Quantum oscillation and unusual protection mechanism of the surface state in nonsymmorphic semimetals

Xue Liu\textsuperscript{1,2}, Chunlei Yue\textsuperscript{1,†}, Yanglin Zhu\textsuperscript{1}, Abin Joshy\textsuperscript{1}, Jinyu Liu\textsuperscript{1}, Ana M Sanchez\textsuperscript{3}, David Graf\textsuperscript{4}, Zhiqiang Mao\textsuperscript{5,1}, Jin Hu\textsuperscript{6,*}, Jiang Wei\textsuperscript{1,*}

\textsuperscript{1}Department of Physics and Engineering Physics, Tulane University, New Orleans, Louisiana 70118, USA

\textsuperscript{2}Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

\textsuperscript{3}Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom

\textsuperscript{4}National High Magnetic Field Lab, Tallahassee, Florida 32310, USA

\textsuperscript{5}Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802, USA

\textsuperscript{6}Department of Physics, Institute for Nanoscience and Engineering, University of Arkansas, Fayetteville, Arkansas 72701, USA

\textsuperscript{†} These authors contributed equally to this work.

*Corresponding to jinhu@uark.edu; jwei1@tulane.edu.
In a topological semimetal with Dirac or Weyl points, the bulk-edge correspondence principle results in a gapless edge mode, given that the surface preserves the essential symmetry protecting the non-trivial bulk bands. The detection of topological surface state is considered as the fingerprint prove of non-trivial bulk band\textsuperscript{1-4}. However, even with broken symmetry at the surface, a new type of surface state, a two dimensional (2D) floating band, is proposed in nonsymmorphic semimetal\textsuperscript{5}. The symmetry reduction at the surface lifts the bulk band degeneracies, leaving an unusual “floating” surface band with trivial topology. Here, we report our quantum transport probing to ZrSiSe thin flakes and reveal signatures of this topologically trivial surface state featuring steady 2D Shubnikov–de Haas (SdH) quantum oscillations. Although not topologically protected, such a surface state carries a robust nature of metallicity with high mobility, implying a new protection mechanism and may open applications for surface-related devices.

The surface electronic state has been a clear focus of condensed matter physics. The conventional surface states, resulting from the termination of the three-dimensional (3D) bulk periodic potential, are generally susceptible to surface defects or impurities which often appear inevitably. Recently, there have been significant breakthroughs in search of robust surface states in the emerging topological quantum materials. In topological insulators, robust surface states, characterized by the linearly dispersed Dirac bands and protected by the time-reversal or spatial crystalline symmetries, have been found\textsuperscript{6-8}. In topological semimetals, a direct manifestation of the topological aspects of the bulk electronic bands is the unusual surface state of Weyl semimetals or Dirac semimetals\textsuperscript{1-3}, which appear as the discontinuous Fermi arcs or joint arcs curving in opposite directions, respectively. These surface states have been observed on various topological semimetals\textsuperscript{9-12} with angle-resolved photoemission spectroscopy (ARPES) measurements and viewed as hallmarks of topological quantum states. More interestingly, even with broken symmetry, there exists a new class of surface state – the surface floating band, which is predicted to
originate from surface symmetry reduction in nonsymmorphic semimetals. Indeed, further explorations to its physical properties are highly desired.

The transport properties of the surface have been extensively studied in topological insulators. Distinct electrical properties originating from the topologically protected surface or edge states, e.g., quantum Hall and quantum spin Hall effects, provide great opportunities for the surface state-based technology applications. In contrast, for topological semimetals which possess bulk Dirac or Weyl fermions, although topological surface states have been directly probed in ARPES experiments, their transport properties are not well-explored, due to the challenge in separating the bulk transport from the surface state transport. One practical approach to probe the transport of surface states is to increase the surface-to-bulk ratio. Recently, quantum oscillations and quantum Hall effect arising from the Weyl orbit, a cyclotron orbit which connects one surface Fermi arc to the opposite Fermi arc by coupling to bulk states, have been reported in the nanostructures of the Dirac semimetal Cd₃As₂. Despite these successes in artificial structures, achieving nanostructures with desired pristine surface quality is generally difficult for most topological semimetals, which imposes a significant obstacle for probing surface state transport properties.

