Realization of insulating state and superconductivity in the Rashba semiconductor BiTeCl

Jian-Jun Ying, Viktor V. Struzhkin, Zi-Yu Cao, Alexander F. Goncharov, Ho-Kwang Mao, Fei Chen, Xian-Hui Chen, Alexander G. Gavriliuk, and Xiao-Jia Chen

Phys. Rev. B **93**, 100504 — Published 28 March 2016

DOI: 10.1103/PhysRevB.93.100504

Realization of insulating state and superconductivity in Rashba semiconductor BiTeCl

Jian-Jun Ying,[1, 2] Viktor V. Struzhkin,[2] Zi-Yu Cao,[3, 1] Alexander F. Goncharov,[2, 3] Ho-Kwang Mao,[2, 1] Fei Chen,[4, 1] Xian-Hui Chen,[4] Alexander G. Gavriliuk,[5, 6] and Xiao-Jia Chen[1, 2, *]

[1] *Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China*
[2] *Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, U.S.A.*
[3] *Key Laboratory of Materials Physics, Institute of Solid State Physics,*
Chinese Academy of Sciences, Hefei 230031, China
[4] *Hefei National Laboratory for Physical Science at Microscale and Department of Physics,*
University of Science and Technology of China, Hefei, Anhui 230026, China
[5] *Institute of Crystallography, Russian Academy of Sciences, Leninsky pr. 59, Moscow 119333, Russia*
[6] *Institute for Nuclear Research, Russian Academy of Sciences, Troitsk, Moscow 142190, Russia*

(Dated: March 9, 2016)

Measurements of the resistivity, Hall coefficient, and Raman spectroscopy are performed on a Rashba semiconductor BiTeCl single crystal at high pressures up to 50 GPa. We find that applying pressure first induces the theoretically predicted insulating state followed by a superconducting phase with the insulating normal state. Upon heavy compression, another different superconducting phase is entered with the metallic normal state. The dome-like evolution of the superconducting transition temperature with pressure is obtained with the crossover from the electron to hole carriers across the boundary of the two superconducting phases. These findings imply the possible realization of topological state of the insulating and superconducting phases in this material.

PACS numbers: 74.25.Dw, 74.70.-b,74.62.Fj

Topological insulators represent the newly discovered phase of matter with insulating bulk state but topologically protected metallic surface state due to the time-reversal symmetry and strong spin-orbital interaction [1–4]. The experimental discovery of the three-dimensional topological insulating phase [5] opened a new era in fundamental topological physics. Superconductivity has been found in some topological insulators mainly in compressed V_2VI_3 binary compounds such as Bi_2Te_3 [6–9], Bi_2Se_3 [10], Sb_2Te_3 [11], and intercalated $Cu_xBi_2Se_3$ [12]. However, the identification of their topological superconductivity is still a hard task and under debate [13]. In most cases, pressure is needed to drive topological insulator to superconductor. Superconductivity is usually accompanied by the electronic topological transition and/or structural transition [7,10]. It remains unclear whether such a transition is essential to induce superconductivity in topological insulators.

Searching for the topological superconductivity is being driven by the exploration of fundamental physics and the potential applications in topological quantum computation [1,2]. Layered non-centrosymmetric bismuth tellurohalides (BiTeX with X=Cl, Br, I) with large Rashba-type splittings in the bulk bands [14–16] are being examined as the inversion asymmetric topological insulators [17,18]. These materials are potential candidates for building the spintronic devices. Unlike the previously discovered three-dimensional topological insulators with inversion symmetry, the inversion symmetry is naturally broken by the crystal structure in asymmetric topological insulators. It is highly possible to realize the topological magneto-electric effects and the topological superconductivity [18–20]. The experimental realization and identification of these interesting effects are thus desired.

Pressure-induced topological insulating state was theoretically predicted for Rashba semiconductor BiTeI [17]. However, controversial conclusions were drawn from experiments on this material [21,22]. Recently, BiTeCl was discovered to be the first example of inversion asymmetric topological insulator from angle-resolved photoemission spectroscopy experiment [18]. This was supported by the transport measurements [23]. However, quantum oscillation measurements failed to detect the Dirac surface state in BiTeCl single crystals [24,25]. Such contradiction may come from the strong surface polarity which would generate large effective pressure along the c axis. The applied pressure could drive the several surface layers into a topological insulator as the case in BiTeI [17,18]. Therefore, pressure is highly required to examine whether topological phase transition could happen in this kind of materials and whether topological superconductivity would be induced. Meanwhile, pressure-induced superconductivity from topological insulators was limited in V_2VI_3-type compounds. Finding new superconducting family from topological insulators would add a new opportunity for exploring topological superconductivity. In this work we choose BiTeCl to address these issues.

