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# Spectroscopic evidence for bulk-band inversion and three-dimensional massive Dirac fermions in ZrTe<sub>5</sub>

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**Three-dimensional topological insulators (3D TIs) represent states of quantum matters in which surface states are protected by time-reversal symmetry and an inversion occurs between bulk conduction and valence bands. However, the bulk-band inversion, which is intimately tied to the topologically nontrivial nature of 3D TIs, has rarely been investigated by experiments. Besides, 3D massive Dirac fermions with nearly linear band dispersions were seldom observed in TIs. Recently, a van der Waals crystal, ZrTe<sub>5</sub>, was theoretically predicted to be a TI. Here, we report an infrared transmission study of a high-mobility [ $\sim 33,000 \text{ cm}^2/(\text{V} \cdot \text{s})$ ] multilayer ZrTe<sub>5</sub> flake at magnetic fields ( $B$ ) up to 35 T. Our observation of a linear relationship between the zero-magnetic-field optical absorption and the photon energy, a bandgap of  $\sim 10 \text{ meV}$  and a  $\sqrt{B}$  dependence of the Landau level (LL) transition energies at low magnetic fields demonstrates 3D massive Dirac fermions with nearly linear band dispersions in this system. More importantly, the reemergence of the intra-LL transitions at magnetic fields higher than 17 T reveals the energy cross between the two zeroth LLs, which reflects the inversion between the bulk conduction and valence bands. Our results not only provide spectroscopic evidence for the TI state in ZrTe<sub>5</sub> but also open up a new avenue for fundamental studies of Dirac fermions in van der Waals materials.**

band inversion | Dirac fermions | topological insulators | Landau levels | Zeeman splitting

Topologically nontrivial quantum matters, such as topological insulators (1–8), Dirac semimetals (9–19), and Weyl semimetals (20–27), have sparked enormous interest owing both to their exotic electronic properties and potential applications in spintronic devices and quantum computing. Therein, intrinsic topological insulators have insulating bulk states with odd  $Z_2$  topological invariants and metallic surface or edge states protected by time-reversal symmetry (4–6, 28). Most of the experimental evidence to date for TIs is provided by the measurements of the spin texture of the metallic surface states. As a hallmark of the nontrivial  $Z_2$  topology of TIs (4–6, 28), an inversion between the characteristics of the bulk conduction and valence bands occurring at an odd number of time-reversal invariant momenta has seldom been probed by experiments. An effective approach for identifying the bulk-band inversion in TIs is to follow the evolution of two zeroth Landau levels (LLs) that arise from the bulk conduction and valence bands, respectively. As shown in Fig. 1A, for TIs, due to the bulk-band inversion and Zeeman effects, the two zeroth bulk Landau levels are expected to intersect in a critical magnetic field and then separate (3, 29); and for trivial insulators, the energy difference between their two zeroth Landau levels would become larger with increasing magnetic field. Therefore, an intersection between the two zeroth bulk LLs is a significant signature of the bulk-band inversion in TIs. However, a spectroscopic study of the intersection between the two zeroth bulk LLs in 3D TIs is still missing. In addition, many typical 3D TIs, such as Bi<sub>2</sub>Se<sub>3</sub>, show massive bulk Dirac fermions with parabolic band

dispersions, which are effectively described by massive Dirac models (6, 28, 29). By contrast, 3D massive Dirac fermions with nearly linear bulk band dispersions (7), which are interesting topics following 2D massive Dirac fermions in gapped graphene (30, 31), were rarely observed in 3D TIs.

A transition-metal pentatelluride, ZrTe<sub>5</sub>, embodies both 1D chain and 2D layer features (32), shown in Fig. 1B. One Zr atom together with three Te (1) atoms forms a quasi-1D prismatic chain ZrTe<sub>3</sub> along the  $a$  axis ( $x$  axis). These prismatic ZrTe<sub>3</sub> chains are connected through zig-zag chains of Te (2) atoms along the  $c$  axis ( $y$  axis) and then construct quasi-2D ZrTe<sub>5</sub> layers. The bonding between ZrTe<sub>5</sub> layers is van der Waals type (33, 34). Thus, as displayed in Fig. 1C, bulk ZrTe<sub>5</sub> crystals can be easily cleaved down to a few layers. Recently, the ab initio calculations indicate that monolayer ZrTe<sub>5</sub> sheets are great contenders for quantum spin Hall insulators—2D TI and that 3D ZrTe<sub>5</sub> crystals are quite close to the phase boundary between strong and weak TIs (33). Scanning tunneling microscopy measurements have shown that edge states exist at the step edges of the ZrTe<sub>5</sub> surfaces (35, 36). Nonetheless, further investigations are needed to check whether the observed edge states in ZrTe<sub>5</sub> are topologically nontrivial or not. Studying the bulk-band inversion or the intersection between the two zeroth bulk LLs can provide a crucial clue to clarifying the nature of the edge states in ZrTe<sub>5</sub>. Except the edge states within the energy gap of the bulk bands around the Brillouin zone center (i.e.,  $\Gamma$  point) of ZrTe<sub>5</sub> (36, 37), 3D massless Dirac fermions with

## Significance

Experimental verifications of the theoretically predicted topological insulators (TIs) are essential steps toward the applications of the topological quantum phenomena. In the past, theoretically predicted TIs were mostly verified by the measurements of the topological surface states. However, as another key feature of the nontrivial topology in TIs, an inversion between the bulk bands has rarely been observed by experiments. Here, by studying the optical transitions between the bulk LLs of ZrTe<sub>5</sub>, we not only offer spectroscopic evidence for the bulk-band inversion—the crossing of the two zeroth LLs in a magnetic field, but also quantitatively demonstrate three-dimensional massive Dirac fermions with nearly linear band dispersions in ZrTe<sub>5</sub>. Our investigation provides a paradigm for identifying TI states in candidate materials.