The recently discovered topological semimetals \( WHM (W = Zr, Hf, or rare earth; H = Si, Ge, Sn; M = S, Se, or Te) \) provide a rare opportunity for probing the transport of surface states. These materials crystallize in layered tetragonal structure (Fig. 1a) and possess two types of Dirac states. One is the nodal-line Dirac state which is protected by the \( C_{2v} \) symmetry and gaped by spin-orbit coupling; the other is the 2D gapless nodal-point Dirac state protected by the nonsymmorphic symmetry. The different combinations of \( W, H, \) and \( M \) elements further gives rise to great tunability in spin-orbit coupling, magnetism, and structural dimensionality, etc., leading to rich electronic properties of various \( WHMs \) such as large magnetoresistance, high Dirac fermion density, strong spin splitting, and magnetic field-mediated tunable Dirac and Weyl states. These properties, together with the feasibility in obtaining the atomically thin crystals for several \( WHMs \) demonstrated as in our previous studies, make this material family a versatile platform for investigating exotic phenomena of relativistic fermions in
nanostructures. In this work, taking advantage of the suppressed bulk contributions in the exfoliated ZrSiSe flakes, we have successfully probed transport of the surface floating band. Unlike the topological nontrivial surface states in many other topological nodal point semimetals, such floating surface band is topological trivial\(^5\). Surprisingly, we have observed clear quantum oscillations and high mobility which are generally not expected for a topologically trivial band, which implies a new protection mechanism for the surface state.

The crystal structure of ZrSiSe is composed of stacking of Se-Zr-Si-Zr-Se slabs as shown in Fig.1a. In each slab, the square net of Si atoms is sandwiched by the Se-Zr layers. The weak inter-slab bonding strength allows for the mechanic exfoliation of ZrSiSe to atomically thin layers\(^22\), as demonstrated in Fig. 1b. The quality of the obtained flakes has been examined by the Scanning Transmission Electron Microscope (STEM). The atomic resolution images of the as-exfoliated flakes have revealed good crystallinity for the inner parts (Fig. 1c) with shallow amorphous oxidation layers (~5 nm) on the top and bottom surface (Fig. 1d and Supplementary Fig. 1). The stacking of Zr, Si, and Se atoms precisely match the expected lattice structure of ZrSiSe (Fig. 1c inset).

We have fabricated ZrSiSe devices through the standard electron beam lithography (Fig. 1b, inset). Before we conducted magnetotransport measurements at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee (see Methods), the devices have been performed current annealing to burn the oxidation layer and achieve ohmic contacts between metal and ZrSiSe flakes (see Methods). With the magnetic field applied perpendicular to the sample surface (i.e., along the c-axis), we observed clear Shubnikov-de Haas (SdH) oscillations in magnetoresistance (MR) for all ZrSiSe thin flakes with various thickness at low temperatures (see Supplementary Fig. 3). Surprisingly, the oscillatory components of the longitudinal resistivity \(\Delta\rho_{xx}\) obtained by subtracting the smooth MR background exhibit different signatures between very thick and thin flakes. In Fig. 2a we present the \(\Delta\rho_{xx}\) for typical thick (176 nm) and thin (28.2 nm) samples. For the thicker sample (176 nm), the oscillation pattern contains only a single frequency of \(F_B = 210\) T as revealed by the fast Fourier transform (FFT) analysis (Fig. 2a, inset), consistent with the
observation in the single crystal bulks. In contrast, the oscillation pattern of the thinner sample (28.2 nm) clearly deviates from the “bulk-like” behavior (Fig. 2a) with an additional frequency occurring around \( F_s = 445 \) T (Fig. 2a, inset). Although \( F_s \) appears to be close to \( 2 \times F_B \), it should not be regarded as a harmonic frequency of \( F_B \) because of their distinct angular dependences as will be shown later. Such a surprising, additional frequency component is reproducible for all thin flakes below 60 nm (see Supplementary Fig. 4 and Fig. 5).

