Unraveling the Topological Phase of ZrTe\textsubscript{5} via Magneto-infrared Spectroscopy

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For materials near the phase boundary between weak and strong topological insulators (TIs), their band topology depends on the band alignment, with the inverted (normal) band corresponding to the strong (weak) TI phase. Here, taking the anisotropic transition-metal pentatelluride ZrTe\textsubscript{5} as an example, we show that the band inversion manifests itself as a second extremum (band gap) in the layer stacking direction, which can be probed experimentally via magneto-infrared spectroscopy. Specifically, we find that the band anisotropy of ZrTe\textsubscript{5} features a slow dispersion in the layer stacking direction, along with an additional set of optical transitions from a band gap away from the Brillouin zone center. Our work identifies ZrTe\textsubscript{5} as a strong TI at liquid helium temperature and provides a new perspective in determining band inversion in layered topological materials.

Narrow-gap semiconductors and semimetals have regained broad interests in the past decade, as they host a rich variety of topological materials including topological insulators (TIs) and semimetals [1–5]. The low-energy electronic structure of such materials usually exhibits mixing characters of both linear band (LB, $E \propto k$, where $k$ is the wave vector) and parabolic band (PB, $E \propto k^2$), if higher-order terms are neglected. This concept is well reflected in the effective TI model [6, 7], which has been proven successful in describing many topological material systems such as HgTe quantum wells [8–10], Bi\textsubscript{2}Se\textsubscript{3} [6, 11], alkali pnictides A\textsubscript{3}Bi (A =Na, K, Rb) [12], Cd\textsubscript{3}As\textsubscript{2} [13], and transition-metal pentatelluride ZrTe\textsubscript{5} [14, 15].

The rising interest in ZrTe\textsubscript{5} is due to the theoretical prediction of a room-temperature quantum spin Hall insulator phase in its monolayer limit [16] and the experimental observation of the chiral magnetic effect [17], anomalous Hall effect [18], and three-dimensional (3D) quantum Hall effect [19] in bulk material. However, because of the delicate dependence of its band topology on the lattice constants [16, 20], there has not yet been a consensus on the bulk topological phase of ZrTe\textsubscript{5} from experiments [17, 21–25], especially with recent contradicting temperature-dependent studies [26–31]. In these studies, the non-trivial topological phase is either probed through its surface states or relying on the transition behavior of certain indirect parameters such as conductivity. Alternatively, one could also seek to probe the PB component of ZrTe\textsubscript{5}, which is associated with band inversion and thus essential for determining the band topology. However, this direct approach has not been reported to date.

In this Letter, we show that the LB and PB components of the electronic structure of ZrTe\textsubscript{5} can be determined using magneto-infrared (magneto-IR) spectroscopy, combining Faraday and Voigt geometry measurements. The application of a magnetic field ($B$) quantizes the electronic states into Landau levels (LLs). By carefully tracking the magnetic field dependence of the inter-LL transitions, we can extract important band parameters along the three principal crystal axes and reconstruct the 3D electronic structure of ZrTe\textsubscript{5} with great energy resolution. Most saliently, we demonstrate both theoretically and experimentally that the band inversion leads to a second extremum (band gap) away from the Brillouin zone center, giving rise to two distinct sets of inter-LL transitions. Our results unambiguously identify ZrTe\textsubscript{5} as a strong topological insulator (STI) at liquid helium temperature.

The ZrTe\textsubscript{5} single crystals studied in this work were prepared by the Te-assisted chemical vapor transport method [15] or molten Te flux growth [32]. The orthorhombic crystal structure is illustrated in Fig. 1(a). The as-grown samples exhibit a shiny needle-like surface (typically 0.5 mm by 10 mm) in the $ac$-plane but with a thin thickness (typically 0.1 mm) along the $b$-axis. With such high aspect ratio, the commonly used Faraday geometry measurement, where light travels in the magnetic field direction, is only suitable for studying the electronic structure in the $ac$-plane, while the Voigt geometry measurement, where light travels perpendicular to $B$, is more effective for the study in the $ab$- and $bc$-planes. Specifically, to optimize the signal, we employed Faraday transmission measurements with $B \parallel b$-axis and Voigt reflection measurements with $B \parallel a$-axis and $B \parallel c$-axis, respectively. All the measurements were performed at 4.2 K with a magnetic field up to 17.5 T. Further crystal synthesis and experimental details can be found in the Supplementary Material (SM) [33].
FIG. 1. (color online) (a) Schematic view of ZrTe$_5$ unit cell. (b-d) Normalized magneto-IR spectra of ZrTe$_5$ with the magnetic field applied along three principal crystal axes. To optimize the signal [33], the spectra with $B \parallel a$-axis (b) and $B \parallel c$-axis (c) are measured in Voigt reflection, while those with $B \parallel b$-axis (d) are measured in Faraday transmission. In (b-d), the interband LL transitions $L_{-n} \rightarrow L_{n+1}$ are recognized as spectral peaks and labeled with integer $n = 0, 1, 2, \ldots$. All measurements are performed at liquid helium temperature ($T = 4.2$ K), and the spectra are offset vertically for clarity.