High-quality single crystals of BiTeCl were grown by a self-flux method [16]. Pressure was applied at room temperature using the miniature diamond anvil cell [26]. A sample chamber in diameter 130 μm was drilled in the c-BN gasket situated in two diamond anvils with 300 μm culet. BiTeCl single crystal was cut with the dimensions of $65\times65\times15$ μm^3. Four Pt wires were adhered to the sample using the silver epoxy. Daphne oil 7373 was used as a pressure transmitting medium. Pressure was calibrated by using the ruby fluoresce shift at room temperature. Resistivity and Hall coefficient were measured

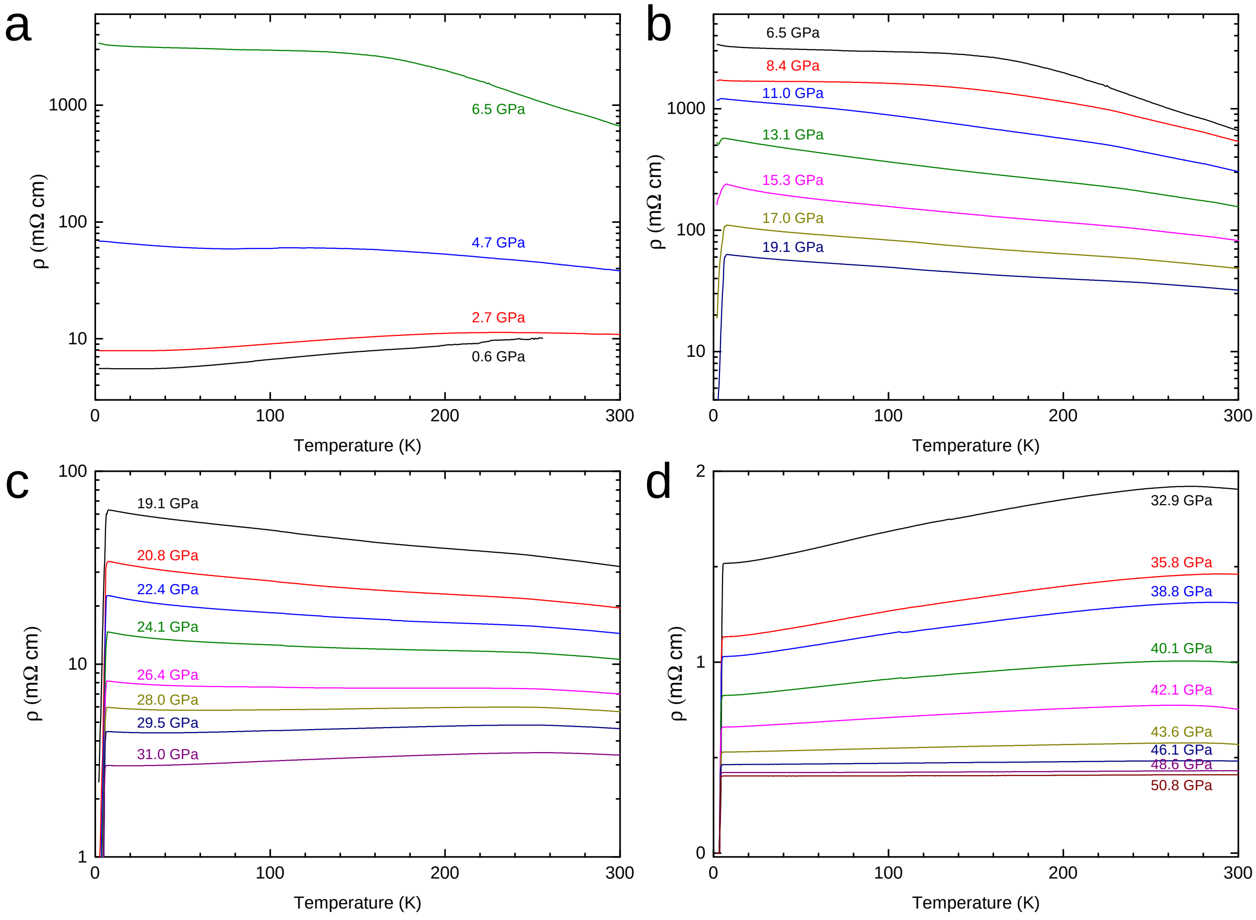

FIG. 1: (color online). Temperature dependence of the resistivity of BiTeCl at various pressures. (a) The sudden change of the resistivity behavior indicates a phase transition from a Rashba semiconductor to an insulator around 5 GPa. (b) The resistivity was gradually suppressed with increasing pressure and superconductivity emerges above 13 GPa. The normal state behaves like an insulator (c) and a metal (d) upon heavy compression.

