High-temperature quantum oscillations of the Hall resistance in bulk Bi$_2$Se$_3$

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Helically spin-polarized Dirac fermions (HSDF) in protected topological surface states (TSS) are of high interest as a new state of quantum matter. In three-dimensional (3D) materials with TSS, electronic bulk states often mask the transport properties of HSDF. Recently, the high-field Hall resistance and low-field magnetoresistance indicate that the TSS may coexist with a layered two-dimensional electronic system (2DES). Here, we demonstrate quantum oscillations of the Hall resistance at temperatures up to 50 K in nominally undoped bulk Bi$_2$Se$_3$ with a high electron density $n$ of about 2·10$^{19}$ cm$^{-3}$. From the angular and temperature dependence of the Hall resistance and the Shubnikov-de Haas oscillations we identify 3D and 2D contributions to transport. Angular resolved photoemission spectroscopy proves the existence of TSS. We present a model for Bi$_2$Se$_3$ and suggest that the coexistence of TSS and 2D layered transport stabilizes the quantum oscillations of the Hall resistance.

Among the new material class of topological insulators (TI), the chalcogenide semiconductor Bi$_2$Se$_3$ has been long subject to intense investigations due to its potential integration in room temperature applications, such as dissipationless electronics and spintronics devices$^{1-4}$. Bi$_2$Se$_3$ has a single Dirac cone at the $\Gamma$-point in the first surface Brillouin zone and a direct band gap of 0.3 eV between the valence and the conduction band$^{5-7}$. Due to the inversion symmetry in Bi$_2$Se$_3$, the topological $\mathbb{Z}_2$ invariant $\nu = (1;000)$ is equal to the charge of parity of the valence band eigenvalues at the time-reversal-invariant points of the first Brillouin zone caused by the band inversion$^8$. In the crystalline modification Bi$_2$Se$_3$ has a tetradymite structure with $R3m$ symmetry. The unit cell consists of 15 atomic layers grouped in three quintuple layers with Se–Bi–Se–Bi–Se order stacked in an A–B–C–A–B–C manner. The quintuple layers are van der Waals bonded to each other by a double layer of Se atoms, the so-called van der Waals gap$^4$. The existence of TSS in Bi$_2$Se$_3$ has been experimentally confirmed through angle resolved photoemission spectroscopy (ARPES)$^3,7,9$ and scanning tunneling microscopy/scanning tunneling spectroscopy (STM/STS)$^{10,11}$. The as-grown crystals of Bi$_2$Se$_3$ are typically $n$-type because of electron doping due to natural selenium vacancies$^{12,13}$. Therefore, the transport properties of Bi$_2$Se$_3$ are generally dominated by bulk conduction. In particular, the temperature dependence of the electrical resistivity $\rho$ is metallic-like$^{14-17}$ and Shubnikov-de Haas (SdH) oscillations in the longitudinal resistivity $\rho_{xx}$ show the characteristic signatures for a 3D Fermi surface$^{14,17}$. For highly Sb-doped samples with lower carrier density $n \sim 10^{17}$ cm$^{-3}$, the SdH can be detected via additional SdH oscillations with a frequency $\nu_{SdH}$ higher than that of the bulk and the Hall resistivity $\rho_{xy}$ exhibits quantum oscillations for a carrier density $n < 5 \cdot 10^{14}$ cm$^{-3}$ (ref.$^{19}$). Different from that, for $n \geq 2 \cdot 10^{19}$ cm$^{-3}$ a bulk quantum Hall effect (QHE) with 2D-like transport behavior was reported$^{5,16}$. Its origin remains unidentified.

In this work we demonstrate that the quantum oscillations of the Hall resistance $R_{xy}$ in high-purity, nominally undoped Bi$_2$Se$_3$ single crystals with a carrier density of $n \approx 2 \cdot 10^{19}$ cm$^{-3}$ persist up to high temperatures. The quantum oscillations in $R_{xy}$ scale with the sample thickness, strongly indicating 2D layered transport. These findings stand out because the Bi$_2$Se$_3$ samples investigated here have a lower carrier mobility $\mu$ of about 600 cm$^{2}$/Vs than materials hosting a typical 2D Fermi gas$^{19-22}$ or 3D Fermi gas$^{23-25}$ showing QHE. We discuss the conditions of the QHE below in detail and present a model for the coexistence of 3D bulk, 2D layered and TSS transport.