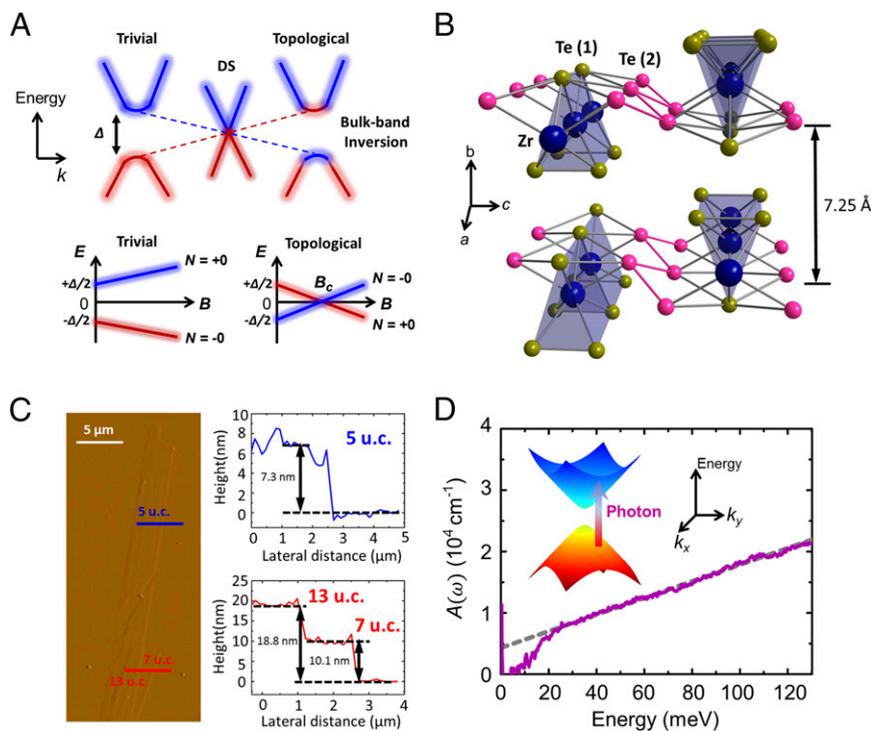
Author contributions: Z.-G.C. designed the research; Z.-G.C. carried out the optical experiments; Z.-G.C. wrote the paper; Z.-G.C., R.Y.C., R.Y., and N.L.W. analyzed the data; R.D.Z., J.S., and G.D.G. grew the single crystals; and C.Z., Y.H., F.Q., and Q.L. performed the basic characterization.

The authors declare no conflict of interest.

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**Fig. 1.** Bulk band and crystal structure of  $\text{ZrTe}_5$ . (A, Top) Schematic of the topological phase transition from trivial to topological insulators. A 3D Dirac semimetal (DS) can be regarded as a quantum critical point with a gapless band structure. Due to the bulk-band inversion in TIs, the conduction and valence band exchange their extrema. Bottom row: energy spectrum for the Landau-index  $N = +0$  and  $-0$  LLs with a Zeeman splitting. (B) Atomic structure of  $\text{ZrTe}_5$ . Each unit cell contains two  $\text{ZrTe}_5$  layers. (C, Left) AFM image of  $\text{ZrTe}_5$  flakes. (Right) thicknesses along the colored lines on the left. Thicknesses from 5 to 13 unit cells (u.c.) are shown. (D) Absorption coefficient  $A(\omega)$  of the  $\text{ZrTe}_5$  flake with thickness  $d \sim 180$  nm as a function of photon energy at  $B = 0$  T. The linear energy dependence of  $A(\omega)$  is mainly associated with interband transitions of 3D Dirac electrons. A sudden drop in  $A(\omega)$  at low energies implies the modification of the band structures within an energy range, namely the bandgap. D, Inset depicts the interband absorption in gapped  $\text{ZrTe}_5$ .

the linearly dispersing conduction and valence band degenerate at the  $\Gamma$  point were suggested to exist in this material by previous angle-resolved photon emission spectroscopy, transport, and optical experiments (38–41). Considering that (i) our  $\text{ZrTe}_5$  thick crystals were experimentally shown to be Dirac semimetals hosting 3D massless Dirac fermions, (ii)  $\text{ZrTe}_5$  monolayers were theoretically predicted to be quantum spin Hall insulators, and (iii) the bulk state of  $\text{ZrTe}_5$  is very sensitive to its interlayer distance, which might be a discrepancy in different samples (33, 40); it is significant to quantitatively verify whether 3D massive Dirac fermions with a bandgap and nearly linear bulk-band dispersions can be realized in dramatically thinned flakes of our  $\text{ZrTe}_5$  crystals.