using the Quantum Design PPMS. Diamond anvil cell with 300 μm culet was used for high-pressure Raman measurements with incident laser wavelength of 488 nm. Neon was loaded as the pressure transmitting medium.

Figure 1 shows the temperature dependence of the resistivity for BiTeCl at various pressures up to 50.8 GPa. At low pressures below 4 GPa, the resistivity shows a metallic behavior similar to that at ambient pressure as reported before[27,28], though this material was thought to be a Rashba semiconductor. This is probably due to the off-stoichiometry which is mostly caused by a slight Cl atom deficiency. When pressure is increased to 5 GPa, the resistivity suddenly increases almost three magnitude of orders, exhibiting an insulating behavior with a resistivity maximum around 150 K [Fig. 1(a)]. This indicates a phase transition from a Rashba semiconductor to an insulator around 5 GPa in BiTeCl. The realization of topological insulator from such a kind of Rashba semiconductor by applied pressure has been theoretically predicted[17] but has never been observed experimentally. The current work may provide the first experimental evidence for the topological insulating state in compressed bismuth tellurohalides. Further increasing pressure, the resistivity is gradually reduced and the resistivity maximum shifts downwards to lower temperatures. Although the origin for such a maximum remains unclear, some competing orders such as charge density wave may occur in these low-dimensional electronic systems[29]. In-

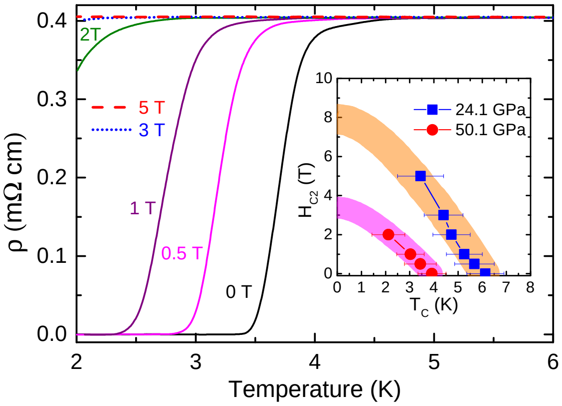

FIG. 2: (color online). Temperature dependence of the resistivity of BiTeCl at pressure of 50.8 GPa with applied magnetic fields. Inset: Upper critical field H_{c2} for the pressure of 24.1 GPa and 50.8 GPa, respectively. T_c was determined from the 90% resistivity transition. The color area represents the calculated H_{c2} from the Werthamer-Helfand-Hohenberg equation.

terestingly, superconductivity emerges when the resistivity maximum is completely suppressed around 13 GPa. However, its normal state still exhibits an insulating behavior. This behavior is different from the other superconducting phases obtained from topological insulators under pressure[7,10], classifying BiTeCl as a new type of superconductor. If the topological insulator is really realized at high pressures, this newly discovered superconductor may possess topological superconductivity. The unique spin-orbit interaction of a Rashba system contributes its superconductivity with the mixing of the singlet and triplet pair states and the Majorana channels[30]. Further increasing pressure, the normal state behaves like a metal above 28 GPa. Superconductivity persists up to the highest pressure of 50.8 GPa studied. The discovery of superconductivity with novel normal-state properties in BiTeCl add insight into the new physics in Rashba system with strong spin-orbital coupling.

The obtained superconductivity in BiTeCl was further supported by the evolution of the resistivity-temperature curve with the applied magnetic fields (Fig. 2). The curve gradually shifts towards the lower temperatures with increasing magnetic field. The magnetic field was applied along the crystallographic c axis. It seems likely that 5 T is sufficient to suppress superconductivity at 50.8 GPa. However, much higher field is needed to suppress superconductivity at 24.1 GPa. These two pressures yield different normal-state behaviors – metallic for the former but insulating for the latter (Fig. 1). The different behaviors of the upper critical field H_{c2} also reflect the different physical properties of the two superconducting phases.