In principle, a periodic quantum oscillation pattern with a specific frequency corresponds to an extremal Fermi surface cross-section. Therefore, the additional frequency in thin samples indicates that an additional electronic band starts to play a substantial role in transport only in the samples with reduced thickness. The modification of band structure due to 2D quantum confinement is widely observed in 2D materials, such as the Dirac state in graphene and the direct band gaps in transition metal dichalcogenides. However, it is unlikely that quantum confinement takes effect at a thickness of \(-60\) nm where the \( F_s \) component already becomes visible (Fig. 2b). As will be demonstrated below, this peculiar frequency is most likely a manifestation of a surface state.

First, the weight of the \( F_s \) band in transport grows with the reducing sample thickness. As shown in Fig. 2b, the relative ratio between the FFT peak amplitudes of \( F_s \) and \( F_B \) increases remarkably when the flake thickness is reduced, indicating the increased weight of the \( F_s \) component in thinner samples. This agrees well with the surface origin of the \( F_s \) band and is a natural consequence of the enhanced surface-to-bulk ratio with reducing the thickness.

Secondly, the 2D character of the \( F_s \) band is also in line with a surface state. We have performed systematic SdH oscillation experiments on a number of ZrSiSe flakes at various magnetic field orientations, and obtained the oscillatory components for both the longitudinal (\( \Delta \rho_{xx} \)) and Hall (\( \Delta \rho_{xy} \)) resistivity. As shown in Fig. 3a, for a typical sample thickness of 36 nm, the SdH oscillation (\( T=0.6K \)) gradually weakens when the magnetic field is rotated away from the perpendicular direction (\( \theta = 0^\circ \)), which has also been
observed in bulk ZrSiSe\textsuperscript{22} and other WHM compounds\textsuperscript{28,31,34}. From the FFT of the oscillatory resistivity $\Delta \rho_{xy}$ (Fig. 3b), one can immediately find that the angular dependences of $F_B$ and $F_S$ are entirely different: Compared to the very weak angular-dependence of $F_B$ up to $\theta = 45^\circ$, $F_S$ varies strongly with $\theta$, indicating it is not a second order harmonic of $F_B$ as mentioned earlier. Such angular dependences for $F_B$ and $F_S$ are highly reproducible with various sample thicknesses (Supplementary Fig. 5). To better illustrate the angular dependences of both frequencies in various samples, we have summarized the data in the polar plot shown in Fig. 3c. Clearly, $F_B$ (blue) appears to be nearly $\theta$-independent up to $\theta = 45^\circ$, consistent with the previous studies on bulk samples\textsuperscript{22}. In contrast, $F_S$ at various $\theta$ obtained from different samples are well-aligned to a vertical line (red dashed lines) in the polar plot, indicating a $1/\cos \theta$ dependence. Such a $1/\cos \theta$ dependence is a signature of 2D electronic state, which has not been observed in bulk ZrSiSe\textsuperscript{22} but consistent with the scenario of a 2D surface state proposed above. Indeed, the presence of additional frequency with $1/\cos \theta$ dependence has also been observed in Cd$_3$As$_2$ nano-structures, which has been attributed to the surface state\textsuperscript{14}.