Figure 1(b-d) shows the normalized magneto-IR spectra of ZrTe$_5$ with the magnetic field applied along different crystal axes. In all three cases, one can readily identify a series of peaks (or modes), which blue-shift as $B$ increases and can be attributed to specific inter-LL transitions $L_{-n} \rightarrow L_{n+1}$ labeled by integer $n = 0, 1, 2, \ldots$. In Fig. 2(a-c), we summarize the magnetic field dependence of the transition energies as a function of $\sqrt{B}$ by extracting the central energy of each mode at different magnetic fields. Here, for simplicity, we focus on the central peak of each transition with the strongest optical weight and omit the weak satellite peaks from the splitting of low-lying transitions.

By comparing the three cases in Fig. 2(a-c), one can see the anisotropy in the electronic structure of ZrTe$_5$. On the one hand, the LL transition energies with $B \parallel b$-axis (Fig. 2(c)) exhibit a nearly perfect linear-in-$\sqrt{B}$ dependence, characteristic of Dirac-like dispersion. On the other hand, the transition energies with $B \parallel a$-axis (Fig. 2(a)) and $B \parallel c$-axis (Fig. 2(b)) grow much more slowly with increasing magnetic field and show strong deviations from the $\sqrt{B}$ dependence. A closer inspection of Fig. 2(a,b) also reveals that if one linearly extrapolates the $n \neq 0$ LL transitions to zero magnetic field, a negative energy intercept is obtained. This behavior is very similar to the inverted PB semiconductors [34], except that the energies are plotted here as a function of $\sqrt{B}$ instead of $B$.

Quantitatively, the modes in Fig. 2(c) can be described by a massive Dirac fermion model [15, 35], where the LL energies read

$$E_n = \alpha \sqrt{2e\hbar v_F^2 n B + M^2},$$

with integer $n$ being the LL index, $\alpha = \pm 1$ the band index, $e$ the electron charge, $\hbar$ the reduced Planck’s constant, $v_F$ is the Fermi velocity, and $M$ the Dirac mass. However, this model fails to explain the data in Fig. 2(a,b) because (1) the model predicts a positive zero-field intercept regardless of the sign of $M$; (2) for low-lying LL transitions ($n < 3$), the energy ratio of two adjacent modes significantly deviates from the model prediction; and (3) for high-order LL transitions ($n > 3$), the model predicts a linear-in-$\sqrt{B}$ dependence at high magnetic fields but the experimental data curve up. All these deviations from the massive Dirac fermion model suggest strong band anisotropy in ZrTe$_5$ and the necessity to extend the model to include PB contributions.

Next, we show that all our data can be well explained by a $\mathbf{k} \cdot \mathbf{p}$ model that accounts for the symmetry at $\Gamma$ point, the PB contributions, and the material anisotropy. The effective Hamiltonian [33] reads

$$H(\mathbf{k}) = \begin{pmatrix}
L(\mathbf{k}) & 0 & A_k A_x k_z \\
0 & -L(\mathbf{k}) & A_k k_z - A_k^+ \\
A_k^+ A_x k_z & L(\mathbf{k}) & 0 \\
A_k k_z - A_k^+ & 0 & -L(\mathbf{k})
\end{pmatrix},$$

where $L(\mathbf{k}) = M - (\mathcal{B}_x k_x^2 + \mathcal{B}_y k_y^2 + \mathcal{B}_z k_z^2)$, $A_k = \hbar(v_{Fx} k_z \pm iv_{Fy} k_y)$, and $A_x = \hbar v_{Fx}$. The $x$-, $y$-, and $z$-directions correspond to the $a$-, $c$-, and $b$-axes of ZrTe$_5$, respectively. The electronic structure is then determined by a set of material parameters: (1) LB component $\mathbf{v_F} = (v_{Fx}, v_{Fy}, v_{Fz})$; (2) PB component $\mathcal{B} = (\mathcal{B}_x, \mathcal{B}_y, \mathcal{B}_z)$, which is also called the band inversion parameter; and (3) Dirac mass $M$. Both $v_F$ and $\mathcal{B}$ carry anisotropy. The resulting LL spectrum of ZrTe$_5$ reads