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Results

Experimental data. High-resolution ARPES dispersions measured at a temperature of 12 K for two representative photon energies of $h\nu = 16$ eV and 21 eV are shown in Fig. 1a and b, respectively. We clearly observe distinct intensity contributions from the bulk conduction band (BCB) and bulk valence band (BVV) coexisting with sharp and intense Dirac cone representing the TSS. The BCB crossing the Fermi level indicates that the crystals are intrinsically $n$-type, in agreement with our Hall measurements on the same samples. At binding energies higher than the Dirac node ($E_D \approx 0.35$ eV), the lower half of the TSS overlaps with the BVV. By changing the photon energy we select the component of the electron wave vector perpendicular to the surface $k_z$. Since the lattice constant of Bi$_2$Se$_3$ is very large along the z axis ($c = 28.64$ Å), the size of the bulk Brillouin zone (BBZ) is very small ($\sim 0.2$ Å$^{-1}$). With photon energies between 16 to 21 eV we cross practically the complete BBZ, enhancing the sensitivity to the out-of-plane dispersion of the bulk bands. We note that the ARPES intensity changes with the photon energy as well due to the $k_z$-dependence of the photoemission transitions. Differently from the BCB or BVV, the TSS exhibits no $k_z$-dependence due to its 2D character. Consistent with the direct nature of the gap, we find the BCB minimum ($\approx \Gamma$-point of the BBZ) at a binding energy of $\sim 0.154$ eV, while the BVV maximum is at $\sim 0.452$ eV. In particular, from the ARPES measurements, we estimate a bulk carrier density of $n_{BCB} = 1.77 \times 10^{19}$ cm$^{-3}$ and a sheet carrier density of $n_{TSS} = k_{TSS}^2/(4\pi) = 1.18 \times 10^{13}$ cm$^{-2}$, with $k_{TSS} = 0.064$ Å$^{-1}$ and $k_{TSS} = (0.086 \pm 0.001)$ Å$^{-1}$, respectively.

In the following, we present data measured on one Bi$_2$Se$_3$ macro flake. However, similar results were obtained for other samples from the same source bulk single crystal. The longitudinal resistance $R_{xx}$ and the Hall resistance $R_{xy}$ were measured simultaneously in a temperature range between 0.3 K and 72 K in tilted magnetic fields up to 33 T. $R_{xx}$ as a function of perpendicular magnetic field $B$ measured at $T = 0.47$ K is shown in Fig. 1c as symmetrized raw data $R_{xy}^{raw}(B) = [R_{xy}^{raw}(+B) + R_{xy}^{raw}(-B)]/2$. The temperature-dependent $R_{xy}$ at zero magnetic field shows metallic-like behavior (see inset of Fig. 1c). A residual resistance ratio $R_{xx}(288$ K)/$R_{xx}(4.3$ K) = 1.63 indicates a high crystalline quality (see Supplementary Information Sec. 1).

The longitudinal resistivity $\rho_{xx}$ and the Hall resistivity $\rho_{xy}$ as a function of the perpendicular magnetic field $B$ at a temperature of $T = 0.47$ K are shown in Fig. 1d ($\rho_{xx}$: blue curve, left axis; $\rho_{xy}$: red curve, right axis). The onset of quantum oscillations with plateau-like features in $\rho_{xy}$ and SdH oscillations in $\rho_{xx}$ can be observed at fields $B \geq 10$ T. The low-field slope of $\rho_{xy}$ yields a carrier density of $n_{tall} = 1.97 \times 10^{19}$ cm$^{-2}$ and a carrier mobility of $\mu_{tall} = 594$ cm$^2/(Vs)$. In order to analyze the plateau-like features in $\rho_{xy}$, we use the high-field anti-symmetrized Hall resistance $R_{xy}^{asy}(B) = [R_{xy}^{raw}(+B) - R_{xy}^{raw}(-B)]/2$ for $T = 0.47$ K and an angle of $\theta = 0^\circ$. $\theta$ denotes the angle between the direction of $B$ and the surface normal $\hat{N}$ of the Bi$_2$Se$_3$ macro flake (i.e. $\theta = 0^\circ$ means $B \parallel \hat{N}$). $\hat{N}$ is parallel to the c-axis of the single crystal. The scaling behaviour of $\Delta R_{xy}^{asy} = R_{xy}^{asy}(N) - R_{xy}^{asy}(N+1)$ with the thickness leads to $Z' = [(1/N - 1/(N+1))/\Delta R_{xy}^{asy}] \cdot (h/(2e^2))$ as the number of 2D spin-degenerate layers contributing to the transport. Conclusively, an average number of 2D layers of $Z' = 25250$ is derived. The variation of $Z'$ for different Landau level (LL) index $N$ is given in the inset of Fig. 2a.