The agreement of the oscillation frequency with the previous ARPES observations\textsuperscript{35} provides further support for the surface origin of $F_S$. The quantum oscillation frequency $F$ is directly linked to the Fermi surface cross-sectional area $A$ that is perpendicular to the external magnetic field, as described by Onsager relation $F = hA/2\pi e$. Therefore, performing the angular dependence measurement has been a traditional approach to map out the size and morphology of the Fermi surface. The $F_S$ frequency in ZrSiSe corresponds to a Fermi surface cross-section area of 4.25 nm\textsuperscript{2} at $\theta = 0^\circ$, which matches well with the area of the ellipse-like electron pocket around the Brillouin zone X point probed in ARPES experiment (estimated to be ~4.58 nm\textsuperscript{2})\textsuperscript{35}. Given no other Fermi pocket with comparable size has been observed in ARPES\textsuperscript{35}, the $F_S$ frequency most likely reflects such an electron pocket which has already been established as a surface-related state in WHM compounds\textsuperscript{5}.

What is the mechanism of the formation of such surface band? Generally, a surface state is expected for any materials due to the termination of the bulk potential or the surface defects/adsorbates in
conventional material, or caused by the non-trivial band topology in a topological insulator\textsuperscript{6-8} or semimetal\textsuperscript{1-4}. As will be discussed below, the surface state probed in quantum oscillations on ZrSiSe does not fall into any of these categories, but can be understood in terms of a recently-predicted novel mechanism associated with the nonsymmorphic symmetry reduction at the crystal surface.

The mechanism of surface defects or adsorbates can be easily excluded. Quantum oscillations, which rely on the formation of complete cyclotron orbits and high mobility (i.e., sharp Landau levels), are generally not expected for “dirty” materials. Given defects or adsorbates are strong scattering centers, quantum oscillation from a surface state is rarely seen in conventional materials. However, in ZrSiSe, $F_5$ and its angular dependence are highly reproducible as long as the sample is thin ($\leq 60$ nm), even with significant amorphous oxidation layers. Such robustness is also inconsistent with the cause of surface chemistry often involves some foreign reactant or surface defects.

In a typical \textit{nodal-point} topological semimetal with isolated bulk Dirac or Weyl points, the bulk-edge correspondence principle results in a gapless mode at the edge when the symmetry group protecting the bulk bands’ topology is unbroken on the edge\textsuperscript{4}. However, this mechanism can also be excluded. ZrSiSe and related \textit{WHM} compounds exhibit the coexistence of nodal-line and nodal-point Dirac states protected by different symmetries\textsuperscript{17,18,26}, but neither of them should lead to a topological surface state. First of all, unlike the scenario of the topological nodal-point states, a nodal-line state is protected by mirror (like in ZrSiSe) and/or screw rotation symmetries, which are not preserved at any crystal surface\textsuperscript{4}. Although “drumhead” surface states have been probed in several other nodal-line semimetals\textsuperscript{36,37}, they do not arise from bulk-edge correspondence principle and thus are not topologically protected\textsuperscript{4}. For the other nodal-point Dirac state protected by the nonsymmorphic symmetry\textsuperscript{17,26}, the Dirac point is too far away from the Fermi level (by $\sim 0.5$eV)$^{26,35}$, so it should not lead to observable effects. Indeed, in these \textit{WHM} materials, a topological surface state arising from the bulk band’s topological properties has not been revealed in either band structure calculation\textsuperscript{18} or ARPES experiments\textsuperscript{17,19,35}.\textsuperscript{18}}
After ruling out the surface chemistry and bulk-edge correspondence, we argue that this robust $F_S$ surface band revealed in our quantum oscillation experiments represents the recently predicted novel surface states derived from the surface symmetry reduction in nonsymmorphic semimetals. In the isostructural compound ZrSiS, it has been shown that the bulk symmetry with nonsymmorphic space group $P4/\text{nmn}$ is reduced to the symmorphic wallpaper group $P4\text{mm}$ at the natural cleavage (001) surface. Such nonsymmorphic symmetry reduction significantly deforms the orbital, which lifts the degeneracy of the bulk bands at Brillouin zone X point and consequently causes an unpinned surface band floating on top of the bulk band. This predicted “floating” surface state is quantitatively consistent with the ARPES observations of the Fermi pocket with the 2D character at X. The similar X point electron pocket in ZrSiSe should also be ascribed to the floating surface state due to the similarities in crystal and electronic structures between ZrSiS and ZrSiSe. Given the matching of the Fermi pocket size with the $F_S$ oscillation frequency as mentioned before, we believe this new surface floating band is the $F_S$ surface band observed in our quantum oscillations experiments.