$$E_{n=0} = s[M - \mathcal{B} k_B^2],$$

$$E_{n\neq0} = -s\mathcal{B} k_B^2 + \alpha \sqrt{2\hbar^2 v_F^2 n k_B^2 + (M - M_B)^2},$$

$$\mathcal{B} = \frac{\mathcal{B}_x}{k_x}, \frac{\mathcal{B}_y}{k_y}, \frac{\mathcal{B}_z}{k_z}$$

and

$$M_B = \frac{M}{\sqrt{k_x^2 + k_y^2 + k_z^2}}.$$
FIG. 2. (color online) (a-c) Magnetic field dependence of the extracted LL transition energies from Fig. 1(b-d) for $B \parallel a$-axis (a), $B \parallel c$-axis (b), and $B \parallel b$-axis (c). The dash lines are best fits to the data using Eq. (2). The LL transitions $L_n \rightarrow L_{n+1}(n)$ are labeled by integer $n = 0, 1, 2, ...$, consistent with that in Fig. 1(b-d). (d) Representative Landau fan diagram for the case of $B \parallel a$-axis. The red and blue lines correspond to the $s = \pm 1$ LLs, respectively.

where $s = \pm 1$, $k_B = \sqrt{eB/\hbar}$ is the inverse magnetic length, and $M_B = 2\mathcal{B}n\ell_0^2$ is the field induced gap. This model is an extension of the effective TI model [6, 7], but due to the band anisotropy, parameters $\mathcal{B}$ and $\bar{v}_F$ now represent the geometric average of their values in the plane perpendicular to the magnetic field [33]. That is, if the field is applied along the $b$-axis, then $\mathcal{B} = \sqrt{\mathcal{B}_a\mathcal{B}_c}$ and $\bar{v}_F = \sqrt{v_{F_a}v_{F_c}}$. We note that there is a sign freedom in Eq. (2) since simultaneously reversing the signs of $\mathcal{B}$ and $M$ will not affect the results. In this work, we fix the sign of $M$ to be positive and allow the sign of $\mathcal{B}$ to vary. A positive (negative) $\mathcal{B}$ represents an inverted (normal) band, respectively.

With the above model, one can produce excellent fits to the experimental data in all configurations, as shown in Fig. 2(a-c). Here, we only consider the electric dipole transitions, $\Delta n = \pm 1$ and $\Delta s = 0$, while leaving the discussion of possible $\Delta n = 0$ and $\Delta s = \pm 2$ transitions to SM [33]. Our fitting results of $B \parallel a$-axis and $B \parallel c$-axis clearly show that the $M_B$ term breaks the $\sqrt{B}$ energy dependence in Eq. (2) via introducing a linear-in-$B$ mass term (PB contribution). This PB component is comparable with the LB component, suggesting that the average $\bar{v}_F$ is relatively small in these two configurations and/or the average $\mathcal{B}$ is relatively large. When $B \parallel b$-axis, however, the LB component dominates the LL transition energies due to the large $\bar{v}_F$. In this case, the PB contribution is relatively small, rendering the determination of the $\mathcal{B}$ value less accurate in this direction [36]. More importantly, we note that the sign of $\mathcal{B}$ cannot be solely determined from the data shown in Figs. 1 and 2, as the most influential PB contribution in Eq. (2), $(M - M_B)^2 \approx M_B^2$ for a small $M$, insensitive to the sign of $\mathcal{B}$.

Fortunately, we find an intriguing scenario that can help circumvent the above situation and resolve the topological phase of ZrTe$_5$. This is shown in Fig. 3(a,b), where we plot the band dispersion along the $b$-axis with different $v_{F_b}$ values for an inverted ($\mathcal{B} > 0$) and normal ($\mathcal{B} < 0$) band, respectively. For the inverted band (Fig. 3(a)), the electronic structures exhibit a local extremum not only at $\Gamma$ point but also at a non-zero $k_b$-vector (denoted by $Z$ point) when $v_{F_b}$ is sufficiently small. As $v_{F_b}$ increases, the extremum at $Z$ point gradually disappears. On the contrary, such extremum at $Z$ point never occurs in the normal band case (Fig. 3(b)) regardless of the magnitude of $v_{F_b}$. From our experimental data shown in Figs. 1 and 2, one can extract the $v_{F}$ values along all three crystal axes with $v_{F_b}$ as small as $\sim 0.5 \times 10^5$ m/s, close to the violet lines in Fig. 3(a,b). Therefore, the presence of a second extremum at $Z$ point signifies band inversion in ZrTe$_5$. In addition, the electronic structures depicted in Fig. 3(a,b) reproduce those in strong and weak topological insulator (STI and WTI) phases obtained from first-principles calculations [16, 20, 32]. The identification of an additional extremum in the electronic structure of ZrTe$_5$ would thus provide a smoking gun evidence for the STI phase.

