (DNLs)[23–34] and beyond [35], have currently Weyl semimetals (TWs)[10–22], and topological nodal line (DNL) semimetals, formed by a closed loop of the inverted bands in the bulk, result in the nearly flat drumhead-like surface states with a high electronic density near the Fermi level. The high catalytic active sites associated with the high electronic densities, the good carrier mobility, and the proper thermodynamic stabilities with \(\Delta G_H\approx0\) are currently the prerequisites to seek the alternative candidates to precious platinum for catalyzing electrochemical hydrogen (HER) production from water. Within this context, it is natural to consider whether or not the DNLs are a good candidate for the HER because its non-trivial surface states provide a robust platform to activate possibly chemical reactions. Here, through first-principles calculations we reported on a new DNL TiSi-type family with a closed Dirac nodal line consisting of the linear band crossings in the \(k_y\) plane. The hydrogen adsorption on the (010) and (110) surfaces yields the \(\Delta G_H\) to be almost zero. The topological charge carries have been revealed to participate in this HER. The results are highlighting that TiSi not only is a promising catalyst for the HER but also paves a new routine to design topological quantum catalyst utilizing the topological DNL-induced surface bands as active sites, rather than edge sites-, vacancy-, dopant-, strain-, or heterostructure-created active sites.

Topological semimetals[1], which have been classified into topological Dirac semimetal (TDs)[2,3], topological Weyl semimetals (TWs)[10–22], and topological nodal line semimetals (DNLs)[23–43] and beyond [35], have currently attracting extensively interest in condensed matter physics and materials science. In difference from both TDs and TWs which exhibit isolated Dirac cones and Weyl nodes in its bulk phase, the class of DNLs [23–43] shows a fully closed line nearly at the Fermi level in its bulk phase. The projection of the DNLs into a certain surface would result in a closed ring in which the topological surface states (usually flat bands) occur due to the non-trivial topological property of its bulk phase. This kind of exotic band structures exhibit various novel properties, such as giant surface Friedel oscillation in beryllium [27], flat Landau level [52] and long-range Coulomb interaction [40]. Currently, only the DNL-induced topological surface bands has been directly confirmed in beryllium [27] and the DNLs have been, partially or indirectly, observed in several bulk materials, such as PtSn [41], TiTaSe [42] and PbTaSe [43] and ZrSiS [44–46] as well as in a two-dimensional DNL monolayer of Cu2Si [47].

Most recently, TWs (NbP, TaP, NbAs and TaAs) have been considered to serve as excellent candidates of catalysts because of the remarkable performance of the hydrogen evolution reaction (HER) [48]. This key concept of TWs as catalysts is extremely nice by alternatively providing a way to create the active sites with topological surface states, rather than by traditionally increasing the active edge sites or vacancies [49–55]. The possible bottleneck of TWs as catalyst may be its much lower carrier density around the Fermi level (Fig. 1h), because that the strength of electrostatic screening in TWs is much weaker than the normal metal (e.g., Pt). However, a DNL material shows two distinguishing features from both TDs and TWs [48]. In its bulk phase, a DNL results in a certain carrier density around the Fermi level (Fig. 1b) and its topologically protected nearly flat drumhead-like non-trivial surface states provide an unusually high electronic density around the Fermi level (Fig. 1b), as seen in pure metal beryllium [27]. Besides these advantages, in similarity to both TDs and TWs the DNL-induced surface states certainly provides sufficient active plane (Fig. 1b) and the carrier mobilities are, in principle, high, because the DNL is formed by the continuously linear crossings of energy bands around the Fermi level (Fig. 1b). Therefore, DNLs would fit better catalyst for the HER due to three combined advantages: (i) non-trivial drumhead-like surface states as robust active sites, (ii) good mobilities of carriers, (iii) a certain density of carriers around the Fermi level. In addition, the crucial thermodynamic descriptor [48–59] of \(\Delta G_H\) as good catalysts should be zero as close as possible, which can be screened well through first-principles calculations.