The negative differentiated Hall resistivity $-d\rho_{xy}/dB$ vs magnetic field $B$ is shown for different angles $\theta$ at constant $T = 1.47$ K in Fig. 2c, and for different temperatures $T$ at constant $\theta = 0^\circ$ in Fig. 2d. In accordance with the angular and the temperature dependence of the SdH oscillations, as shown in Figs 3a and 4a, respectively, a decreasing amplitude of the differentiated Hall resistivity with increasing $\theta$ and increasing $T$ is detected. At a constant $T = 1.47$ K the typical signatures of quantum oscillations of the Hall resistance are observed up to $\theta = 71.5^\circ$ and an angle of $\theta = 0^\circ$ means $B \parallel \hat{N}$. For $\theta = 0^\circ$ the temperature of the SdH oscillations for a bulk carrier density $n_{BCB} = 1.77 \times 10^{19}$ cm$^{-3}$ is $0.16$ K and $k_{BCB} = 0.001$ Å$^{-1}$.

The SdH oscillations in the longitudinal resistivity $\rho_{xx}$ are periodic functions of the inverse magnetic field $1/B$. The SdH oscillations in the longitudinal resistivity $\rho_{xx}$, deduced from the periodicity in the $1/B$ dependence. These values are in agreement with those determined from the slopes of the lines in the LL fan diagram (Fig. 2b) and fast Fourier transforms of the same data. The absence of additional frequencies and beatings, as well as the angular dependence of $\rho_{xx}$, are significant evidence of a single 3D (non-spherical) Fermi surface (see Supplementary Information Sec. 3).

The temperature dependence of $\Delta_{\rho_{xx}}$ is shown in Fig. 4a. The amplitude decreases with increasing temperature $T$, and oscillations are not observed for $T > 71.5$ K. From the fitting of the relative longitudinal resistivity ratio $\Delta_{\rho_{xx}}(T) = \Delta_{\rho_{xx}}(T = 1.47$ K), we deduce an effective mass of the charge carriers of $m^* \approx 0.16$ m$_e$ ($m_e = 9.10938356 \times 10^{-31}$ kg denotes the electron rest mass) and a Fermi velocity of $v_F = \sqrt{k_{TSS}^2/m^*} = 0.46 \times 10^6$ m/s, with $k_{TSS} = 0.064$ Å$^{-1}$.
Figure 1. Electronic structure, temperature-dependent resistance and magnetotransport properties of Bi$_2$Se$_3$.