The quantum oscillation properties of the $F_S$ band provide further support of this argument. The surface floating band is formed by lifting the bulk band’s degeneracy and is thus topological trivial, which can be revealed by Berry phase analysis. We have separated the $F_B$ and $F_S$ oscillation components and extracted the Berry phase for both bands using the Landau fan diagram (see Methods). As shown in Fig. 4a, for ZrSiSe flakes with a range of thickness, the linear fits of the Landau indices $n$ yield intercepts $n_0$ around 0 and -0.5 for $F_S$ and $F_B$ bands, respectively. Berry phase $\phi_B$ can be derived via $2\pi(n_0+\delta)$, where $\delta = \pm 1/8$ for the 3D band (e.g., the bulk $F_B$ band) and 0 for the 2D band (e.g., the surface $F_S$ band). As summarized in Fig. 4b, the Berry phase is trivial ($\phi_B \approx 0$) for the surface $F_S$ band in each sample, in sharp contrast with that of the bulk $F_B$ band which exhibits an average Berry phase of $\phi_B^{\text{Bulk}} \approx -0.68\pi \pm 1/4 \pi$. This result is further verified through directly fitting the oscillation pattern using the multiband Lifshitz-Kosevich model (see Methods), which confirms the distinct topology of the bulk and the surface floating bands in ZrSiSe.
Furthermore, the effective cyclotron mass of the $F_S$ band also agrees with the scenario of the surface floating band. The formation of the floating band at the surface of our material can be modeled by breaking the nonsymmorphic glide plane symmetry and introducing large mass for S and Zr orbitals\(^5\), so such surface state is expected to be more massive, which is indeed observed in ZrSiSe. We have extracted effective masses for both bulk $F_B$ and surface $F_S$ bands from the temperature dependence of FFT amplitude for ZrSiSe samples with various thicknesses (see Methods) (Fig. 4c). As summarized in Fig. 4d, the effective cyclotron mass for the surface floating band $m_S^*$ is around $0.39m_0$ ($m_0$: free electron mass) for all analyzed samples, which is twice as large as that of the bulk band ($m_B^* \sim 0.19m_0$).

Our above discussions have established that the additional $F_S$ component observed in the quantum oscillation of ZrSiSe nano-flakes originates from the surface floating band. The observation of quantum oscillations caused by such topological trivial surface state is surprising, because the lack of a protection mechanism is generally expected to lead to a vulnerable surface state with low mobility that is not favorable to quantum oscillations. However, in our ZrSiSe samples, the LK-fitting (see Methods) has revealed high quantum mobility of $1.20 \times 10^3$ cm\(^2\)V\(^{-1}\)s\(^{-1}\) at 1.7K for the surface $F_S$ band, which is comparable with the topologically protected bulk band $\mu_q=1.74 \times 10^3$ cm\(^2\)V\(^{-1}\)s\(^{-1}\). This is consistent with the transport mobility derived from our Hall effect measurements by using Three-channel model\(^{38}\). As illustrated by Fig. 4e, in our multichannel system, the Hall signal is contributed from bulk electron, bulk hole, and surface electron (as confirmed by ARPES measurements\(^{34}\)). Then, the conductivity and hall coefficient can be described as

$$\sigma_{xx} = e n_p \mu_p - e n_n \mu_n - e n_t \mu_t,$$

$$R_H = \frac{n_p \mu_p^2 - n_n \mu_n^2 - n_t \mu_t^2}{e[n_p \mu_p + n_n \mu_n + n_t \mu_t]^2}$$