Within this context, through first-principles calculations (details refer to Ref. 60) we report a new DNL family of the TiSi-type materials MX (M = Ti, Zr, Hf; X = Si, Ge, Sn). The DNL exists in the \(k_y\) plane of the bulk Brillouin zone (BZ) and induces the nearly flat drumhead-like topological non-trivial surface states, thereby resulting in a highly high localized electronic density around the Fermi level on the surface. Interestingly, on the two (010) and (110) surfaces of TiSi the hydrogen adsorption free energies \(\Delta G_H\) are derived to be almost zero, being much more closer to zero than those values of all known catalysts for the HER [51,53,56–59], including the most extensively used precious platinum (Pt).

The TiSi samples were first prepared by the arc melted method and then annealed in vacuum for 48 hours at 1200 °C. The X-ray diffraction demonstrate that TiSi crystallizes...
FIG. 1. Schematics of momentum space diagrams and density of states (DOSs) of TWs and DNLs. Panel (a): A pair of Weyl nodes in bulk (left lower panel) and broken Fermi arc surface states (left upper panel) on the surface and their corresponding DOSs (right panels); Panel (b) A DNL in bulk (left lower panel) and the nearly flat drumhead-like non-trivial surface states on the surface (left upper panel) and their corresponding DOSs (right panels).

in the orthorhombic lattice (Fig. 2a) with the space group of \textit{Pnma} (No. 62) and the refinement reveals that Si occupies the Wyckoff 4\textit{e} site (0.0362, 0.2500, 0.1103) and Ti at another Wyckoff 4\textit{e} site (0.1820, 0.2500, 0.6250). Our current experimental findings are supported by our theoretical lattice constants \(a = 6.529\ \text{Å}, \ b = 3.645\ \text{Å}, \) and \(c = 5.004\ \text{Å},\) also in good accord with the previous experimental data [61–64] (supplementary Table S1). In addition, the derived phonon dispersion does not show any imaginary frequencies and is dynamically stable (Fig. 2b).

In standard DFT calculations, as shown in Fig. 3a, the bands near the Fermi energy are mainly contributed from the Ti \(d_{xy}\) and \(d_{xz}\) orbitals. Without the SOC inclusion, there are the two nearly linear band crossings, A and B points, as marked in Fig. 3a. The one (A) locates at 0.1 eV above the Fermi level in the X-\Gamma direction and the other one (B) lies about 0.18 eV below the Fermi level along the \(\Gamma-Z\) direction. They are physically induced by the band inversion. At the centre of the Brillouin zone (BZ, Fig. 1b), \(d_{yz} \rightarrow d_{z^2}\) band inversion (Fig. S1 [60]) occurs between the two bands No. 1 and No. 2, as marked in Fig. 3a. Strikingly, the band crossings not only appear at these two points, but also form a circle-like closed line around the \(\Gamma\) point in the \(k_y = 0\) plane (Fig. 3d). This is the apparent sign of the DNL appearance. The band crossings between No.1 and No.2 bands do not occur at the same en-
energy level, but show a wave-like closed curve upon the $k$ vectors around the centered Γ point. Certainly, this DNL stability is highly robust, protected by the inversion and time-reversal symmetry without the spin-orbit coupling (SOC) effect. Because of the light masses of Ti and Si, its SOC effect is rather weak; therefore, it does not affect the electronic band structure, apparently (Fig. S2[60]). Furthermore, the non-trivial topology order of TiSi is confirmed by the non-Abelian Berry connection method [66–68], as shown in Fig. 3(b) and 3(c).

In the $k_z = 0$ plane in which the DNL locates, the loop of the Wannier center evolution change partners from $k_z = 0$ to $k_z = \pi$. However, in the $k_y = \pi$ plane, no partner changes. Hence, the evolution loop of the Wannier center cuts the reference line odd times in the $k_y = 0$ plane, whereas the crossing between Wannier center evolution loop and the reference line zero or even times in the $k_y = \pi$ plane.