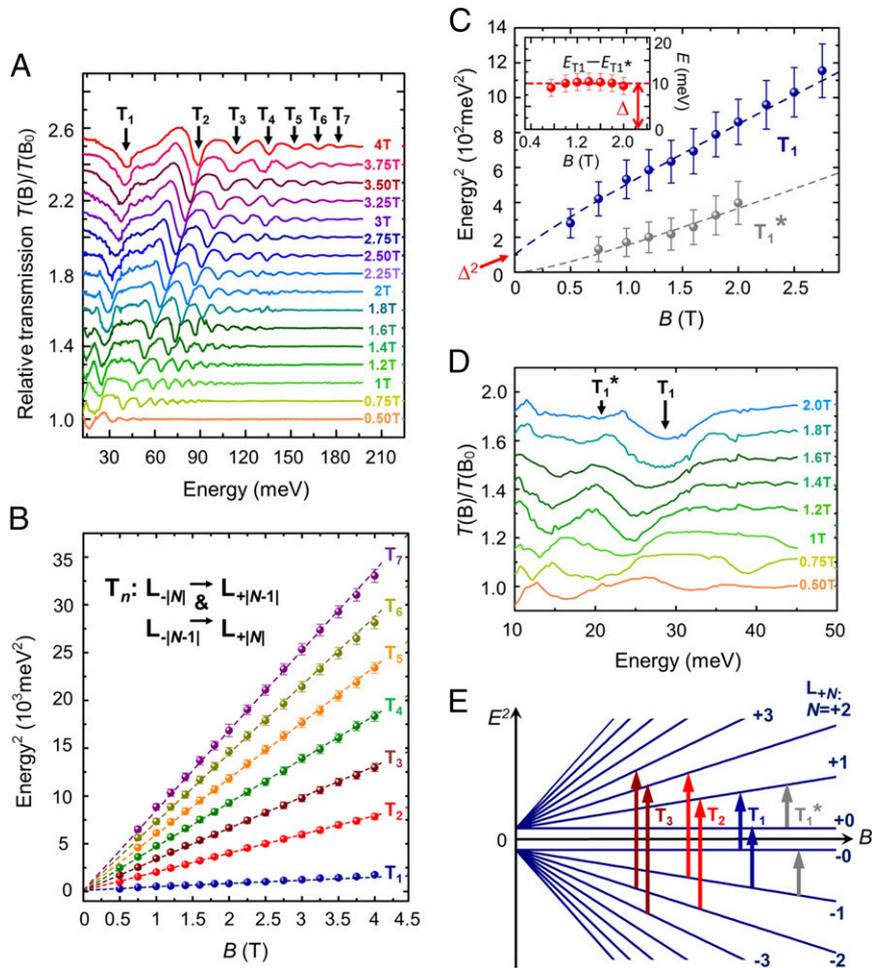
Infrared spectroscopy is a bulk-sensitive experimental technique for studying low-energy excitations of a material. Here, to investigate the bulk-band inversion and the nature of the bulk fermions in  $\text{ZrTe}_5$ , we measured the infrared transmission spectra  $T(\omega, B)$  of its multilayer flake with thickness  $d \sim 180$  nm at magnetic fields applied along the wave vector of the incident light (Materials and Methods and Supporting Information). A series of intra- and inter-LL transitions are present in the relative transmission spectra  $T(B)/T(B_0 = 0 \text{ T})$  of the  $\text{ZrTe}_5$  flake. The linear  $\sqrt{B}$  dependence of the LL transition energies at  $B \leq 4$  T and the nonzero intercept of the LL transitions at  $B = 0$  T, combined with the linear relationship between the zero-magnetic-field optical absorption and the photon energy, indicates 3D massive Dirac fermions with nearly linear band dispersions in the  $\text{ZrTe}_5$  flake. Moreover, a 3D massive Dirac model with a bandgap of  $\sim 10$  meV can quantitatively explain the magnetic-field dependence of the measured LL transition energies very well. At high magnetic fields, we observed fourfold splittings of the LL transitions. In addition, our analysis of the split LL transitions shows that the intra-LL transitions, which are associated to the two zeroth LLs and disappear at  $B \sim 2.5$  T, reemerge at  $B > 17$  T. Considering

that the zeroth LL crossing in a Zeeman field would make the two zeroth bulk LLs intersect with the chemical potential here and then alter the carrier occupation on the zeroth LLs, we attribute the reemergence of the intra-LL transitions in the  $\text{ZrTe}_5$  flake to the energy crossing of its two zeroth bulk LLs, which originates from the bulk-band inversion. These results strongly support the theoretically predicted 3D TI states in 3D  $\text{ZrTe}_5$  crystals.