Within the weak-coupling BCS theory, the upper critical field at T = 0 K can be determined by the Werthamer-Helfand-Hohenberg equation[31]: $H_{c2}(0) = 0.693[-(dH_{c2}/dT)]_{T_c}T_c$. The colorful areas shown in the inset of Fig. 2 are the temperature dependence of H_{c2} calculated based on this equation for the superconductivity at 24.1 and 50.8 GPa, respectively. The $H_{c2}(0)$ at 50.8 GPa is about 3.5 T. This value is comparable with that of superconducting Bi_2Se_3 phase[10]. The calculated $H_{c2}(0)$ of almost 8 T at 24.1 GPa is twice larger than that at 50.8 GPa. The large difference of $H_{c2}(0)$ at 24.1 and 50.8 GPa indicates the different origins of superconductivity of those two high-pressure phases. Differing from V_2VI_3-type topological materials, the normal state of superconducting BiTeCl shows both insulating and metallic behaviors with different values of $H_{c2}(0)$. Our results indicate that the first superconducting phase with insulating normal state is followed Rashba semiconductor-insulator transition but it develops to the second one with metallic normal state upon heavy compression. The large upper critical field in the first superconducting phase results from the strong spin-orbit interaction in a Rashba system. The similarity of the normal state together with the comparable $H_{c2}(0)$ value between the second superconducting phase and V_2VI_3 compounds classifies them as conventional superconductors. Pressure-induced insulating behavior together with the followed superconductivity with insulating normal state is the central discovery of this work. If the obtained insulating state is exactly the same as the theoretically predicted one[17], it should possess topological order. The following superconductivity could have topological feature as well. Topological superconductivity could have been realized in BiTeCl, though the identification from both experimental and theoretical sides is highly desired.

Raman spectroscopy is a powerful tool to probe the changes in lattice and thus can provide valuable information on structural evolution and phase transition. Figure 3 shows the Raman spectra of BiTeCl at various pressures up to 39.4 GPa. At ambient pressure, BiTeCl crystalizes in a trigonal layer structure with space group of $P6_3mc$. This phase has seven Raman active modes ($2A_1$+$2E_1$+$3E_2$). Both E-type modes belong to the inplane vibration of the Bi, Te, and Cl layers, while the lower E mode has a large contribution of the Cl atom vibration. The two out-of-plane A_1 modes include the vibration with higher frequencies. Our Raman measurements reproduced all these modes below 5 GPa. The obtained modes marked by the arrows are also similar to those reported previously at ambient pressure[28,32]. The two E modes with the lowest (16 cm^{-1}) and highest (120 cm^{-1}) frequencies and one A_1 mode with the highest frequency (153 cm^{-1}) have the strong intensities. Applying pressure shifts the lowest frequency E mode and the highest A_1 mode to the high frequencies, while the highest E_1 mode first softens and then hardens. The E mode around 100 cm^{-1} and the A_1 mode around 140 cm^{-1} behave in a similar way as the highest frequency E_1 mode. The

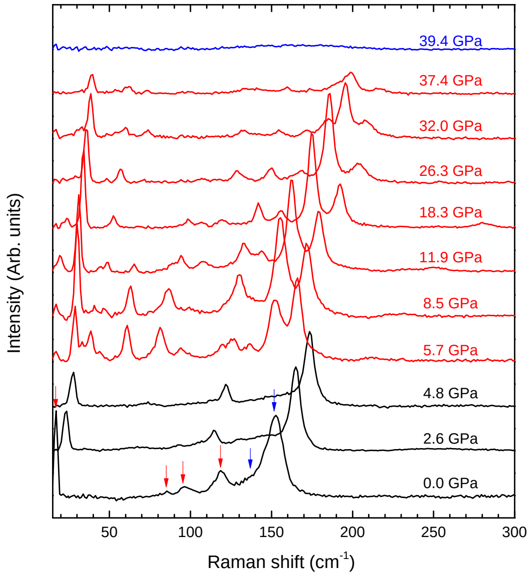

FIG. 3: (color online). Raman spectra of BiTeCl at various pressures up to 39.4 GPa. The vibrational modes in the initial Rashba semiconductor are marked by arrows. The different spectra above 5 GPa and the absence of Raman peaks above 39 GPa are consistent with the different normal-state behaviors of the two superconducting phases.

softening of these intermediate modes may contribute to the strong electron-phonon coupling favoring superconductivity.