We have also considered the isoelectronic and isostructural TiGe, TiSn, HfSi, HfGe, HfSn and ZrSi, ZrGe and ZrSn. As shown in supplementary Table S1 and Fig. S1-S6 [60], the electronic band structures of ZrSi and GeSi are qualitatively the same physics as TiSi does (see Fig. 3(e) and f).

To inspect the topological surface bands for TiSi, we have calculated the electronic structures of the (010) surface by varying the thickness of the slabs (Fig. S7[64]). As expected, the robust surface electronic bands (topological SF-band 1 in Fig. 3a) appear, when the slab’s thickness is above eight atomic layers along the $b$-axis. From Fig. 4, outside the Dirac nodal ring on the (010) surface projected by the DNL of its bulk phase, the two-fold degenerated topological SF-band 1 clearly separates: one goes to the unoccupied conduction bands integrating with the projection of the electronic bands of bulk phase and the other one emerges into the valence bands overlapping with the projected bulk bands. With other words, these separated surface bands outside the projected Dirac nodal ring are the topologically trivial states and not correlated with the bulk DNL states. These separated trivial surface bands mainly originates from the Ti $d_{xz}$, $d_{yz}$ and $d_{xy}$-like states. This means that the topological non-trivial surface bands SF-band 1 only occur within the DNL-projected Dirac nodal ring on the (010) surface. The topologically protected SF-band 1 around the Γ point are mainly comprised with the $d_{xz}$ and $d_{xy}$-like electronic states from the topmost atomic layer, reflecting well the $d_{xz} \rightarrow d_{xy}$ band inversion in its bulk phase (Fig. 2a). This SF-band 1 is two-fold degenerated, half-filled when the surface is electrically neutral, in similarity to the case of Be [27].

Importantly, the three main features of the DNLs in TiSi motivates us to consider its activities as catalysts, as conceptually shown in Fig. 5. Firstly, the nearly flat drumhead-like non-trivial topological surface states (SF-band 1 in Fig. 4) on the (010) surface disperses parabolically and its lowest-energy part exactly cuts the Fermi level of 0 eV at Γ, suggesting the possibility of robust active planes for catalyst against defects, impurities, and other surface modifications. Secondly, from Fig. 3b the Dirac nodal points on the NDLs around the Fermi level are expected to exhibit high mobility because the linear band crossing. In similarity to TDs and TWs, it will be favorable for the free and quick diffusion of electrons. Thirdly, the topology carrier density is not low due to the DNL presence around the Fermi level.

Following the theoretical suggestions [49,59], we evaluate the HER activities of the two (010) and (110) planes, where the hydrogen adsorption free energy $\Delta G_H^*$ was determined by varying different adsorption sites on the specified surface (see method [60]). Theoretically, $\Delta G_H^*$ is known to scale with activation energies and has been successfully used as a descriptor for correlating theoretical predictions with experimental measurements of catalytic activity for various systems [49,59].

FIG. 4. The surface electronic band structures of the TiSi (010) surface. Panels (a and b): the comparison of the derived surface electronic structures on the 50-atomic-layer (010) surface without and with the top and bottom hydrogen adsorption, respectively. Noted that the topologically protected non-trivial surface bands (marked as the topological non-trivial SF-band 1) has been highlighted and the trivial surface bands (trivial SF-band 2) has been also marked in panels along $\Gamma$-$X$. 

(a) 50 layers

(b) 50 layers+H
FIG. 5. The effects of the topological DNLs on the HER activity of TiSi. Panel (a): Schematic of the HER reaction of the DNL-induced half-filled nontrivial surface states to provide active plane and the DNL states to provide high mobile and quickly diffused electrons. Panel (b): the visualized localized charges of the topological states on the (010) surface. The charges are characteristic of $d_{yz}$-like orbitals from the topmost Ti atoms. Panel (c): The visualized localized charge accumulations of hydrogen on the (010) surface. Panel (d): the visualized localized charge depletion surrounding Ti atoms. Panel (e): Free energy versus the reaction coordinate of the HER of TiSi in comparison with several other compounds. The data of MoS$_2$ (-0.08 eV for the edge states), Pt (-0.09 eV) and Hydrogenase (-0.05 eV) are all taken from Ref. [50]. Panel (f): Volcano plot for the HER of TiSi in comparison with various pure metals (the experimental data [59] of Pt, Pd, Ni, Ir, Co, Rh, Ag, Cu, Mo and W), TWs (the calculated data [48] of NbP, TaP, NbAs and TaAs), and other candidates (the theoretical data [48] of TaS$_2$(2H), MoTe$_2$(1T′), MoTe$_2$(Td), and TaS$_2$(1T)).