## Results

**Three-Dimensional Massive Dirac Fermions.** At zero magnetic field, the measured absolute transmission  $T(\omega)$  corresponds to the absorption coefficient:  $A(\omega) = -[\ln T(\omega)]/d$ , where  $d$  is the thickness of the sample and  $\omega$  is the photon energy (see the methods section of ref. 42). In solids, the absorption coefficient is determined by the joint density of state  $D(\omega)$ :  $A(\omega) \propto D(\omega)/\omega$ . Three-dimensional electron systems with linear band dispersions along three momentum directions have the  $D(\omega)$  proportional to  $\omega^2$ , and for 2D linear dispersions,  $D(\omega) \propto \omega$ . Thus, in stark contrast to the  $\omega$ -independent absorption of 2D Dirac materials like graphene (43), the linear  $\omega$  dependence of  $A(\omega)$  in Fig. 1D indicates 3D linear band dispersions in  $\text{ZrTe}_5$ . Moreover, at low energies, the absorption coefficient apparently deviates from the linear relationship with  $\omega$ , implying the opening of a bandgap at the original Dirac point. The 3D linear band dispersions, together with the possible bandgap, suggest the presence of 3D massive Dirac fermions in the exfoliated  $\text{ZrTe}_5$  flake.

To confirm the 3D massive Dirac fermions in  $\text{ZrTe}_5$ , we further performed infrared transmission experiments at magnetic fields applied perpendicular to the  $ac$  plane ( $xy$  plane) of the crystal (Faraday geometry). The low-field relative transmission  $T(B)/T(B_0 = 0 \text{ T})$  spectra in Fig. 2A show seven dip features  $T_n$  ( $1 \leq n \leq 7$ ) directly corresponding to the absorption peaks of LL



**Fig. 2.** Low-magnetic-field Landau level transitions in ZrTe<sub>5</sub>. (A) Absorption features  $T_n$  ( $1 \leq n \leq 7$ ) in  $T(B)/T(B_0)$  spectra. The spectra are displaced from one another by 0.1 for clarity. (B, C) Squares of  $T_n$  and  $T_1^*$  energies plotted as a function of magnetic field ( $B \leq 4$  T).  $T_n$  correspond to the interband LL transitions:  $LL_{-|N|} \rightarrow LL_{+|N-1|}$  (or  $LL_{-|N-1|} \rightarrow LL_{+|N|}$ ). The nonzero  $E_{T_1}^2(B)$  at zero field reveals a bandgap  $\Delta$ . C, Inset shows the energy difference between  $T_1$  and  $T_1^*$ , which equals to the bandgap. (D) Absorption features  $T_1^*$  in  $T(B)/T(B_0)$  spectra.  $T_1^*$ , which is located at energies lower than  $T_1$ , arises from the intraband LL transition  $LL_{+0} \rightarrow LL_{+1}$  (or  $LL_{-1} \rightarrow LL_{-0}$ ). (E) Schematic of the Landau level spectrum without a Zeeman splitting and the allowed optical transitions, shown in a  $E^2$ - $B$  plot.

transitions. All of these dip features systematically shift to higher energies, as the magnetic field increases. Here, we define the energy positions of the transmission minima in  $T(B)/T(B_0)$  as the absorption energies, which is a usual definition in thin film systems, such as Bi<sub>2</sub>Se<sub>3</sub> films and graphene. Then, we plotted the square of the  $T_n$  energies ( $E_{T_n}^2$ ) as a function of magnetic field in Fig. 2B. The linear  $B$  dependence of  $E_{T_n}^2$  (i.e., linear  $\sqrt{B}$  dependence of  $E_{T_n}$ ) reveals the LL transitions of Dirac fermions (31, 44, 45). In Fig. 2C, the nonzero intercept of the linear fit to  $E_{T_1}^2$  at zero magnetic field is an important signature of a nonzero Dirac mass or a bandgap (31). Therefore, the linear relationship between  $E_{T_n}^2$  and  $B$ , together with the nonzero intercept, provides further evidence for 3D massive Dirac fermions in the ZrTe<sub>5</sub> flake.

To quantitatively check the 3D massive Dirac fermions in the ZrTe<sub>5</sub> flake, we use a 3D massive Dirac Hamiltonian, which was derived from the low-energy effective  $k \cdot p$  Hamiltonian based on the spin-orbital coupling, the point group and time-reversal symmetries in ZrTe<sub>5</sub>, and includes the spin degree of freedom (40). According to the 3D massive Dirac Hamiltonian expanded to the linear order of momenta, we can obtain the nearly linear band dispersions of ZrTe<sub>5</sub> at zero magnetic field:  $E(k_{x,y,z}) = \pm \sqrt{\hbar^2(k_x^2 v_x^2 + k_y^2 v_y^2 + k_z^2 v_z^2) + (\Delta/2)^2}$ , where  $k_{x,y,z}$  are the wave vectors in momentum space,  $v_{x,y,z}$  are the Fermi velocities

along three momentum directions,  $\Delta$  is the bandgap and describes the mass of Dirac fermions  $m_{x,y,z}^D = \Delta/(2v_{x,y,z}^2)$  and  $\hbar$  is Planck's constant divided by  $2\pi$ . In a magnetic field applied perpendicular to the  $ac$  plane, the LL spectrum of ZrTe<sub>5</sub> without considering Zeeman effects has the form:

$$E_N(k_z) = \pm \delta_{N,0} \sqrt{(\Delta/2)^2 + (v_z \hbar k_z)^2} + \text{sgn}(N) \sqrt{2e\hbar v_F^2 B |N| + (\Delta/2)^2 + (v_z \hbar k_z)^2}, \quad [1]$$