with $n_n = n_e \times d$, $n_p = n_h \times d$, where $n_e$, $n_h$ are bulk state hole and electron carrier density, $d$ is the sample thickness, $n_t$ is the surface state carrier density, and $\mu_n$, $\mu_p$, $\mu_t$ are bulk hole, bulk electron, and surface electron mobilities respectively. By fitting the thickness dependent $\sigma_{xx}$ and $R_H$ (as plotted in Fig.
4f), we can derive $\mu_{c} = 1.84 \times 10^{3}$ cm$^2$V$^{-1}$s$^{-1}$ for the surface band and $\mu_{p} = 1.39 \times 10^{4}$ cm$^2$V$^{-1}$s$^{-1}$, $\mu_{n} = 1.03 \times 10^{4}$ cm$^2$V$^{-1}$s$^{-1}$ for bulk band. These derived quantum and transport mobilities of the surface electrons are comparable with that of the topological protected bulk electrons in many other topological semimetals$^{39}$. Such high mobility of topological trivial surface state and its robustness is unexpected and may benefit from a sort of protection mechanism that deserves further investigation. One possible interpretation could be the connection with the bulk topological band: given the surface floating band for nonsymmorphic ZrSiSe is caused by lifting degeneracy of the bulk band at the surface$^{5}$, it could be robust when the corresponding bulk band is topologically protected. In ZrSiSe, the surface floating band is related to the bulk Dirac band protected by the nonsymmorphic symmetry$^{5,17}$. Therefore, an “indirectly” protected surface bands with trivial topology could appear in ZrSiSe, which represents a novel protection mechanism in crystalline solid.

In summary, we have systematically studied quantum oscillations of exfoliated ZrSiSe nano-flakes and successfully detected a new 2D, trivial surface state, which can be attributed to the surface floating state caused by symmetry reduction at the surface. Our results also suggest such a surface is trivial but robust and likely protected via a new mechanism. Our findings provide a new arena for the study of exotic surface states in topological quantum materials.
Figure captions

**Figure 1** | **ZrSiSe crystal structure and microscopy characterizations.** a, Crystal structure of ZrSiSe, showing the Se-Zr-Si-Zr-Se slabs and the cleavage plane (red arrow) b, Optical microscope image of a 28.2nm ZrSiSe nano-flake on Si/SiO$_2$ wafer obtained through micromechanical exfoliation. Inset, atomic force microscope image of a Hall bar device. c, d, Atomic resolution annular dark-field (ADF) aberration-corrected scanning transmission electron microscopy (STEM) images of (c) the bulk along the [100] zone and (d) exfoliated ZrSiSe flakes along the [110] zone. Inset in c, the [100] zone (cross-section) image matches well with the crystal structure.

**Figure 2** | **Thickness dependent SdH oscillations.** a, The oscillatory components $\Delta \rho_{xx}$ of thick (176nm) and thin (28.2nm) ZrSiSe samples with magnetic field normal to the sample surface. Inset, the fast Fourier transform of the corresponding oscillation patterns. The FFT for the 28.2nm sample is normalized to the 176nm sample according to the $F_B$ for clarity. The additional frequency of $F_S=445T$ appears for the thin sample. b, Thickness dependence of the relative FFT amplitude (FFTA) between $F_S$ and $F_B$ bands. Inset, corresponding FFT spectrums for different thicknesses, normalized to the 176nm sample according to the $F_B$ peak for clarity.