(a) and (b) Electronic structure of the Bi$_2$Se$_3$ bulk single crystal before mechanical exfoliation. The panels show high resolution ARPES $E(k)$ dispersions measured at a temperature of $T = 12$ K and at a photon energy of $h\nu = 16$ eV and $21$ eV, respectively. In (a), the TSS, the bulk conduction band (BCB) and the bulk valence band (BVB) are indicated. (c) Longitudinal resistance $R_{xx}$ vs perpendicular magnetic field $B$ as symmetrized raw data measured at $T = 0.47$ K. Inset: Longitudinal resistance $R_{xx}$ vs temperature $T$ measured for $B = 0$. (d) Longitudinal resistivity $\rho_{xx}$ (blue curve, left axis) and Hall resistivity $\rho_{xy}$ (red curve, right axis) vs perpendicular magnetic field $B$ measured at $T = 0.47$ K.
In a first step we assumed 2D transport in accordance with some other investigations \(14,15,26\). The Dingle plots (inset of Fig. 4b) at temperatures of \(T = 1.47 K, 4.22 K, 15.3 K, \text{and} 26 K\) yield the following Dingle scattering time (also known as single-particle relaxation time) \(\tau_D\) and the Dingle temperature \(T_D = h/(4\pi^2k_B\tau_D)\), assuming the fit function \(-\pi m^*/(e\tau_D B)\) with \(m^* = 0.16 m_e; \tau_D = 5.8 \cdot 10^{-14} s (T_D = 20.8 K), 5.1 \cdot 10^{-14} s (23.7 K), 3.9 \cdot 10^{-14} s \).
Figure 4. 2D and 3D analysis of the temperature dependence of the Shubnikov-de Haas oscillations. (a) Relative longitudinal resistivity $\Delta \rho_{xx}$ vs magnetic field $B$ measured for an angle $\theta = 0^\circ$ at different temperatures $T$. The black arrows indicate values of magnetic field $B$ shown in panel b vs temperature $T$. (b) Relative longitudinal resistivity ratio $\Delta \rho_{xx}(T)/\Delta \rho_{xx}(1.47 \text{ K})$ vs temperature $T$ for a magnetic field of $B = 30.4 \text{ T}$ (violet squares), 25.7 T (orange circles), and 22.3 T (dark cyan triangles). Dashed lines represent best linear fits to data assuming the function $\chi(T) = (4\pi^2 m e T)/(\hbar e B)$, with $\chi(T) = (4\pi^2 m e T)/(\hbar e B)$. Inset: Dingle plots of the SdH oscillations with 2D transport (maxima of relative longitudinal resistivity $\Delta \rho_{xx}$ as shown in panel (a)) at $T = 1.47 \text{ K}$ (blue squares), 4.22 K (pink circles), 15.3 K (green triangles), and 26 K (cyan diamonds). Dashed lines represent best linear fits to data with the function $-\pi m^* / (e B T)$, with $m^* = 0.16 m_e$. (c) Relative longitudinal resistivity $\Delta \rho_{xx}$ vs magnetic field measured for $\theta = 0^\circ$ at $T = 1.47 \text{ K}$ (blue squares) and 26 K (pink circles). For clarity, only every fifth data point is shown. The curves are best fits to the Lifshitz-Kosevich formula for 2D transport (given in the legend), with $B_{\text{D}}^{2D} = 166 \text{ T}$ (cf. Fig. 3b and text). (d) Same data as in (c): The curves are best fits to the Lifshitz-Kosevich formula for 3D transport (given in the legend), with $B_{\text{D}}^{2D} = 169.5 \text{ T}$ and the parameter $F = 2\pi k_B T \tau_D / (\hbar \omega_c)$ and $m^* = 0.16 m_e$. The parameter $r$ denotes the number of harmonic oscillations. In the present study we considered a range of values of $1 \leq r \leq 20$.

$s \approx 30.9 \text{ K}$ and $2.7 \cdot 10^{-14} \text{ s} \approx 45.5 \text{ K}$, respectively. For a more detailed analysis we have fitted the magnetic-field dependence of $\Delta \rho_{xx}$ (see Supplementary Information Sec. 4) and have used as fit function the Lifshitz-Kosevich formula for 2D transport. We found a reasonably good agreement between experimental data and the calculated behavior for $\Delta \rho_{xx}(B)$ (cf. Fig. 4c).

However, in a second step we also performed fits under the assumption of 3D transport (cf. Fig. 4d), because the angular dependence of the SdH frequency $B_{\text{SdH}}$ in Fig. 3b clearly follows the function for 3D transport. In this case, we find for all curves a single value for the Dingle temperature $T_D = 23.5 \text{ K}$ and hence a single value for the Dingle scattering time $\tau_D = 5.2 \cdot 10^{-14} \text{ s}$, consistent with a nearly constant $k_B T_D \approx 23.5 \text{ K}$ up to $T = 30 \text{ K}$ (see inset of Fig. 1c). From $\tau_D$ and the effective mass $m^* = 0.16 m_e$, we determined a carrier mobility of $\mu_D = e T_D / m^* = 572 \text{ cm}^2/(\text{Vs})$.