where  $v_F$  is the effective Fermi velocity of LLs, the integer  $N$  is Landau index,  $\delta_{N,0}$  is the Kronecker delta function,  $\text{sgn}(N)$  is the sign function, and  $e$  is the elementary charge. The  $\sqrt{B}$  dependence is a hallmark of Dirac fermions (31, 44, 45). According to Eq. 1, the magnetic field makes the 3D linear band dispersions evolve into a series of 1D non-equally-spaced Landau levels (or bands), which disperse with the momentum component along the field direction. Specifically, because the 3D massive Dirac Hamiltonian of ZrTe<sub>5</sub> involves the spin degree of freedom of this system, two zeroth LLs indexed by  $N = +0$  and  $N = -0$  locate at the hole and electron band extrema, respectively, and have energy dispersions  $E_{\pm 0}(k_z) = \pm \sqrt{(\Delta/2)^2 + (v_z \hbar k_z)^2}$ , which is different from the case that when the spin degree of freedom was not

considered in materials with the hexagonal lattice, only one zeroth nondegenerate Landau level is present in each valley (46). The optical selection rule for ZrTe<sub>5</sub> only allows the LL transitions from LL<sub>N</sub> to LL<sub>N'</sub>:  $\Delta N = |N| - |N'| = \pm 1$  and with the  $k_z$ -momentum difference  $\Delta k_z = 0$  (40). Due to the singularities of the density of states (DOS) at  $k_z = 0$ , magneto-optical response here, which is determined by the joint DOS, should be mainly contributed by the LL transitions at  $k_z = 0$  (29, 40). Thus, the energies of the interband LL (inter-LL) transitions  $LL_{-|N|} \rightarrow LL_{+|N-1|}$  (or  $LL_{-|N-1|} \rightarrow LL_{+|N|}$ ) and the intraband LL (intra-LL) transitions  $LL_{+|N-1|} \rightarrow LL_{+|N|}$  (or  $LL_{-|N|} \rightarrow LL_{-|N-1|}$ ),  $E_N^{Inter}$  and  $E_N^{Intra}$  at  $k_z = 0$ , are given by:

$$E_N^{Inter} = \sqrt{2e\hbar v_F^2 B |N| + (\Delta/2)^2} + \sqrt{2e\hbar v_F^2 B |N-1| + (\Delta/2)^2} \quad [2]$$

$$E_N^{Intra} = \sqrt{2e\hbar v_F^2 B |N| + (\Delta/2)^2} - \sqrt{2e\hbar v_F^2 B |N-1| + (\Delta/2)^2}. \quad [3]$$

From T<sub>1</sub> to T<sub>7</sub>, the slopes of the linear fits to  $E_{T_n}^2$  in Fig. 2B scale as 1: 5.7: 9.3: 13.1: 16.7: 20.5: 24.1, respectively, which is close to the approximate ratio of the theoretical inter-LL transition energies based on Eq. 2, 1:  $(\sqrt{2} + \sqrt{1})^2$  ( $\sim 5.8$ ):  $(\sqrt{3} + \sqrt{2})^2$  ( $\sim 9.9$ ):  $(\sqrt{4} + \sqrt{3})^2$  ( $\sim 13.9$ ):  $(\sqrt{5} + \sqrt{4})^2$  ( $\sim 17.9$ ):  $(\sqrt{6} + \sqrt{5})^2$  ( $\sim 21.9$ ):  $(\sqrt{7} + \sqrt{6})^2$  ( $\sim 25.9$ ). Therefore, the absorption features T<sub>n</sub> are assigned as the inter-LL transitions:  $LL_{-|N-1|} \rightarrow LL_{+|N|}$  (or  $LL_{-|N|} \rightarrow LL_{+|N-1|}$ ) (Fig. 2B) and we have  $n = |N|$ , where  $1 \leq n \leq 7$ . Fitting  $E_{T_n}^2$  based on Eq. 2 from a least square fit yields a bandgap  $\Delta \sim 10 \pm 2$  meV, the effective Fermi velocities  $v_F^{T_1} \approx (4.76 \pm 0.04) \times 10^5$  m/s and  $v_F^{2 \leq n \leq 7} \approx (5.04-4.95 \pm 0.04) \times 10^5$  m/s (Supporting Information).

As another signature of the bandgap or the nonzero Dirac mass, the absorption feature T<sub>1</sub>\* is present at energies lower than the lowest-energy inter-LL transition T<sub>1</sub> in Fig. 2D. The feature T<sub>1</sub>\* is attributed to the intra-LL transition  $LL_{+0} \rightarrow LL_{+1}$  (or  $LL_{-1} \rightarrow LL_{-0}$ ), illustrated by the gray arrows in Fig. 2E (Supporting Information). According to Eqs. 2 and 3, the energy difference ( $E_{T_1} - E_{T_1^*}$ ) between the transitions T<sub>1</sub> and T<sub>1</sub>\* in the inset of Fig. 2C directly gives the bandgap value  $\Delta = E_{T_1} - E_{T_1^*} \approx 10 \pm 2$  meV, which is consistent with the value obtained by the above fitting. Furthermore, the field dependence of the T<sub>1</sub>\* energy in Fig. 2C can be well fitted by Eq. 3 with  $\Delta \sim 10 \pm 2$  meV and  $v_F^{T_1^*} \approx (4.63 \pm 0.04) \times 10^5$  m/s.