Since each local extremum in electronic structure carries a large density of states, it can host a set of LL transitions under a magnetic field. This is indeed the case observed in our experiment when the magnetic field is applied in the slow $v_{F_b}$ direction (when $B \parallel b$-axis), as shown in Fig. 3(c). Here, due to the high quality of our ZrTe$_5$ samples, clear interband LL transitions $(n = 1, 2, 3, ...)$ occur in a very low field and unambiguously exhibit a doublet structure (marked by black and red up-triangles) before the field-induced linewidth broadening takes place. The energy splitting of the doublet at such a low magnetic field cannot originate from field-induced effects such as $g$-factor or band asymmetry [37]. Linear extrapolation of the magnetic field depen-
FIG. 3. (color online) (a,b) Zero-field band structures of ZrTe$_5$, calculated in the STI (a) and WTI (b) phases with different Fermi velocities along the $b$-axis. The PB component is kept the same in the calculation but with a positive (negative) sign for the STI (WTI) phase. For STI, two band extrema keep the same in the calculation but with a positive (negative) sign for the STI (WTI) phase. For STI, two band extrema occur at $\Gamma$ (red arrow) and $Z$ (black arrow) points when $v_{Fb}$ is sufficiently small. (c) Normalized magneto-transmission spectrum, $-T(B)/T(0T)$, of ZrTe$_5$ measured at $B = 0.4$ T and $B \parallel b$-axis. The up-triangles label the energy positions of the LL transitions from $Z$ (black) and $\Gamma$ (red) points. (d,e) Best fits to the magnetic field dependence of the LL transitions from $\Gamma$ (d) and $Z$ (e) points using the simple massive Dirac fermion model of Eq. (1).

| ZrTe$_5$ at $\Gamma$ point | $k \parallel a$ | $k \parallel b$ | $k \parallel c$ |
|---------------------------|----------------|----------------|----------------|
| $v_F$ (10$^3$ m/s)        | 6.85           | 0.50           | 4.10           |
| $\mathcal{B}_b$ (eV·nm$^2$) | 0.12          | 0.21           | 0.08           |
| $M_z$ (meV)             | 7.5            | 7.5            | 7.5            |

TABLE I. Extracted band parameters (at $\Gamma$ point) along the three principal crystal axes of ZrTe$_5$ using the anisotropic $\mathbf{k} \cdot \mathbf{p}$ model.

Anisotropy of $\mathcal{B}$ is now fully resolved with improved accuracy. Similarly, the anisotropy of $v_F$ at $\Gamma$ point can be deduced using the extracted $\bar{v}_F$ values from Fig. 3(d) and Fig. 2(a,b).

In Table I, we summarize the extracted band parameters of ZrTe$_5$ along the three principal crystal axes. As one can see, owing to the small $v_{Fb}$, the low-energy electronic structure along the $b$-axis is dominated by the PB component, leading to a much weaker dispersion than those along the LB dominated $a$- and $c$-directions. Our findings are consistent with recent transport and IR experiments [35, 38–41].

In conclusion, we have performed a magneto-IR spectroscopy study of the band anisotropy in ZrTe$_5$. We find that the LB dispersion (characterized by $v_F$) along its $b$-axis is about one order of magnitude smaller than those along the $a$- and $c$-axes, enabling investigation of the interplay between the LB and PB components. Specifically, we show that when $v_F$ is small, the PB component can strongly modify the band dispersion, and the presence of a second extremum in the slow $v_F$ direction ($b$-direction for the case of ZrTe$_5$) indicates band inversion. Incorporating prior results of first-principles calculations, we further identify ZrTe$_5$ as an STI at low temperatures. Our work provides an experimental approach to directly infer the topological phase of anisotropic materials from their bulk band structure.