Evaluation of experimental data. Most of the investigations of bulk Bi$_2$Se$_3$ conclude that the Fermi surface is 3D, usually from the angular dependence of the SdH oscillations. However, in the search of TSS and QHE some works evaluated the Fermi surface as 2D. Our analysis of the SdH oscillations (see above) indicates that the Fermi surface is 3D. This is confirmed by our following analysis of the angular dependence of the SdH frequencies.

The angle dependence of the SdH oscillations determines that the Fermi surface has an ellipsoidal shape. For a plane 2D Fermi surface, the SdH oscillation frequency is equal to $B_{\text{SdH}}^{2D}(\theta) = \frac{B}{\cos \theta}$, with $B_{\text{SdH}}^{2D}(\theta) \rightarrow \infty$ for $\theta \rightarrow 90^\circ$ (blue curve in Fig. 3b), and for an ellipsoidal 3D Fermi surface it is $B_{\text{SdH}}^{3D}(\theta) = B_1 B_2 / \sqrt{(B_1 \cos \theta)^2 + (B_2 \sin \theta)^2}$ (red curve in Fig. 3b), with $B_1 = B_{\text{SdH}}^{3D}(\theta = 0^\circ) = B_{\text{SdH}}^{2D}(\theta = 0^\circ) = 166$
and $B_\parallel = B_{SdH}(\theta = 90^\circ) = 328$ T. Previous data\textsuperscript{15,16} may also be interpreted as 3D ellipsoidal Fermi surface (see Supplementary Information Sec. 3).

We estimate the ellipsoidal cross-section of the 3D Fermi surface with the wave vectors $k_{F_{SdH}}^{(a)} = k_{F_{SdH}}^{(b)} = \sqrt{2eB/hc} = 0.071 \text{ Å}^{-1}$ and $k_{F_{SdH}}^{(c)} = 2eB/(h(k_{F_{SdH}}^{(a)})) = 1.14 \text{ Å}^{-1}$. With these values we deduced an eccentricity for the 3D non-spherical Fermi surface of $k_{F_{SdH}}^{(a)}/k_{F_{SdH}}^{(c)} = 1.98$. Köhler\textsuperscript{30} and Hyde et al.\textsuperscript{31} show, that the eccentricity of the Fermi surface decreases with decreasing carrier density $n$. In accordance with the present study, Eto et al.\textsuperscript{14} deduced for a Bi$_2$Se$_3$ bulk single crystal with a lower carrier density of $n = 3.4 \cdot 10^{18} \text{ cm}^{-3}$ an eccentricity of $k_{F_{SdH}}^{(a)}/k_{F_{SdH}}^{(c)} = 1.62$, consistent with eccentricities obtained by Köhler\textsuperscript{30}. Assuming a parabolic dispersion and using the values of $k_{F_{SdH}}^{(a)}$ and $k_{F_{SdH}}^{(c)}$ from the SdH analysis and of $E_F$ from the ARPES measurements, we estimate with $E_F = (\langle k_F^2 \rangle / (2m^*)$ for the effective masses $m^*_F = m^*_c = 0.125 m_e$ and $m^*_c = 0.485 m_e$. An average value for the effective mass is then given by $^{11} 1/m^*_c = (1/m^*_e + 2/m^*_c)/3$, which yields $m^*_c = 0.166 m_e$. This value is consistent with the value obtained from the temperature dependence of the SdH oscillations: $m^*_SdH = 0.16 m_e$.