The carrier-charge mobility  $\mu$  in the ZrTe<sub>5</sub> flake can be calculated using the general equation (47):  $\mu = e\hbar/(\Gamma m^*)$ , where  $\Gamma$  is the transport scattering rate and  $m^*$  is the carrier effective mass on the anisotropic Fermi surface (48, 49). Here, the transport scattering rate  $\Gamma$  within the *ac* plane can be roughly estimated from the width of the T<sub>1</sub> feature at low fields:  $\Gamma \sim 9$  meV at  $B = 0.5$  T. Moreover, considering the absence of Pauli blocking of the T<sub>1</sub> transition at  $B = 0.5$  T, we get the Fermi energy in ZrTe<sub>5</sub>,  $E_F < |E_{LL+1(or-1)}| = E_{T_1} \approx 15$  meV (Supporting Information), which means the Fermi level in our sample is quite close to the band extrema. In this case, the average effective mass  $m^*$  of the carriers within the *ac* plane can be described by (30):  $m_{ac}^* \approx \Delta/[2(v_F^{ac})^2] \approx 3.54 \times 10^{-33}$  kg  $\approx 0.00389 m_0$ , where  $m_0$  is the free electron mass and the average Fermi velocity within the *ac* plane  $v_F^{ac}$  is approximately equal to the effective Fermi velocity of the LLs,  $v_F^{ac} \approx 4.76 \times 10^5$  m/s. Finally, we can estimate the mobility of the carriers within the *ac* plane of our ZrTe<sub>5</sub> sample:  $\mu \approx 33,000$  cm<sup>2</sup>/(V · s), which is comparable to those in graphene/h-BN heterostructures (50, 51).

**Bulk-Band Inversion.** As shown in Fig. 3A, applying a higher magnetic field enables us to observe the splitting of the T<sub>1</sub> transition, which indicates a nonnegligible Zeeman effect in ZrTe<sub>5</sub> (40). For TIs, due to the Zeeman field, each LL except the two zeroth LLs splits into two sublevels with opposite spin states, while the

LL<sub>-0</sub> and LL<sub>+0</sub> are spin-polarized and have spin-up and -down state, respectively (3, 29). The energy of the sublevel has the form (40):

$$E_{N,\xi} = E_N(k_z = 0) + 1/2 \xi g_N B, \quad [4]$$

where  $\xi$  is equal to +1 for spin-up and -1 for spin-down and  $g_N$  is the effective Landé  $g$  factor of LL<sub>N</sub>. The spin-orbit coupling (SOC) in ZrTe<sub>5</sub> mixes the spin states of the two sublevels, so two extra optical transitions between the sublevels with different spin indices become possible. The inter- and intra-LL transition energies including the Zeeman effect can be written as (40):

$$E_{N,\xi,\xi'}^{Inter} = E_N^{Inter} + 1/2 (\xi g_N - \xi' g_{(N-1)}) B \quad [5]$$

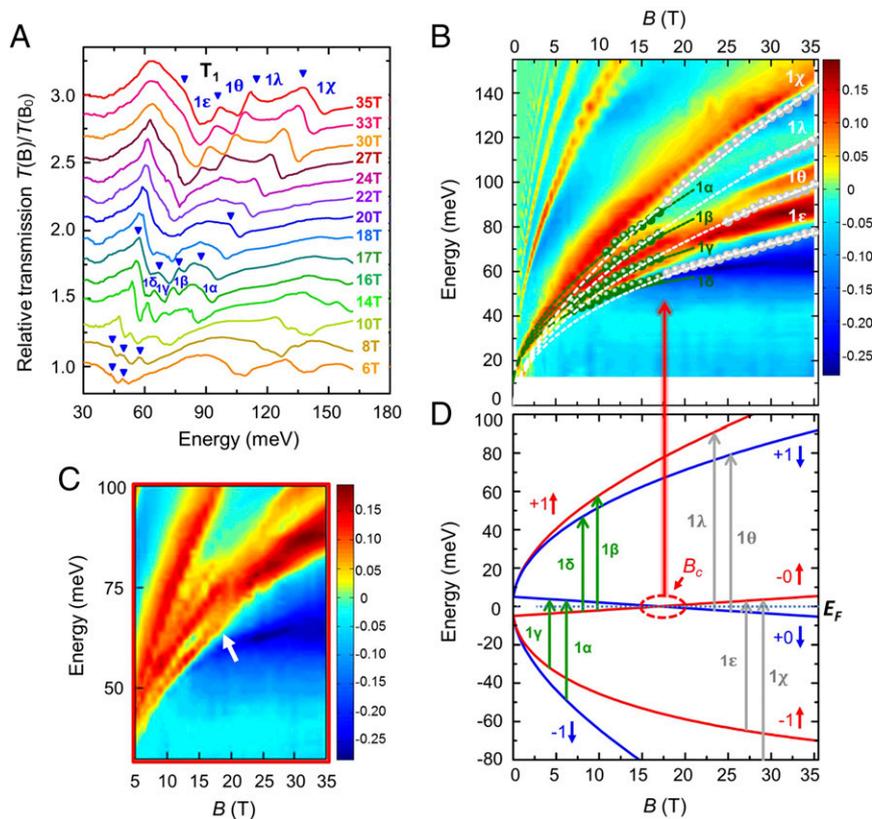
$$E_{N,\xi,\xi'}^{Intra} = E_N^{Intra} + 1/2 (\xi g_N - \xi' g_{(N-1)}) B, \quad [6]$$

where  $\xi$  and  $\xi'$  correspond to the spin states of the two sublevels, respectively.