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[36] Note that the Dirac mass obtained from fitting the data in Fig. 2(c) is slightly smaller than that from Fig. 2(a,b). This is because the band gap along the b-axis is not at Γ point, as discussed in the context of Fig. 3.
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Supplementary Material: Unraveling the Topological Phase of ZrTe$_5$ via Magneto-infrared Spectroscopy

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SAMPLE GROWTH AND EXPERIMENT SETUP

In this work, the single-crystal ZrTe$_5$ samples were synthesized by both the Te-assisted chemical vapor transport (CVT) method [1] and the molten Te flux growth [2]. For the CVT growth, we first prepared polycrystalline ZrTe$_5$ by reacting appropriate ratio of Zr ($\geq$ 99.9%) and Te ($\geq$ 99.9999%) in an evacuated quartz tube at 450 °C for one week. Next, 2 g of polycrystalline ZrTe$_5$ and transport agent (100 mg 99.9999% Te) were sealed in a quartz tube and placed horizontally in a tube furnace. The sample (source) was placed at the center of the furnace and was heated up to 530 °C at a rate of 60 °C per hour. The growth zone (sink) was 12 cm away, and its temperature was measured to be 450 °C.

In the flux growth, elemental Zr ($\geq$ 99.9%) and Te ($\geq$ 99.9999%) were directly mixed in the molar ratio of 1:49 and sealed under vacuum in a quartz tube. The mixture was heated to 1000 °C at a rate of 100 °C per hour, and held at this temperature for 12 hours. Then, we cooled down the mixture in two steps: first to 650 °C at a rate of 100 °C per hour; and next to 460 °C at a rate of 3 °C per hour. Finally, the crystals were separated from the flux by centrifuging at 460 °C.

Broad-band magneto-infrared (magneto-IR) spectroscopy measurements were performed using a Bruker 80v Fourier-transform IR spectrometer. The unpolarized IR light from a globar source was delivered to the sample through evacuated light pipes. Lights were focused onto the sample and collected into a Si bolometer detector using parabolic focusing cones. The sample was placed at the center of a $B = 17.5$ T superconducting magnet in a helium exchange gas environment. During the measurement, IR spectra were taken at selected magnetic fields and normalized to the zero-field spectrum to show the magnetic field induced change.

Figure S1 shows the schematics of two experiment configurations. In Faraday configuration (where the light propagation direction is parallel to the magnetic field), transmission measurements were performed with $B \parallel b$-axis. The ZrTe$_5$ sample was prepared by repeatedly exfoliating the material with an IR-transparent Scotch tape. The resulting ZrTe$_5$ flakes have an average thickness of $\sim$1 µm. Although transmission measurement is also preferred in Voigt configuration (where the light propagation direction is perpendicular to the magnetic field), one has to align the thin ZrTe$_5$ flakes in the same orientation while maintaining a relatively uniform thickness and full coverage on the tape. This is a challenging task.
FIG. S1. (color online) Schematics of Voigt and Faraday measurement configurations. In the Voigt (Faraday) configuration, the incident and reflected (transmitted) IR lights travel in the bc-plane (ab-plane) while the magnetic field $B$ is applied along the $a$-axis ($b$-axis). $a$, $b$, and $c$ label the principal crystal axes of ZrTe$_5$.

Instead, we carried out reflection measurements in Voigt configuration for $B \parallel a$-axis and $B \parallel c$-axis, in which we only need to align fewer, larger-size ZrTe$_5$ crystals on the tape.

ANISOTROPIC $k \cdot p$ MODEL

In this section, we introduce the $k \cdot p$ model describing the anisotropy of ZrTe$_5$. The anisotropic Hamiltonian was previously constructed [1, 3] up to $k^2$ terms with the following bases: $\{(|+,\uparrow\rangle,|+,\downarrow\rangle,|-,\uparrow\rangle,|-,\downarrow\rangle\}$, where the orbitals and spins are denoted by $\pm$ and $\uparrow, \downarrow$, respectively. The three-dimensional (3D) anisotropic $k \cdot p$ Hamiltonian for ZrTe$_5$ reads

$$H(k) = (M - \Sigma_i \mathcal{B}_i k_i^2) \tau^z + \hbar (v_{F,x} k_x \tau^x \sigma^z + v_{F,y} k_y \tau^y + v_{F,z} k_z \tau^z \sigma^x). \quad (S1)$$

Here, $k = (k_x, k_y, k_z)$ is the wave vector, index $i = x, y, z$ labels the three principal axes ($a$-, $c$-, and $b$-axes) of ZrTe$_5$, $\hbar$ is the reduced Planck’s constant, and $\tau$ and $\sigma$ are the Pauli matrices for orbital and spin, respectively. The material parameters are the same as those described in the main text: (1) Fermi velocity $v_F = (v_{F,x}, v_{F,y}, v_{F,z})$; (2) band inversion parameter $\mathcal{B} = (\mathcal{B}_x, \mathcal{B}_y, \mathcal{B}_z)$; and (3) Dirac mass $M$. Both $v_F$ and $\mathcal{B}$ carry anisotropy.