**Discussion**

Generally, a bulk or 3D QHE is attributed to parallel 2D conduction channels, each made from one or a few stacking layers. A bulk QHE, where quantized values of the Hall resistance $R_H$, inversely scale with the sample thickness, has been observed in a number of anisotropic, layered electronic bulk materials, e.g., GaAs/AlGaAs multi-quantum wells\textsuperscript{32,33}, Bechgaard salts\textsuperscript{34,35} and also in Fe-doped Bi$_2$Se$_3$ bulk samples\textsuperscript{36}, where transport by TSS was excluded. However, the observation of the quantum oscillations of the Hall resistance in Bi$_2$Se$_3$ at elevated temperatures calls for a special condition considering the usual requirement of $B > 1$. In the present case $B_{max} = 33$ T and the carrier mobility $\mu \approx 600 \text{ cm}^2/(\text{V}\cdot\text{s})$ yields only $\mu B_{max} \approx 2$. Furthermore, the deduced effective mass $m^*_c = 0.16 m_e$ yields for a magnetic field of $B = 10$ T, where we observe the onset of the quantum oscillations, a value for the LL energy splitting of $\hbar \omega_c = eB/m^*_c \approx 7 \text{ meV}$. However, the thermal energy amounts to $k_B T \approx 4 \text{ meV}$ at $T = 50$ K, while $\hbar \omega_c \gg k_B T$ is usually required for a QHE. Nevertheless, we observe unambiguous quantum oscillations even $\sim 10 \text{ K}$ as signature of a QHE.

In order to explain the experimental observations, we propose the following model. The Bi$_2$Se$_3$ bulk sample investigated here may consist of three different conducting regions: a semiconducting-like core region, surrounded by a metallic-like shell region and the topological surface (see Fig. S1 in Supplementary Information Sec. 5). The semiconducting-like core was proven by the preparation of semiconducting micro flakes\textsuperscript{37}. The metallic-like shell region due to Se depletion dominates the transport mechanism observed here as metallic and 2D layered effects. From our experiments, we assume the shell to form a stacked system of 2D layers with a peri-

inter-layer coupling, it is expected that in the quantum Hall state the edge states of the stacked 2D layers form a

in the miniband gap, which could be the result of an interaction with the existing TSS. Theoretically, due to the

oscillations in $\rho_{osc}$, $\theta_{SdH}$, core  corresponds to a slow-changing background which

oscillations at $\theta = 0^\circ$ for the three regions the following values: $B_{SdH} = 4.82$ T, $B_{SdH} = 2.3$ T and $B_{SdH} = 4.8$ T. The small value $B_{SdH}$ corresponds to a slow-changing background which is out of the measurement range of our experimental setup. The larger value of the TSS is caused only by the small number of surface electrons with respect to the large number of bulk electrons ($N_{SdH,SdH} = N_{shell} = 2 \cdot 10^{13} \text{ cm}^{-2}$ and $N_{SdH,TSS} \approx 3 \cdot 10^{11} \text{ cm}^{-2}$) resulting in a maximum contribution of the bulk (core + shell) in the transport behavior. A periodic modulation of the charge carrier density along the $c$-direction would result in a miniband structure for the LLs and, as long as the Fermi level is in a gap between these minibands, the Hall resistivity $\rho_{xy}$ will be quantized and scale with the periodicity of the potential\textsuperscript{29}.

According to our estimate of the width of the LLs (see above), the persistence of the quantum oscillations in the Hall resistance up to high temperatures requires a special condition: We propose a Fermi level pinning in the miniband gap, which could be the result of an interaction with the existing TSS. Theoretically, due to the inter-layer coupling, it is expected that in the quantum Hall state the edge states of the stacked 2D layers form a sheath at the surface\textsuperscript{44}. Due to the finite width of the wave functions at the surface, this sheath can interact with the TSS. This opens the possibility that the TSS act as electron reservoirs to pin the Fermi level in a miniband gap as the magnetic field is varied over a finite range. Therefore, we conclude that the observation of the quantum oscillations of the Hall resistance at higher temperatures in Bi$_2$Se$_3$ ($\eta \approx 2 \cdot 10^{15} \text{ cm}^{-3}$) with a majority of non-Dirac fermions is related to the existence of the TSS. Based on our results, we propose that other 3D materials with TSS and a periodic potential modulation may show quantization effects in the Hall resistance at elevated temperatures.