Fig. 3B displays the false-color map of the  $-\ln[T(B)/T(B_0)]$  spectra of the ZrTe<sub>5</sub> flake. Interestingly, a cusplike feature around 18 T, which is indicated by a white arrow, can be observed in Fig. 3C (i.e., the magnified image of a region in Fig. 3B). To quantitatively investigate the physical meaning of this cusplike feature, we plot the energies of the four split T<sub>1</sub> transitions [i.e., 1 $\alpha$ , 1 $\beta$ , 1 $\gamma$ , and 1 $\delta$  (green dots)] around 16 T in Fig. 3B, which are defined by the onsets of the absorption features due to the Zeeman splitting (see figure 3 of the Supplemental Material of ref. 40 and Supporting Information). As displayed by the green dashed lines in Fig. 3B, fitting the energy traces of the inter-LL transitions, 1 $\alpha$ , 1 $\beta$ , 1 $\gamma$ , and 1 $\delta$ , based on Eq. 5 with the obtained values of the Fermi velocity  $v_F^{T_1}$  and the bandgap  $\Delta$  yields the  $g$  factors of the two zeroth LLs and  $LL_{\pm 1}$ :  $g_{\text{eff}}(LL_{+0}) = g_{\text{eff}}(LL_{-0}) \sim 11.1$ ,  $g_{\text{eff}}(LL_{-1}) \sim 31.1$  and  $g_{\text{eff}}(LL_{+1}) \sim 9.7$  [or  $g_{\text{eff}}(LL_{+1}) \sim 31.1$  and  $g_{\text{eff}}(LL_{-1}) \sim 9.7$ ] (Supporting Information).

It is known that as a hallmark of TIs, the band inversion causes the exchange of the characteristics between the valence- and conduction-band extrema (2, 6, 28), so as shown in Fig. 1A and 3D, the LL<sub>-0</sub> and LL<sub>+0</sub>, which come from the inverted band extrema, have reversed spin states and cross at a critical magnetic field (3, 29). According to Eq. 4 with the above values of  $g_{\text{eff}}(LL_{\pm 0})$  and  $\Delta$ , we estimated the critical magnetic field  $B_c \sim 17$  T. In Fig. 2A and D, the disappearance of the intra-LL transition T<sub>1</sub>\* around  $B \sim 2.5$  T indicates that LL<sub>+0</sub> (or LL<sub>-0</sub>) becomes fully depleted (or occupied) with increasing magnetic field and that at  $B > 2.5$  T, the chemical potential of ZrTe<sub>5</sub> can be considered to be located at zero energy. In this case, the two zeroth LLs intersect with the chemical potential at the same magnetic field  $B_c$ . More importantly, this intersection means at  $B > B_c \sim 17$  T, LL<sub>-0</sub> and LL<sub>+0</sub> becomes empty and occupied, respectively, which leads to the gradual replacement of the inter-LL transitions T<sub>1</sub>, 1 $\alpha$ , 1 $\beta$ , 1 $\gamma$ , and 1 $\delta$ , by the intra-LL transitions T<sub>1</sub>\*, 1 $\lambda$ , 1 $\lambda$ , 1 $\theta$ , and 1 $\varepsilon$ , explained in Fig. 3D. Furthermore, in Fig. 3B, the energy traces of the four split transitions (gray dots) observed at  $B > 17$  T are shown to follow the white theoretical curves for the intra-LL transitions T<sub>1</sub>\*, which are based on Eq. 6. Therefore, the four split transitions observed at  $B > 17$  T in Fig. 3B can be assigned as the intra-LL transitions T<sub>1</sub>\*, 1 $\lambda$ , 1 $\lambda$ , 1 $\theta$ , and 1 $\varepsilon$ . Because the energy traces of the split intra-LL transitions T<sub>1</sub>\* deviate markedly from those of the inter-LL transitions T<sub>1</sub>, the reemergence of the T<sub>1</sub>\* transitions at  $B > 17$  T causes the cusplike feature, which provides experimental evidence for the bulk-band inversion in the ZrTe<sub>5</sub> flake.