By diagonalizing the Hamiltonian, one can arrive at the 3D zero-field band dispersion
around Γ point

\[ E(k) = \alpha \sqrt{\sum_i \hbar^2 v_i^2 k_i^2 + (M - \sum_i B_i k_i^2)^2}, \]

where \( \alpha = \pm 1 \) denotes conduction and valence bands, respectively. The dispersion along each principal axis can then be described as

\[ E = \alpha \sqrt{\hbar^2 v^2 k^2 + (M - B k^2)^2}. \]  (S2)

Particularly, around \( Z \) point \((0,0,Z)\), the dispersion in the \( k_x - k_y \) plane can be written as

\[ E(k) = \alpha \sqrt{\hbar^2 v_{Fx}^2 k_x^2 + \hbar^2 v_{Fy}^2 k_y^2 + \bar{M}_Z^2} \]

where \( \bar{M}_Z^2 = h^2 v_{Fx}^2 k_Z^2 + (M - \bar{B}_Z k_Z^2 - \bar{B}_x k_x^2 - \bar{B}_y k_y^2)^2 \). If \( k_x \ll \sqrt{M/\bar{B}_x} \) and \( k_y \ll \sqrt{M/\bar{B}_y} \), then \( \bar{M}_Z^2 \approx h^2 v_{Fx}^2 k_Z^2 + (M - \bar{B}_Z k_Z^2)^2 \). From Table I of the main text, one can estimate \( \sqrt{M/\bar{B}_x} \sim \sqrt{M/\bar{B}_y} \sim 0.28 \text{ nm}^{-1} \), which is equivalent to a magnetic field of 52 T in terms of magnetic length. Therefore, the above approximation is justified in our low-field fitting, and one can model the charge carriers near \( Z \) point as massive Dirac fermions with a renormalized Dirac mass \( M_Z \).

**LANDAU LEVELS IN ANISOTROPIC k · p MODEL**

We now consider the magnetic field effects. We first consider the \( B \parallel b \)-axis case, and for convenience, we make the following scaling:

\[ \bar{B}_i = \bar{B}'_i / \hbar^2 v_{Fi}^2. \]  (S3)

To produce analytic solution, we need to make an approximation by replacing the in-plane anisotropy \( \bar{B}'_x, \bar{B}'_y \) with an effective average \( \bar{B}' \), which we will further discuss in the next section.

We consider the extremum point \( k_z = 0 \) (or \( k_b = 0 \)) as its large density of states provides dominant contributions in the magneto-optical response. The Hamiltonian can be transformed into two decoupled diagonal blocks by a unitary transformation

\[ H' = U^\dagger H U, \quad \text{with} \quad U = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \]
which essentially rearranges the basis function into \(|+,↑⟩,|−,↑⟩,|+,↓⟩,|−,↓⟩\). The transformed Hamiltonian now reads
\[
H' = \begin{pmatrix}
H_1 & 0 \\
0 & H_2
\end{pmatrix},
\]
where
\[
H_1 = \begin{pmatrix}
M - \mathcal{B}'(v_{F_x}^2 k_x^2 + v_{F_y}^2 k_y^2) & \hbar v_{F_x} k_x + i\hbar v_{F_y} k_y \\
\hbar v_{F_x} k_x - i\hbar v_{F_y} k_y & -M + \mathcal{B}'(v_{F_x}^2 k_x^2 + v_{F_y}^2 k_y^2)
\end{pmatrix}.
\]

To obtain the Landau lever (LL) spectrum, we perform the standard Peierls substitution using the Landau-gauge vector potential \(A = (-By,0,0)\). By defining
\[
\Delta = \sqrt{2e\hbar v_{F_x} v_{F_y} B} \quad \text{and} \quad \hat{b} = \hbar(v_{F_x} \hat{k}_x - i v_{F_y} \hat{k}_y)/\Delta,
\]
with \(e\) being the electron charge, we get
\[
[\hat{b}, \hat{b}^\dagger] = 1 \quad \text{and} \quad \hbar^2(v_{F_x}^2 k_x^2 + v_{F_y}^2 k_y^2) = (\hat{b}^\dagger \hat{b} + \frac{1}{2})\Delta^2.
\]

Next, we implement the ansatz that the trial wavefunction for \(H_1\) is \(\psi_\uparrow = (c_1 \phi_n, c_2 \phi_{n-1})\), where \(\phi_n\) is the eigenwavefunction of Harmonic oscillator, \(n\) denotes the LL index, and \(c_1\) and \(c_2\) are the coefficients to be determined. Now, \(H_1\) in a magnetic field becomes
\[
H_1 = \begin{pmatrix}
M - \mathcal{B}'(n + \frac{1}{2})\Delta^2 & \Delta \sqrt{n} \\
\Delta \sqrt{n} & -M + \mathcal{B}'(n - \frac{1}{2})\Delta^2
\end{pmatrix}.
\]