**Methods**

High-quality single crystalline Bi$_2$Se$_3$ was prepared from melt with the Bridgman technique. The growth time, including cooling was about 2 weeks for a $\sim 50 \text{ g}$ crystal. The whole crystal was easily cleaved along the [001] growth direction, indicating crystal perfection. The macro flake was prepared by cleaving the bulk single crystal with a thickness of around 110 $\mu\text{m}$ to investigate bulk properties.
We explored the structural properties of the bulk single crystal with atomic force microscopy (AFM), scanning transmission electron microscopy (STEM) and high-resolution transmission electron microscopy (HRTEM). The composition and surface stability were investigated using energy-dispersive x-ray spectroscopy (EDX) and spatially resolved core level X-ray PEEM. Structural analysis using HRTEM and STEM was carried out at a JEOL JEM2200FS microscope operated at 200 kV. The sample preparation for HRTEM characterization consisted of ultrasonic separation of the flakes from the substrate, followed by their transfer onto a carbon-coated copper grid. Using adhesive tape, the surface was prepared by cleavage of the crystal along its trigonal axis in the direction perpendicular to the van-der-Waals-type (0001) planes. The ARPES measurements were performed at a temperature of 12 K in an ultra-high vacuum (UHV) chamber at a pressure of ~5 × 10⁻¹² mbar with a VG Scienta R8000 electron analyzer at the UE112-PMG2a beamline of BESSY II using p-polarized undulator radiation.

Magnetotransport experiments were performed using standard low-noise lock-in techniques (Stanford Research Systems SR830 with a Keithley 6221 as current source), with low excitation to prevent heating of the sample. The Bi₂Se₃ macro flake was mounted in a flow cryostat (1.3 K to 300 K), as well as in a ³He insert (down to 0.3 K), in a Bitter magnet with a bore diameter of 32 mm and magnetic fields up to 33 T at the High Field Magnet Laboratory of the Radboud University Nijmegen. In both setups, a Cernox thermometer in the vicinity of the sample was used to monitor the temperature in situ. In the ³He system, the temperature between 0.3 K and 1.3 K was stabilized by the ³He vapour pressure prior to the magnetic field sweep to assure a constant temperature. However, the temperature between 1.3 K and 4.2 K was stabilized by the ⁴He pressure. Above a temperature of 4.2 K, we have used the flow cryostat and stabilized the temperature using a capacitance.