The previous theoretical suggestions that for the best activity the optimal value of $\Delta G^*_{H^+}$ should be 0 eV, where hydrogen is bound neither too strongly nor weakly with active sites on the surface [56]. Surprisingly, our calculated results demonstrate that $\Delta G^*_{H^+}$ of HER on different TiSi surfaces are very close to zero. It shows us that on the (010) surface $\Delta G^*_{H^+} = -0.03$ eV when hydrogen bridges two nearest neighboring Ti atoms (Fig. 5c) and -0.05 eV with hydrogen bridging Ti and Si on the topmost atomic layer. The (110) surface even yields, $\Delta G^*_{H^+} = -0.005$ eV, of an almost zero value. In comparison with some typical catalysts (MoS$_2$, Pt and hydrogenase) in Fig. 5e, the HER activities on the TiSi surfaces are highly attractive. It can be seen that the values of $\Delta G^*_{H^+}$ of TiSi show a much closer value to zero than both the typical catalysts of Pt ($\Delta G^*_{H^+} = -0.09$ eV) [50] and the edge states ($\Delta G^*_{H^+} = 0.082$ eV) [50] of MoS$_2$. Furthermore, we have plotted the Volcano curves for the HER of TiSi in comparison with some data known. Remarkably, among all known data TiSi exhibits a $\Delta G^*_{H^+}$ most close to zero. In particular, in comparison with these TWs [48] in Fig. 5f, TiSi possibly shows a more excellent HER performance, because their $\Delta G^*_{H^+}$ values of TiSi are almost at the top of the Volcano curve. However, the $\Delta G^*_{H^+}$ of both NbP and TaP are much lower than that of Pt, and their asenides even have the corresponding values as negative as -0.75 eV and -1.0 eV, respectively.

Mechanically, the calculations demonstrate that, after the hydrogen adsorption on the (010) surface, the topological SF-band 1 (Fig. 4b) becomes unoccupied above the Fermi level. The hydrogen atom will obtain the charges and disperse in the deep energy region below the Fermi level. This process can be made more clear by visualizing the local charges in Fig. 5b,c,d. On the clean (010) surface, the charges of the topological SF-band 1 are clearly localized at two nearest neighboring Ti atoms with the $d_{yz}$ orbitals (Fig. 5b). After the hydrogen adsorption, the topological charges are indeed transferred to the hydrogen. As evidenced in Fig. 5c, a lone-pair $s$-like orbital appears in terms of the charge accumulations. Correspondingly, the charge depletion of the two nearest neighboring Ti atoms are highly visualized in Fig. 5d, which also refers to the position of the localized topological charges on the H-free adsorption (010) surface in Fig. 5c. This fact indicates that the topology carrier on the SF-band 1 states are fully transferred.
into hydrogen s-like orbitals, indicating that the bulk DNLs play an important role in the HER as a potential catalyst.

Summarizing, we have reported on the new DNLs’ family (TiSi, TiGe and ZrSi) and theoretically demonstrate that they have the promising potential as excellent catalyst for the HER performance because of the active sites provided by the robust nearly flat drumhead-like non-trivial surface states, a stable supply of itinerant electrons from the certain carrier density and the high mobilities related with the DNLs, and the most suitable $\Delta G_{\text{HER}} \approx 0$ for the HER.

Acknowledgments Work was supported by the “Hundred Talents Project” of the Chinese Academy of Sciences and by the National Natural Science Foundation of China (Grant Nos. 51671193 and 51474202) and by the Science Challenging Project No. JCKY2016212A504. All calculations have been performed on the high-performance computational cluster in the Shenyang National University Science and Technology Park and the National Supercomputing Center in Guangzhou (TH-2 system)

These authors contributed equally to this work.