**Figure 3** | **Angular-dependent SdH oscillations.** a, Angular-dependent oscillatory components $\Delta \rho_{xy}$ of the 36nm ZrSiSe device at 0.6K. Inset, The measurement setup. b, Fast Fourier transform of the SdH oscillation pattern shown in a. c, Polar plot of the angular-dependence of bulk frequency $F_B$ (blue) and surface frequency $F_S$ (red) from all measured devices (see Supplementary Fig. 4 and 5 for oscillation patterns and their FFT). The dashed straight line (red) indicates the $1/\cos\theta$ dependence for $F_S$. 
Figure 4 | Property comparison between the bulk and surface bands. a, Landau Level (LL) fan diagram for the bulk $F_B$ and surface $F_S$ states of four ZrSiSe nano-devices with thicknesses of 28.2nm, 33.9nm, 36nm, and 46.2nm. The solid lines represent linear fits of the Landau indices, which intercept around 0 for the surface band and -0.34 for the bulk band. Inset, zoom-in view showing different intercepts for surface and bulks. b, Berry phases derived from the LL fan diagram shown in a for samples with different thicknesses. c, The temperature-dependence of the FFT amplitude for bulk and surface bands for the same four samples in a. The solid lines indicate the fits to the thermal damping term of the LK-model. d, Effective masses for bulk and surface states derived from the fitting shown in c. e, Schematic drawing of the multi-channel contributions to the Hall effect. f, Thickness dependent longitudinal conductivity and Hall coefficient. The solid lines indicate the fits to the three-channel model.

Methods

Sample preparation. The ZrSiSe single crystal was synthesized by using a chemical vapor transport (CVT) method. The stoichiometric mixture of Zr, Si and Se powder was sealed in a quartz tube with iodine being used as a transport agent (2 mg/cm³). Plate-like single crystals with metallic luster can be obtained via the vapor transport growth with a temperature gradient from 950 ºC to 850 ºC. The composition and phase of the single crystals were examined by Energy-dispersive x-ray spectroscopy and x-ray diffraction, respectively. The thin flakes of ZrSiSe were obtained through a micromechanical exfoliation. The thickness of thin flakes was precisely determined by atomic force microscope. The ZrSiSe devices with the standard four-terminal resistivity or six-terminal Hall bar geometry were fabricated by using the standard electron beam lithography, followed by the deposition of 5nm Ti/50nm Au as contacts via electron beam evaporation.

Scanning Transmission Electron Microscopy: Atomic-resolution Annular Dark Field STEM images of the flakes were recorded with a JEOL ARM200F over collection angles 45–180 mrad. High
signal-to-noise images were formed by averaging multiple, rapidly acquired frames to remove scan distortions.

**Current annealing process.** The fabricated ZrSiSe devices were conducted current annealing between every two electrodes of the Hall bar device geometry, which has been used for cleaning or improving contacts of graphene devices\(^{40,41}\). By using a parameter analyzer, a DC voltage was applied and swept step by step from 0V up to 2.5V with the current recorded. A typical annealing process has been shown by Supplementary Fig.2, before annealing the I-V sweeps show nonlinear behavior with high resistance \(\sim 0.4 \text{ M}\Omega\) indicating a large contact resistance caused by the oxidation layer between the metal and ZrSiSe single crystals; when the voltage sweeps up around 2.4V, the current suddenly jumps to 1 mA which is the preset current limitation. Then, after stabilizing for a few sweeps, the I-V sweep becomes linear and the two-probe resistance decreases down to \(\sim 1 \text{ K}\Omega\). By processing current annealing, the oxidation layer under the electrodes has been broken down to achieve a nearly ohmic contacts between metal and ZrSiSe crystals.

**Magneto-transport measurements.** Prior to the high field experiments, the ZrSiSe devices were tested by an in house 9T-PPMS. The high field magneto-transport measurements were performed at National High Magnetic Field Laboratory (NHMFL) in Tallahassee by using an 18T superconducting magnet and a 31T resistive magnet. The a.c. currents used for all devices were between 20 \(\mu\text{A}\) to 50 \(\mu\text{A}\) supplied by Keithley 6221 AC and DC Current Source. The longitudinal/transverse voltages were measured using lock-in amplifiers with the frequencies triggered with the a.c. currents. The noise ratio was reduced by twisted pairs between two voltage cables and two current cables, respectively.