The LL energies and the coefficients \(c_1\) and \(c_2\) can be calculated from solving the eigenvalue problem of this algebraic Hamiltonian. \(H_2\) can be calculated in a similar fashion. Altogether, we have the following LL energies,
\[
E_0^\uparrow = M - \frac{\mathcal{B}'}{2}\Delta^2, \quad E_0^\downarrow = -M + \frac{\mathcal{B}'}{2}\Delta^2,
\]
\[
E_s^{n\neq 0,\alpha} = -\frac{s\mathcal{B}'}{2}\Delta^2 + \alpha\sqrt{\Delta^2 n + (M - n\mathcal{B}'\Delta^2)^2},
\]
where \(s = \pm 1\). Comparing to the LLs in the main text, one can immediately see that \(\bar{v}_F = \sqrt{v_{F_x} v_{F_y}}\) and \(\mathcal{B}' = \mathcal{B}'\hbar^2 \bar{v}_F^2\).

A similar procedure can be applied to the \(B \parallel a\)-axis and \(B \parallel c\)-axis cases, and the resulting LLs have similar expressions. There is only one subtlety: when \(B \parallel c\)-axis, \(s\) no longer denotes the spin. To see this, one can make a unitary transformation \(U = e^{i\sigma_z \pi/2}\) to rotate the spin directions, leading to \(\sigma^x \rightarrow \sigma^x, \sigma^y \rightarrow -\sigma^z, \sigma^z \rightarrow \sigma^y\). The new Hamiltonian reads
\[
H(k) = (M - \sum_i \mathcal{B}_i k_i^2) \tau^z + \hbar(v_{F_x} k_x \tau^+ \sigma^y + v_{F_y} k_y \tau^y + v_{F_z} k_z \tau^z \sigma^z).
\]
At \( k_y = 0 \) (or \( k_c = 0 \)), it is again possible to rotate the Hamiltonian into a diagonal block form \( H' = \begin{pmatrix} H_1 & 0 \\ 0 & H_2 \end{pmatrix} \) with another unitary transformation \( \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} \). This is equivalent to transform the basis to \((|+\uparrow\rangle, |-\downarrow\rangle, |+\downarrow\rangle, |-\uparrow\rangle)\). As one can see, the upper and lower blocks are no longer composed of spin-polarized states. Therefore, the spin is no longer a good quantum number to differentiate the LLs within the same index.

**EXTRACTING THE ANISOTROPIC BAND PARAMETERS**

In this section, we discuss how we extract the anisotropic band parameters from the experiment. To avoid confusion, we note that the barred variables are the fitting parameters from the data with their subscripts indicating the magnetic field directions, while the unbarred variables are the band parameters (summarized in Table I of the main text).

The extraction of \( v_F \) is straightforward. Since the relation between the fitting parameters and the Fermi velocity are \( \bar{v}_F_i = \sqrt{v_{F_j} v_{F_k}} \), where \( i, j, k = a, b, c \), one can translate them into \( v_{F_i} = (\bar{v}_{F_j} \bar{v}_{F_k})/\bar{v}_{F_i} \).

The extraction of \( B \) requires some additional information. First, although one can directly extract \( \bar{B}_a \) and \( \bar{B}_c \) from the fitting results of Fig. 2(a,b) of the main text, the extraction of \( \bar{B}_b \) for the \( B \parallel b \)-axis case from Fig. 2(c) of the main text is less accurate, because (1) the observed LL transitions are actually from the \( Z \) point, not the \( \Gamma \) point of the Brillouin zone; and (2) the large \( \bar{v}_{Fb} \) in this direction makes the linear band component dominate the electronic structure. Instead, we extract \( \bar{B}_b \) directly with Eq. (S2) from the gap difference between the \( Z \) and \( \Gamma \) points.