Above 5 GPa, the spectra suddenly change, indicating the appearance of a new high-pressure phase. The similar phase transition to an orthorhombic $Pnma$ structure with a semiconducting feature has been reported in the sister system BiTeI[33]. The $Pnma$ phase has more Raman vibrational modes ($6A_g$+$3B_{1g}$+$6B_{2g}$+$3B_{3g}$). Above 39 GPa, no Raman modes were detected, suggesting a phase transition to a high symmetric structure with a possible cubic unit cell. This is consistent with the obtained metallic normal state of this high-pressure phase from the resistivity measurements [Fig. 1(d)]. Previously, an orthorhombic $P4/nmm$ structure was suggested for dense BiTeI from combined XRD measurements and calculations[33]. This $P4/nmm$ phase corresponds to more rich Raman active modes with nine E_g modes besides A_{1g}, B_{1g}, and B_{2g}. Our Raman data does not support the existence of the $P4/nmm$ BiTeCl. The metallic phase of BiTeCl is possibly a substitutional alloy similar to Bi_2Te_3 system[34]. The Raman spectra also reveal the different physical properties of BiTeCl.

Combining the resistivity and Raman measurements, we can map out the phase diagram of BiTeCl (Fig. 4). Below 5 GPa, BiTeCl keeps its initial phase as a Rashba semiconductor (S) but behaves in reality like a metal or semimetal [Fig. 1(a)][27,28]. Above that, it evolves to a superconductor with an insulating (I) normal state up to the phase boundary starting at 28 GPa. Above 39 GPa, superconductivity remains unchanged with pressure but the material possesses a metallic (M) normal state. T_c first exhibits a dome-like shape with pressure and then becomes almost constant upon heavy compression. Meanwhile, the sign of the measured Hall coefficient at 10 K gradually changes from negative to positive above 28 GPa (lower panel of Fig. 4). This provides the dominant electron and hole carrier character for the two superconducting phases. The electron doping agrees with the negative thermopower[35]. The large hole carrier density in the latter is consistent with the character of the substitutional alloy indicated from Raman measurements. The relatively weak pressure dependence of the carrier density provides a natural explanation for the almost constant T_c and the conventional character of superconductivity of this phase.

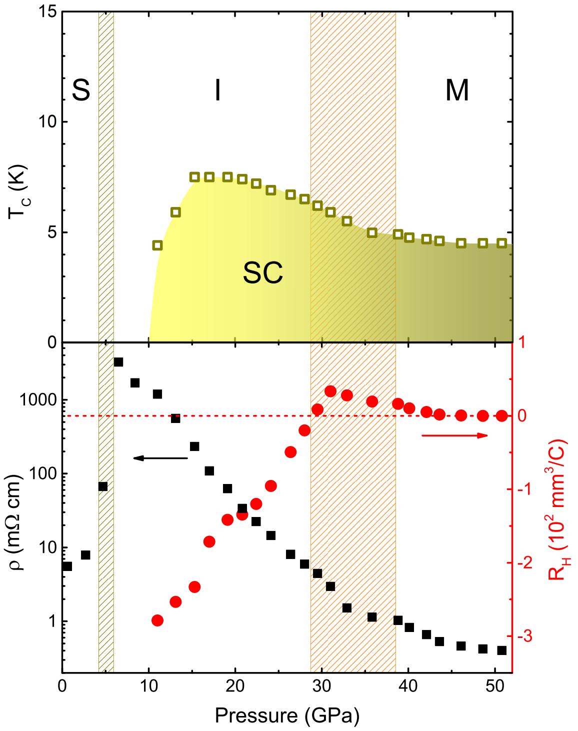

FIG. 4: (color online). Phase diagram of BiTeCl at high pressures. Lower panel shows the pressure dependence of the resistivity and Hall coefficient measured at 10 K. The dashed regions represent the phase borders of semiconductor (S), insulator (I), and metal (M). Two high-pressure superconducting phases with the insulating and metallic normal states. The dashed area represents the coexistence of two phases.