---

1. M. Z. Hasan, S.-Y. Xu, and G. Bian, Topological insulators, topological superconductors and Weyl fermion semimetals: discoveries, perspectives and outlooks, Phys. Scr. **T164**, 014001 (2015).

2. S. M. Young, S. Zaheer, J. C. Y. Teo, C. L. Kane, E. J. Mele, and A. M. Rappe, Dirac Semimetal in Three Dimension, Phys. Rev. Lett. **108**, 140405 (2012).

3. Z. J. Wang, Y. Sun, X.-Q. Chen, C. Franchini, G. Xu, H. M. Weng, X. Dai, and Z. Fang, Dirac semimetal and topological phase transitions in $A_2$Bi (A=Na, K, Rb), Phys. Rev. B **85**, 195320 (2012).

4. Z. K. Liu, B. Zhou, Y. Zhang, Z. J. Wang, H. M. Weng, D. Prabhakaran, S.-K. Mo, Z. X. Shen, Z. Fang, X. Dai, Z. Hussain, and Y. L. Chen, Discovery of a Three-Dimensional Topological Dirac Semimetal, $Na_2$Bi, Science **343**, 864 (2014).

5. X. Y. Cheng, R. H. Li, Y. Sun, X.-Q. Chen, D. Z. Li, and Y. Y. Li, Ground-state phase in the three-dimensional topological Dirac semimetal $Na_2$Bi, Phys. Rev. B **89**, 245201 (2014).

6. S.-Y. Xu, C. Liu, S. K. Kushwaha, R. Sankar, J. W. Krizan, I. Belopolski, M. Neupane, G. Bian, N. Alidoust, T. R. Chang, H. T. Jeng, C. Y. Huang, W. F. Tsai, H. Lin, P. P. Shibayev, F. C. Chou, R. J. Cava, and M. Z. Hasan, Observation of Fermi arc surface states in a topological metal, Science **347**, 294 (2015).

7. Z. J. Wang, H. M. Weng, Q. S. Wu, X. Dai, and Z. Fang, Three-dimensional Dirac semimetal and quantum transport in $Cd_3$As$_2$, Phys. Rev. B **88**, 125427 (2013).

8. M. Neupane, S. Y. Xu, R. Sankar, N. Alidoust, G. Bian, C. Liu, I. Belopolski, T. R. Chang, H. T. Jeng, H. Lin, A. Bansil, F. Chou, and M. Z. Hasan, Observation of a three-dimensional topological Dirac semimetal phase in high-mobility $Cd_3$As$_2$, Nat. Commun. **5**, 3786 (2014).

9. Z. K. Liu, J. Jiang, B. Zhou, Z. J. Wang, Y. Zhang, H. M. Weng, D. Prabhakaran, S. K. Mo, H. Peng, P. Dudin, T. Kim, M. Hoesch, Z. Fang, X. Dai, Z. X. Shen, D. L. Feng, Z. Hussain, and Y. L. Chen, A stable three-dimensional topological Dirac semimetal $Cd_3$As$_2$, Nature Mater. **13**, 677-681 (2014).

10. X. Wan, A. M. Turner, A. Vishwanath, and S. Y. Savrasov, Topological semimetal and Fermi-arc surface states in the electronic structure of pyrochlore iridates, Phys. Rev. B **83**, 205101 (2011).

11. H. M. Weng, C. Fang, Z. Fang, B. A. Bernevig, and X. Dai, Weyl Semimetal Phase in Noncentrosymmetric Transition-Metal Monophosphides, Phys. Rev. X **5**, 011029 (2015).

12. S. M. Huang, S. Y. Xu, I. Belopolski, C. C. Lee, G. Q. Chang, B. K. Wang, N. Alidoust, G. Bian, M. Neupane, C. L. Zhang, S. Jia, A. Bansil, H. Lin, and M. Z. Hasan, A Weyl Fermion semimetal with surface Fermi arcs in the transition metal monopnicotride TaAs class, Nat. Commun. **6**, 7373 (2015).