In summary, using magnetoinfrared spectroscopy, we have investigated the Landau level spectrum of the multilayer ZrTe<sub>5</sub> flake. The magnetic-field dependence of the LL transition energies



**Fig. 3.** Crossing of the two zeroth LLs of ZrTe<sub>5</sub>. (A) Split  $T_1$  transitions in the  $T(B)/T(B_0)$  spectra at  $B \geq 6$  T. The energies of the split  $T_1$  transitions are defined by the onsets of the dip features indicated by the blue triangles. Around 16 T, four modes are present. Four modes reemerge around 27 T. (B) Color scale map of the  $-\ln[T(B)/T(B_0)]$  spectra as a function of magnetic field and energy. (C) Magnified view of a region in  $B$  to better present the cusplike feature that is indicated by a white arrow around 18 T. The measured  $T_1$  (green dots) and  $T_1^*$  (gray dots) energies are plotted as a function of magnetic field in  $B$ . Here, the green and gray dots in  $B$  can be extracted from the lower-energy edges (i.e., the onsets) of the peak-feature traces in the color intensity plots (i.e.,  $B$  and C) of the  $-\ln[T(B)/T(B_0)]$  spectra. These dots in  $B$  have the intensities of the color scale, respectively: 0.025 for  $1\alpha$ ,  $1\beta$ ,  $1\gamma$ , and  $1\theta$ ,  $-0.025$  for  $1\delta$ ,  $1\chi$ , and  $1\lambda$  and  $-0.075$  for  $1e$ . The theoretical  $T_1$  and  $T_1^*$  energies, based on Eqs. 5 and 6 with the  $g$  factors:  $g_{\text{eff}}(\text{LL}_{-1}) = 31.1$ ,  $g_{\text{eff}}(\text{LL}_{+1}) = 9.7$ , and  $g_{\text{eff}}(\text{LL}_{+0}) = g_{\text{eff}}(\text{LL}_{-0}) = 11.1$ , the bandgap  $\Delta = 10$  meV, the Fermi velocities  $v_F^{T_1} = 4.76 \times 10^5$  m/s, and  $v_F^{T_1^*} = 4.63 \times 10^5$  m/s, are shown by the green and gray dashed curves, respectively. (D) Schematic of the split  $T_1$  (green arrows) and  $T_1^*$  (gray arrows) transitions. The LL spectrum is produced with the above values of the  $g$  factors, the bandgap and the Fermi velocity  $v_F^{T_1}$ . The two zeroth LLs cross at a critical magnetic field  $B_c \sim 17$  T. The chemical potential is roughly at zero energy when the magnetic field is high enough. At  $B > B_c$ , the interband LL transitions ( $1\alpha$ ,  $1\beta$ ,  $1\gamma$ , and  $1\delta$ ) are gradually replaced by the intraband LL transitions ( $1\chi$ ,  $1\theta$ ,  $1\lambda$ , and  $1e$ ), which causes the cusplike feature shown in C.

here, together with the photon-energy dependence of the absorption coefficient at zero field, quantitatively demonstrates 3D massive Dirac fermions with nearly linear dispersions in the ZrTe<sub>5</sub> flake. Due to the Zeeman splitting of the LLs, the energy splitting of the LL transitions was observed at  $B \geq 6$  T. Interestingly, the intra-LL transitions  $T_1^*$  reemerge at  $B > 17$  T. We propose that the reemergence of the  $T_1^*$  transitions results from the band-inversion-induced crossing of the two zeroth LLs,  $\text{LL}_{+0}$  and  $\text{LL}_{-0}$ . Our results make ZrTe<sub>5</sub> flakes good contenders for 3D TIs. Moreover, due to the 3D massive Dirac-like dispersions and the high bulk-carrier mobility [ $\sim 33,000$  cm<sup>2</sup>/(V · s)], the ZrTe<sub>5</sub> flake can also be viewed as a 3D analog of gapped graphene, which enables us to deeply investigate exotic quantum phenomena.

## Materials and Methods

**Sample Preparation and Characterizations.** Bulk single crystals of ZrTe<sub>5</sub> were grown by Te flux method. The elemental Zr and Te with high purity were sealed in an evacuated double-walled quartz ampule. The raw materials were heated at 900 °C and kept for 72 h. Then they were cooled slowly down to 445 °C and heated rapidly up to 505 °C. The thermal-cooling cycling between 445 and 505 °C lasts for 21 d to remelt the small size crystals. The multilayer ZrTe<sub>5</sub> flake (ac plane) for magnetotransmission measurements were fabricated by mechanical exfoliation, and deposited onto double-side-polished SiO<sub>2</sub>/Si substrates with 300 nm SiO<sub>2</sub>. The flake thickness  $\sim 180$  nm and the chemical composition were characterized by atomic force

microscopy (AFM) and energy dispersion spectroscopy (EDS), respectively (Supporting Information).

**Infrared Transmission Measurements.** The transmission spectra were measured at about 4.5 K in a resistive magnet in the Faraday geometry with magnetic field applied in parallel to the wave vector of incident light and the crystal  $b$  axis. Nonpolarized IR light (provided and analyzed by a Fourier transform spectrometer) was delivered to the sample using a copper light pipe. A composite Si bolometer was placed directly below the sample to detect the transmitted light. The diameter of IR focus on the sample is  $\sim 0.5$ –1 mm. Owing to the mismatch between the size of the IR focus and the ZrTe<sub>5</sub> flake, an aluminum aperture was placed around the sample. The transmission spectra are shown at energies above 10 meV, corresponding to wavelengths shorter than 124  $\mu\text{m}$ . The wavelength of infrared light here is smaller than the size of the measured sample, and thus the optical constants can be used for a macroscopic description of the data.

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