The temperature dependence of the resistivity of

BiTeCl shown in Fig. 1(b) exhibits a more complicated feature. There is a maximum around 150 K for the pressure of 6.5 GPa. Applying pressure shifts it down to lower temperatures. However, the maximum feature is gradually suppressed and superconductivity appears spontaneously. The emergence of superconductivity and the destruction of the resistivity maximum at the same pressure indicate a close connection between them. The resistivity maximum is the common feature for the materials with the charge density wave. This superconducting phase is possible to come after the suppression of the charge density wave. It possesses an insulating normal state [Figs. 1(b) and 1(c)]. This dramatic change of the electrical transport with pressure is also reflected by the resistivity value. The lower panel of Fig. 4 also summarizes the resistivities measured at various pressures and at 10 K. An anomaly is clearly observed across the phase boundary of the phase S and I. The crossover of the carrier character suggests the change of their different Fermi surfaces. The Rashba semiconducting phase at ambient pressure can be tuned into an insulating phase above 5 GPa. The huge enhancement of the resistivity with three magnitude of orders indicates the possible realization of the topological insulator upon compression suggested previously [17]. Although the estimated pressure of the surface polarity along the *c* axis for BiTeCl is only about 1 GPa in the angle-resolved photoemission spectroscopy measurement [18], our measurements were performed at the quasi-hydrostatic pressure condition which is quite different with the nonhydrostatic environment in the angle-resolved photoemission spectroscopy experiment. The pressure-induced topological phase transition at 4-5 GPa has also been observed in the sister BiTeI [33,36]. These results together contribute BiTeCl the possible topological feature in its insulating state and even its superconducting state.

In conclusion, we have carried out the high-pressure resistivity, Hall coefficient, and Raman spectroscopy measurements on a Rashba semiconductor BiTeCl up to 50 GPa. We have succeeded in detecting an insulating state followed by two superconducting phases with insulating and metallic normal state, respectively. These findings enrich the superconducting family from bismuth tellurohalides. The results also highlight the possible realization of the topological state of both the insulating and superconducting phases from these Rashba semiconductors with strong spin-orbital coupling.

The resistance measurements were supported by the DOE under Grant No. DE-FG02-02ER45955. Raman measurements were supported by the U.S. National Science Foundation Earth Sciences Instrumentation and Facilities (EAR/IF) and DARPA. The sample design and growth were supported by the National Natural Science Foundation of China (Grant No. 11190021), the "Strategic Priority Research Program (B)" of the Chinese Academy of Sciences (Grant No. XDB04040100). A.G.G. acknowledges the support from Russian Foundation for Basic Research (Grant No. 14-02-00483-a), Russian Scientific Foundation (Grant No. 14-12-00848), and "Elementary particle physics, fundamental nuclear physics and nuclear technologies".

---

[*] Electronic address: xjchen@hpstar.ac.cn

[1] C. Nayak, S. H. Simon, A. Stern, M. Freedman, and S. Das Sarma, *Non-Abelian anyons and topological quantum computation.* Rev. Mod. Phys. **80**, 1083-1159 (2008).

[2] J. Alicea, Y. Oreg, G. Refael, F. v. Oppen, and M. P. A. Fisher, *Non-Abelian statistics and topological quantum information processing in 1D wire networks.* Nat. Phys. **7**, 412-417 (2011).

[3] M. Z. Hasan and C. L. Kane, *Colloquium: Topological insulators.* Rev. Mod. Phys. **82**, 3045-3067 (2010).

[4] X. L. Qi and S. C. Zhang, *Topological insulators and superconductors.* Rev. Mod. Phys. **83**, 1057-1110 (2011).

[5] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *A topological Dirac insulator in a quantum spin Hall phase.* Nature (London) **452**, 970-974 (2008).

[6] M. A. Ilina and E. S. Itskevich, *Superconductivity of bismuth telluride.* Sov. Phys. Solid State **13**, 2098-2100 (1972).

[7] M. Einaga, Y. Tanabe, A. Nakayama, A. Ohmura, F. Ishikawa, and Y. Yamada, *New superconducting phase of* Bi_2Te_3 *under pressure above 11 GPa.* J. Phys.: Conf. Ser. **215**, 012036 (2010).

[8] J. L. Zhang, S. J. Zhang, H. M. Weng, W. Zhang, L. X. Yang, Q. Q. Liu, S. M. Feng, X. C. Wang, R. C. Yu, L. Z. Cao, L. Wang, W. G. Yang, H. Z. Liu, W. Y. Zhao, S. C. Zhang, X. Dai, Z. Fang, and C. Q. Jin, *Pressure-induced superconductivity in topological parent compound* Bi_2Te_3*.* Proc. Natl. Acad. Sci. U.S.A. **108**, 24-28 (2011).

[9] K. Matsubayashi, T. Terai, J. S. Zhou, and Y. Uwatoko, *Superconductivity in the topological insulator* Bi_2Te_3 *under hydrostatic pressure.* Phys. Rev. B **90**, 125126 (2014).