Second, we do not know the exact relation between the fitting parameters and the band inversion parameter. To proceed, we rewrite the anisotropic parabolic band terms in the diagonal elements of the LL Hamiltonian using the relations (S4) and (S5):

\[
M - h^2 (C_{x}v_{Fx}^2 k_{x}^2 + C_{y}v_{Fy}^2 k_{y}^2) = M - \frac{C_{x} - C_{y}}{2} (b^\dagger b + \frac{1}{2}) \Delta^2 - \frac{C_{x}'}{4} (b^\dagger b + b^2) \Delta^2, \tag{S7}
\]

where if \( \left| \frac{C_{x}'}{C_{x} - C_{y}} \right| \ll 1 \), one can neglect the last term. This is similar to the commonly known axial approximation [4]. But, in strongly anisotropic materials (like ZrTe\(_5\)), such a
presumption is not guaranteed, and axial approximation may not be a valid approximation. Therefore, in this work, we proceed with a simple “geometric average”, that is, $B_i' = \sqrt{B_j'B_k}$ or equivalently $B_i = \sqrt{B_jB_k}$. This idea is similar to the Onsager reciprocal relation, where we construct an isotropic electronic structure with averaged band parameters while keeping the same area enclosed by the constant energy contour as in the anisotropic structure. This process effectively takes into account the last two terms in Eq. (S7). In addition, the geometric average approximation approaches the axial approximation when $B_x' \approx B_y'$.

Lastly, with the information of $B_a$, $B_c$, $B_b$, and the geometric average approximation, one can obtain $B_a$ and $B_c$ through the following relations $B_a = B_b^2 / B_b$ and $B_c = B_a^2 / B_b$. We note that the accuracy of the geometric average approximation may be affected by the warping of the band structure. Also, the Z point may be far away from the Γ point and thus not well captured with our $k \cdot p$ model. A more accurate determination may require first-principles calculations, which is beyond the scope of our work. Still, the geometric average approximation provides an analytical relation and easy means of understanding the band anisotropy of ZrTe$_5$.

**SELECTION RULES**

The selection rule is determined by the matrix element $\langle I | \frac{\partial H}{\partial k_i} | F \rangle$, where $|I\rangle$ and $|F\rangle$ are the initial and final states, and $i$ denotes the electric field ($E$) polarization of the incident light. Here, we study the case of $B \parallel z$, but the conclusion also applies to the $B \parallel x, y$ cases.

Specifically, if $E \perp B$, then

$$\frac{\partial H}{\partial k_x} = \hbar v_{Fx} \tau^x \otimes \sigma^z, \quad \frac{\partial H}{\partial k_y} = -\hbar v_{Fy} \tau^y,$$

which couples the bases with the same $s$. The $k^2$ terms in the Hamiltonian do not contribute as we are close to Γ point. Therefore, the selection rule for $E \perp B$ reads $\Delta s = 0$ and $\Delta n = \pm 1$, which represents the conventional electric dipole transitions.

If $E \parallel B$, then

$$\frac{\partial H}{\partial k_z} = \hbar v_{Fz} \tau^x \otimes \sigma^x,$$

which couples the bases with opposite $s$. Therefore, the selection rule for $E \parallel B$ is $\Delta s = \pm 2$ and $\Delta n = 0$.  


FIG. S2. (color online) LL transitions with $E \parallel B$ excitation. (a) Landau fan diagram for the case of $B \parallel a$-axis under $E \parallel B$ excitation. The LLs are calculated with the band parameters shown in (b) and color-coded in red ($s = +1$ LLs) and blue ($s = -1$ LLs), respectively. The dark blue (orange) arrows illustrate the allowed transitions following the $\Delta s = +2$ ($\Delta s = -2$) selection rule. (b) Best fits to the $B \parallel a$-axis data (Fig. 2(a) of the main text) with $E \parallel B$ transitions. The allowed transitions $L_{-n} \rightarrow L_{n}$ are labeled with LL index $n = 0, 1, 2, 3...$ and with the same color code as in (a).

In Fig. S2, we show the possible LL transitions with $E \parallel B$ excitation and their best fits to the experimental data in the $B \parallel a$-axis case (i.e., the data in Fig. 2(a) of the main text). Here, although the fits to high-order LL transitions work well, those to low-lying LL transitions deviate from the data significantly. Therefore, we exclude these $\Delta n = 0$, $\Delta s = \pm 2$ transitions when analyzing the data in the main text.

ADDITIONAL DATA FROM THE LOW FIELD MEASUREMENTS

Figure S3(a) shows the normalized magneto-transmission spectra at low magnetic fields complementary to Fig. 3(c) of the main text. The doublet structure at low fields can be consistently reproduced in several samples, as shown in Fig. S3(b).
FIG. S3. (color online) (a) Low-field normalized magneto-transmission spectra, $-T(B)/T(0T)$, of ZrTe$_5$ measured with $B \parallel b$-axis. The up-triangles label the energy positions of the LL transitions from Z (black) and Γ (red) points, as described in the context of Fig. 3 of the main text. (b) Magneto-transmission spectra across three different samples S1, S2, and S3 at $B = 0.5$ T. The S1 sample is used in the main text. The dash lines indicate the positions of the Γ point transition energies.

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