**Landau level fan diagrams.** To examine the Berry phase \(\phi_B\) accumulated along cyclotron orbits for bulk and surface bands, we performed Landau Level fan diagram analysis using the longitudinal conductivity \(\sigma_{xx}\), which was derived via \(\sigma_{xx} = \rho_{xx}/(\rho_{xx}^2 + \rho_{xy}^2)\) where \(\rho_{xx}\) and \(\rho_{xy}\) are longitudinal and transverse resistivity, respectively, as shown in Supplementary Fig 6. Bulk and surface band’s oscillations
are then separated by FFT filter, in order to build the LL fan diagram for each bands. Given the integer LL indices should be assigned when the Fermi level lies between two adjacent LLs where the density of state reachess a minimum$^8$,$^42$, we assign the integer Landau indices to the oscillation maximum of $\sigma_{xx}$$^39$, as shown in Supplementary Fig 7. Berry phase for each band was extracted from the intercept of the linear fit of the LL fan diagram. The slope of each linear fit yield the oscillation frequency, which only differs from the frequency obtained from the FFT by 1-2%. Such consistency indicates the reliability of the obtained intercept and the derived Berry phase$^8$.

**Lifshitz-Kosevich fit.** In addition to LL index fan diagram, we also performed the direct Lifshitz-Kosevich (LK) fitting to extract the Berry phase. In our ZrSiSe system, the SdH oscillations are treated as the linear superposition of bulk and surface frequency ($F_B$, $F_S$) oscillations. Each frequency component can be described as$^{39,43,44}$:

$$\Delta \rho_{xx} = A \frac{5}{2} \left(\frac{B}{2F}\right)^2 e^{-\lambda_D} \frac{\lambda}{\sinh \lambda} \cos[2\pi \left(\frac{F}{B} + \gamma - \delta\right)]$$

The thermal damping factor $\lambda = 2\pi^2 k_B T m^*/(\hbar e B)$, $\lambda_D = 2\pi^2 k_B T_D m^*/(\hbar e B)$, where $m^*$ is the effective mass, $T_D$ is Dingle temperature, $F$ is the frequency, $\gamma$ is defined as $\gamma = 0.5 - \phi_B/2\pi$, and $\delta$ is the phase shift which is $\pm 1/8$ for 3D and 0 for 2D. Typical fittings for 36 nm and 46.2 nm samples are shown in Supplementary Fig. 8. The extracted Dingle temperature for bulk and surface states are 6.49 K and 4.57 K, respectively, from which the quantum relaxation time $\tau_q = \hbar/(2\pi k_B T_D)$ and quantum mobility $\mu_q = e\tau_q/m^*$ can be extracted. Moreover, the fitting also yields Berry phases of $-1.09\pi (\delta = -1/8)$ or $-0.59\pi (\delta_{3D} = 1/8)$ for the bulk and $0.1\pi (\delta_{2D} = 0)$ for the surface, which is in a good agreement with the values derived from LL fan diagram.

**Effective mass.** The effective masses of bulk and surface bands for various samples were obtained from the temperature dependence of the quantum oscillations (1.7 to 20 K) as shown in Supplementary Fig. 9, by fitting the FFT peak intensity to the thermal damping term of the LK-formula$^39$. 
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Author contributions

This project was designed by J.H., Z.Q.M, and J.W. Bulk ZrSiSe crystals were synthesized by J.H. Nanodevices were fabricated by X.L. and C.Y. High field measurement experiments were conducted by X.L., C.Y., Y.Z., A.J., J.L., and D.G. TEM experiments were performed by A.S. The quantum transport data were analyzed by J.H., X.L., C.Y., A.S, and J.W. The manuscript was written by C.Y., X.L., and J.H., and revised by J.H., Z.Q.M., and J.W. All authors contribute to the discussion of manuscript.

Competing financial interests

The authors declare no competing financial interest.
Figure 1
Figure 2

Figure 3
Figure 4