[10] K. Kirshenbaum, P. S. Syers, A. P. Hope, N. P. Butch, J. R. Jeffries, S. T. Weir, J. J. Hamlin, M. B. Maple, Y. K. Vohra, and J. Paglione, *Pressure-induced unconventional superconducting phase in the topological insulator* Bi_2Se_3*.* Phys. Rev. Lett. **111**, 087001 (2013).

[11] J. Zhu, J. L. Zhang, P. P. Kong, S. J. Zhang, X. H. Yu, J. L. Zhu, Q. Q. Liu, X. Li, R. C. Yu, R. Ahuja, W. G. Yang, G. Y. Shen, H. K. Mao, H. M. Weng, X. Dai, Z. Fang, Y. S. Zhao, and C. Q. Jin, *Superconductivity in topological insulator* Sb_2Te_3 *induced by pressure.* Sci. Rep. **3**, 2016 (2013).

[12] Y. S. Hor, A. J. Williams, J. G. Checkelsky, P. Roushan, J. Seo, Q. Xu, H. W. Zandbergen, A. Yazdani, N. P. Ong, and R. J. Cava, *Superconductivity in* $Cu_xBi_2Se_3$ *and its implications for pairing in the undoped topological insulator.* Phys. Rev. Lett. **104**, 057001 (2010).

[13] Takeshi Kondo, Y. Nakashima, Y. Ota, Y. Ishida, W. Malaeb, K. Okazaki, S. Shin, M. Kriener, Satoshi Sasaki, Kouji Segawa, and Yoichi Ando, *Anomalous dressing of Dirac fermions in the topological surface state of* Bi_2Se_3*,*

Bi_2Te_3, and Cu-Doped Bi_2Se_3. Phys. Rev. Lett. **110**, 217601 (2013).

[14] K. Ishizaka, M. S. Bahramy, H. Murakawa, M. Sakano, T. Shimojima, T. Sonobe, K. Koizumi, S. Shin, H. Miyahara, A. Kimura, K. Miyamoto, T. Okuda, H. Namatame, M. Taniguchi, R. Arita, N. Nagaosa, K. Kobayashi, Y. Murakami, R. Kumai, Y. Kaneko, Y. Onose, and Y. Tokura, *Giant Rashba-type spin splitting in bulk BiTeI.* Nat. Mater. **10**, 521-526 (2011).

[15] S. V. Eremeev, I. A. Nechaev, Yu. M. Koroteev, P. M. Echenique, and E. V. Chulkov, *Ideal two-dimensional electron systems with a giant Rashba-type spin splitting in real materials: Surfaces of bismuth tellurohalides.* Phys. Rev. Lett. **108**, 246802 (2012).

[16] G. Landolt, S. V. Eremeev, O. E. Tereshchenko, S. Muff, B. Slomski, K. A Kokh, M. Kobayashi, T. Schmitt, V. N. Strocov, J. Osterwalder, E. V. Chulkov, and J. Hugo Dil, *Bulk and surface Rashba splitting in single termination BiTeCl.* New J. Phys. **15**, 085022 (2013).

[17] M. S. Bahramy, B.-J. Yang, R. Arita, and N. Nagaosa, *Emergence of non-centrosymmetric topological insulating phase in BiTeI under pressure.* Nat. Commun. **3**, 679 (2012).

[18] Y. L. Chen, M. Kanou, Z. K. Liu, H. J. Zhang, J. A. Sobota, D. Leuenberger, S. K. Mo, B. Zhou, S.-L. Yang, P. S. Kirchmann, D. H. Lu, R. G. Moore, Z. Hussain, Z. X. Shen, X. L. Qi and T. Sasagawa, *Discovery of a single topological Dirac fermion in the strong inversion asymmetric compound BiTeCl.* Nat. Phys. **9**, 704-708 (2013).

[19] L. Fu and C. L. Kane, *Topological insulators with inversion symmetry.* Phys. Rev. B **76**, 045302 (2007).

[20] X. L. Qi, T. L. Hughes, and S. C. Zhang, *Topological invariants for the Fermi surface of a time-reversal-invariant superconductor.* Phys. Rev. B **81**, 134508 (2010).

[21] X. X. Xi, C. L. Ma, Z. X. Liu, Z. Q. Chen, W. Ku, H. Berger, C. Martin, D. B. Tanner, and G. L. Carr, *Signatures of a pressure-induced topological quantum phase transition in BiTeI.* Phys. Rev. Lett. **111**, 155701 (2013).