13. B. Q. Lv, H. M. Weng, B. B. Fu, X. P. Wang, H. Miao, J. Ma, P. Richard, X. C. Huang, L. X. Zhao, G. F. Chen, Z. Fang, X. Dai, T. Qian, and H. Ding, Experimental Discovery of Weyl Semimetal TaAs, Phys. Rev. X **5**, 031013 (2015).

14. S.-Y. Xu, I. Belopolski, N. Alidoust, M. Neupane, G. Bian, C. L. Zhang, R. Sankar, G. Q. Chang, J. Z. Yuan, C. C. Lee, S. M. Huang, H. Zheng, J. Ma, D. S. Sanchez, B. K. Wang, A. Bansil, F. C. Chou, P. P. Shibayev, H. Lin, S. Jia, and M. Z. Hasan, Discovery of a Weyl fermion semimetal and topological Fermi arcs, Science **349**, 613 (2015).

15. Z. K. Liu, L. X. Yang, Y. Sun, T. Zhang, H. Peng, H. F. Yang, C. Chen, Y. Zhang, Y. F. Guo, D. Prabhakaran, M. Schmidt, Z. Hussain, S.-K. Mo, C. Felser, B. Yan, and Y. L. Chen, Evolution of the Fermi surface of Weyl semimetals in the transition metal pnictide family, Nature Mater. **15**, 27 (2016).

16. G. Q. Chang, S.-Y. Xu, D. S. Sanchez, S.-M. Huang, C.-C. Lee, T.-R. Chang, G. Bian, H. Zheng, I. Belopolski, N. Alidoust, H.-T. Jeng, A. Bansil, H. Lin, and M. Z. Hasan, A strongly robust type II Weyl fermion semimetal state in Ta$_3$S$_2$, Science Advances **2**, e1600295 (2016).

17. K. Koepernik, D. Kashinathan, D. V. Efremov, S. Khim, S. Borisenko, B. Büchner, and J. van den. Brink, TaIrTe$_2$: A ternary type-II Weyl semimetal, Phys. Rev. B **93**, 201101(R), (2016).

18. A. A. Soluyanov, D. Greshch, Z. J. Wang, Q. S. Wu, M. Troyer, X. Dai, and B. A. Bernevig, Type-II Weyl semimetals, Nature **527**, 495 (2015).

19. F.-Y. Li, X. Luo, X. Dai, Y. Yu, F. Zhang, and G. Chen, Hybrid Weyl Semimetal, Phys. Rev. B **94**, 121105(R) (2016).

20. J. W. Ruan, S.-K. Jian, D. Q. Zhang, H. Yao, H.-J. Zhang, S.-C. Zhang, and D. Y. Xing, Ideal Weyl semimetals in the Chalcoprites CuTiSe$_2$, AgTiTe$_2$, AuTiTe$_2$, and ZnPbAs$_2$, Phys. Rev. Lett. **116**, 226801 (2016).

21. J. W. Ruan, S.-K. Jian, H. Yao, S.-C. Zhang, and D. Y. Xing, Symmetry-protected ideal Weyl semimetal in HgTe-class materials, Nat. Commun. **7**, 11136 (2016).

22. H. M. Weng, C. Fang, Z. Fang, and X. Dai, Coexistence of Weyl fermion and massless triply degenerate nodal points, Phys. Rev. B **94**, 165201 (2016).

23. C. Fang, H. M. Weng, X. Dai, and Z. Fang, Topological nodal line semimetals, Chin. Phys. B **25**, 117106 (2016).

24. S. Ryu, and Y. Hatsugai, Topological Origin of Zero-Energy Edge States in Particle-Hole Symmetric Systems, Phys. Rev. Lett. **89**, 077002 (2002).

25. T. T. Heikkilä, and G. E. Volovik, Dimensional crossover in topological matter: Evolution of the multiple Dirac point in the layered system to the flat band on the surface, JETP Lett. **93**, 59 (2011).