References
1. Xue, Q.-K. Nanoelectronics: A topological twist for transistors. Nature Nanotechnol. 6, 197 (2011).
2. Zhang, H. et al. Topological insulators in Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃ with a single Dirac cone on the surface. Nature Phys. 5, 438 (2009).
3. Chiatti, O. et al. 2D layered transport properties from topological insulator Bi₂Se₃ single crystals and micro flakes. Sci. Rep. 6, 27483 (2016).
4. Ando, Y. Topological InsulatorMaterials. J. Phys. Soc. J. 82, 102001 (2013).
5. Chechelsky, J. G., Hor, Y. S., Cava, R. J. & Ong, N. P. Bulk band gap and surface state conduction observed in voltage-tuned crystals of the topological insulator Bi₂Se₃. Phys. Rev. Lett. 106, 196801 (2011).
6. Betancourt, J. et al. Complex band structure of topological insulator Bi₂Se₃, J. Phys.: Condens. Matter 28, 195901 (2016).
7. Xia, Y. et al. Observation of a large-gap topological-insulator class with a single Dirac cone on the surface. Nature Phys. 5, 398 (2009).
8. Fu, L. & Kane, C. L. Topological insulators with inversion symmetry. Phys. Rev. B 76, 045302 (2007).
9. Bianchi, M. et al. The electronic structure of clean and adsorbate-covered Bi₂Se₃, an angle-resolved photoemission study. Semicond. Sci. Technol. 27, 124001 (2012).
10. Alpichshev, Z. et al. STM Imaging of Impurity Resonances on Bi₂Se₃. Phys. Rev. Lett. 108, 206402 (2012).
11. Liu, Y. et al. Tuning Dirac states by strain in the topological insulator Bi₂Se₃, Nature Phys. 10, 294 (2014).
12. Hyde, G. R., Beale, H. A., Span, I. L. & Woollam, J. A. Electronic properties of Bi₂Se₃ crystals. J. Phys. Chem. Solids 35, 1719 (1974).
13. Yan, B., Zhang, D. & Felser, C. Topological surface states of Bi₂Se₃, coexisting with Se vacancies. Phys. Status Solidi RRL 7, 148 (2013).
14. Eto, K., Ren, Z., Taskin, A. A., Segawa, K. & Ando, Y. Angular-dependent oscillations of the magnetoresistance in Bi₂Se₃ due to the three-dimensional bulk Fermi surface. Phys. Rev. B 81, 195309 (2010).
15. Petrushovsky, M. et al. Probing the surface states in Bi₂Se₃ using the Shubnikov-de Haas effect. Phys. Rev. B 86, 045131 (2012).
16. Cao, H. et al. Quantized Hall Effect and Shubnikov-de Haas Oscillations in Highly Doped Bi₂Se₃; Evidence for Layered Transport of Bulk Carriers. Phys. Rev. Lett. 108, 216803 (2012).
17. Analysis, J. G. et al. Bulk Fermi surface coexistence with Dirac surface state in Bi₂Se₃/A. A comparison of photoemission and Shubnikov-de Haas measurements. Phys. Rev. B 81, 205407 (2010).
18. Analysis, J. G. et al. Two-dimensional surface state in the quantum limit of a topological insulator. Nature Phys. 6, 960 (2010).
19. Beenakker, C. W. J. & van Houten, H. Quantum transport in semiconductor nanostructures. Sol. St. Phys. 44, 1 (1991).
20. Störmer, H. L., Eisenstein, J. P., Gossard, A. C., Wiegmann, W. & Baldwin, K. Quantization of the Hall effect in an anisotropic three-dimensional electronic system. Phys. Rev. Lett. 56, 85 (1986).
21. Novoselov, K. S. et al. Room-Temperature Quantum Hall Effect in Graphene. Phys. Rev. Lett. 95, 206402 (2005).
22. Khoury, T. et al. High-Temperature Quantum Hall effect in Graphene. Science 315, 1379 (2007).
23. Kouwenhoven, L. P. et al. High-temperature quantum Hall effect in finite gapped HgTe quantum wells. Phys. Rev. B 93, 125308 (2016).
24. Halperin, B. I. Possible States for a Three-Dimensional Electron Gas in a Strong Magnetic Field. Jap. J. Appl. Phys. 26, 1913 (1987).
25. Johann, S. T., Brooks, J. S., Kang, W., Chiang, L. Y. & Chakini, P. M. Quantum Hall effect in a bulk crystal. Phys. Rev. Lett. 63, 1988 (1989).
26. Hill, S. et al. Bulk quantum Hall effect in Bi₂Se₃, Phys. Rev. B 58, 10778 (1998).
27. Yan, Y. et al. High-Mobility Bi₂Se₃ Nanoplates Manifesting Quantum Oscillations of Surface States in the Sidewalls. Sci. Rep. 4, 3817 (2014).
28. Lifshitz, E. M. & Pitaevskii, L. P. Statistical Physics. (Pergamon Press, Oxford, 1986).
29. Taskin, A. A. & Ando, Y. Berry phase of nonideal Dirac fermions in topological insulators. Phys. Rev. B 84, 033301 (2011).
30. Ridley, B. K. Quantum Processes in Semiconductors. (Oxford University Press, Oxford, 2013).
31. Kohler, H. Conduction Band Parameters of Bi₂Se₃ from Shubnikov-de Haas Investigations. Phys. Stat. Sol. (b) 58, 91 (1973).
32. Ziman, J. M. Electrons and Phonons–The Theory of Transport Phenomena in Solids. (Clarendon Press, Oxford, 2013).
33. Balicas, L., Kriza, G. & Williams, F. I. B. Sign Reversal of the Quantum Hall Number in (TMTSF)₂PF₆. Phys. Rev. B 56, 85 (1997).
34. Ge, J. et al. Evidence of layered transport of bulk carriers in Fe-doped Bi₂Se₃, topological insulators. Sol. State Commun. 211, 29 (2015).
35. Balents, L. & Fisher, M. P. Chiral Surface States in the Bulk Quantum Hall Effect. Phys. Rev. Lett. 76, 2782 (1996).

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Author Contributions
M.B., O.C., S.P., S.W. and S.F.F. contributed to the transport experiments, analyzed the data and wrote the manuscript, J.S.-B. and O.R. conducted the ARPES experiments and L.V.Y. conducted the bulk crystal growth. All authors contributed to the discussion and reviewed the manuscript.

Additional Information
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