[22] M. K. Tran, J. Levallois, P. Lerch, J. Teyssier, A. B. Kuzmenko, G. Autes, O.V. Yazyev, A. Ubaldini, E. Giannini, D. van der Marel, and A. Akrap, *Infrared- and Raman-spectroscopy measurements of a transition in the crystal structure and a closing of the energy gap of BiTeI under pressure.* Phys. Rev. Lett. **112**, 047402 (2014).

[23] F. X. Xiang, X. L. Wang, and S. X. Dou, *Transport evidence of robust topological surface state in BiTeCl single crystals, the first strong inversion asymmetric topological insulator.* arXiv:1401.6732 (unpublished).

[24] F. Chen, D. Zhao, Z. J. Xiang, C. Shang, X. G. Luo, B. Y. Pan, S. Y. Li, T. Wu, and X. H. Chen, *Quantum oscillations in Rashba semiconductor BiTeCl.* Phys. Rev. B **90**, 201202(R) (2014).

[25] C. Martin, A.V. Suslov, S. Buvaev, A. F. Hebard, P. Bugnon, H. Berger, A. Magrez, D. B. Tanner, *Unusual Shubnikov-de Haas oscillations in BiTeCl.* Phys. Rev. B **90**, 201204(R) (2014).

[26] A. G. Gavriliuk, A. A. Mironovich, and V. V. Struzhkin, *Miniature diamond anvil cell for broad range of high pressure measurements.* Rev. Sci. Instrum. **80**, 043906 (2009).

[27] T. Ideue, J. G. Checkelsky, M. S. Bahramy, H. Murakawa, Y. Kaneko, N. Nagaosa, and Y. Tokura, *Pressure variation of Rashba spin splitting toward topological transition in the polar semiconductor BiTeI.* Phys. Rev. B **90**, 161107(R) (2014).

[28] A. Akrap, J. Teyssier, A. Magrez, P. Bugnon, H. Berger, A. B. Kuzmenko, and D. van der Marel, *Optical properties of BiTeBr and BiTeCl.* Phys. Rev. B **90**, 035201 (2014).

[29] E. Morosan, H. W. Zandbergen, B. S. Dennis, J. W. G. Bos, Y. Onose, T. Klimczuk, A. P. Ramirez, N. P. Ong, and R. J. Cava, *Superconductivity in Cu_xTiSe_2.* Nat. Phys. **2**, 544-550 (2006).

[30] Y. Tanaka, T. Yokoyama, A. V. Balatsky, and N. Nagaosa, *Theory of topological spin current in noncentrosymmetric superconductors.* Phys. Rev. B **79**, 060505 (2009).

[31] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, *Temperature and purity dependence of the superconducting critical field, H_{c2}. III. Electron spin and spin-orbit effects.* Phys. Rev. **147**, 295-302 (1966).

[32] I. Yu. Sklyadneva, R. Heid, K.-P. Bohnen, V. Chis, V. A. Volodin, K. A. Kokh, O. E. Tereshchenko, P. M. Echenique, and E. V. Chulkov, *Lattice dynamics of bismuth tellurohalides.* Phys. Rev. B **86**, 094302 (2012).

[33] Y. Z. Chen, X. X. Xi, W. L. Yim, F. Peng, Y. C. Wang, H. Wang, Y. M. Ma, G. T. Liu, C. L. Sun, C. L. Ma, Z. Q. Chen, and H. Berger, *High-pressure phase transitions and structures of topological insulator BiTeI.* J. Phys. Chem. C **117**, 25677-25683 (2013).

[34] L. Zhu, H. Wang, Y. C. Wang, J. Lv, Y. M. Ma, Q. L. Cui, Y. M. Ma, and G. T. Zou, *Substitutional alloy of Bi and Te at high pressure.* Phys. Rev. Lett. **106**, 145501 (2011).

[35] J. Jacimovic, X. Mettan, A. Pisoni, R. Gaal, S. Katrych, L. Demko, A. Akrap, L. Forro, H. Berger, P. Bugnon, and A. Magrez, *Enhanced low-temperature thermoelectrical properties of BiTeCl grown by topotactic method.* Scr. Mater. **76**, 69-72 (2014).

[36] Yu. S. Ponosov, T. V. Kuznetsova, O. E. Tereshchenko, K. A. Kokh, and E. V. Chulkov, *Dynamics of the BiTeI lattice at high pressures.* JETP Lett. **98**, 557-561 (2013).