26. A. A. Burkov, M. D. Hook, and L. Balents, Topological nodal
current for hydrogen evolution, J. Electrochem. Soc. 152, J23 (2006).

[60] See Supplemental Material http://link.aps.org/supplemental/ for (1) Computational details (which include Refs. 50, 59, 63–78), (2) Comparison of DFT optimized lattice constants with available experimental data, (3) Band inversion in TiSi, (4) DNLs in TiSi-family, (5) Dirac nodal lines and Surface band structures in ZrSi and TiGe, (6) Evolution of thickness-dependent surface electronic band structures of the TiSi (010) surface, and (7) Computations of hydrogen adsorption on the TiSi surfaces.

[61] S. Agarwal, E. J. Cotts, S. Zarembo, R. Kematiick, and C. Myers, The heat capacities of titanium silicides Ti5Si3, TiSi and TiSi2, J. Alloys Comp. 314, 99 (2001).

[62] G. V. Samsonov, N. F. Podgrushko, and L. A. Dvovina, Thermal-Conductivity of silicide phases of transition-metals of groups IV-VI, Inorg. Mater. 13, 1429 (1977).

[63] G. V. Samsonov, L. N. Okhemchuk, N. F. Podgrushko, I. A. Podchernyaeva, and V. S. Fomenko, Inorg. Relations between electron work function and certain physical-properties in silicides of group-IV transition-metals, Inorg. Mater. 12, 720 (1976).

[64] C. E. Brukl, H. Nowotny, O. Schob, and F. Benesovsky, Die Kristallstrukturen von TiSi, Ti(Al,Si)2, Monatsh. Chem. 92, 781 (1961).

[65] L. Fu, C. L. Kane, and E. J. Mele, Topological Insulators in Three Dimensions, Phys. Rev. Lett. 98, 106803 (2007).

[66] A. Soluyanov, Alexey, and D. Vanderbilt, Computing topological invariants without inversion symmetry, Phys. Rev. B 83, 235401 (2011).

[67] R. Yu, X. L. Qi, A. Bernevig, Z. Fang, and X. Dai, Equivalent expression of Z2 topological invariant for band insulators using the non-Abelian Berry connection, Phys. Rev. B 84, 075119 (2011).

[68] Y. Sun, Q.-Z. Wang, S.-C. Wu, C. Felser, C.-X. Liu, and B. H. Yan, Pressure-induced topological insulator in NaBaBi with right-handed surface spin texture, Phys. Rev. B 93, 205303 (2016).

[69] P. Hohenberg, and W. Kohn, Inhomogeneous Electron Gas, Phys. Rev. 136, B864 (1964).

[70] W. Kohn, and L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, Phys. Rev. 140, A1133 (1965).

[71] S. Baroni, S. De Gironcoli, A. Dal Corso, and P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory, Rev. Mod. Phys. 73, 515 (2001).

[72] G. Kresse, and J. Hafner, Ab initio molecular dynamics for liquid metals, Phys. Rev. B 47, 558 (1993).

[73] G. Kresse, and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci 65, 15 (1996).

[74] P. E. Blöchl, O. Jepsen, and O. K. Andersen, Improved tetrahedron method for Brillouin-zone integrations, Phys. Rev. B 49, 16223 (1994).

[75] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865 (1997).

[76] J. C. Slater, and G. F. Koster, Simplified LCAO Method for the Periodic Potential Problem, Phys. Rev. 94, 1498 (1954).

[77] C. Franchini, R. Kovˇe?tk, M. Marsman, S. S. Murthy, J. He, C. Ederer, and G. Kresse, Maximally localized Wannier functions in LaMnO3 within PBE + U, hybrid functionals and partially self-consistent GW: an efficient route to construct ab initio tight-binding parameters for eg perovskites, J. Phys.: Condens. Matter. 24, 235602 (2012).

[78] X. C. Fu, W. X. Shen, T. Y. Yao, and W. H. Hou, (Ed.) Physical and Chemistry, the fifth verion, Higher Education Press, Beijing, (2006).