Magnetic freeze-out and anomalous Hall effect in ZrTe$_5$

Adrien Gourgout,$^1$ Maxime Leroux,$^2$ Jean-Loup Smir,$^3$ Maxime Massoudzadegan,$^2$ Ricardo P. S. M. Lobo,$^1$ David Vignolles,$^2$ Cyril Proust,$^2$
Helmuth Berger,$^4$ Qiang Li,$^{5,6}$ Genda Gu,$^6$ Christopher C. Homes,$^{6,7}$ Ana Akrap,$^8$ and Benoît Fauqué$^{3,6}$

$^1$Laboratoire de Physique et d’Étude des Matériaux (ESPCI Paris - CNRS - Sorbonne Université), PSL Research University, 75005 Paris, France
$^2$LNCMI-EMFL, CNRS UPR3228, Univ. Grenoble Alpes, Univ. Toulouse, Univ. Toulouse 3, INSA-T, Grenoble and Toulouse, France
$^3$JEIP, USR 3573 CNRS, Collège de France, PSL Research University, 11, place Marcelin Berthelot, 75231 Paris Cedex 05, France
$^4$IPHYS, EPFL, CH-1015 Lausanne, Switzerland
$^5$Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11794-3800, USA
$^6$Condensed Matter Physics and Materials Science Division, Brookhaven National Laboratory, Upton, New York 11973-5000, USA
$^7$National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, USA
$^8$Department of Physics, University of Fribourg, 1700 Fribourg, Switzerland

(Dated: 5 May 2022)

The ultra-quantum limit is achieved when a magnetic field confines an electron gas in its lowest spin-polarised Landau level. Here we show that in this limit, electron doped ZrTe$_5$ shows a metal-insulator transition followed by a sign change of the Hall and Seebeck effects at low temperature. We attribute this transition to a magnetic freeze-out of charge carriers on the ionised impurities. The reduction of the charge carrier density gives way to an anomalous Hall response of the spin-polarised electrons. This behaviour, at odds with the usual magnetic freeze-out scenario, occurs in this Dirac metal because of its tiny Fermi energy, extremely narrow band gap and a large $g$-factor. We discuss the different possible sources (intrinsic or extrinsic) for this anomalous Hall contribution.

I. Introduction

In the presence of a magnetic field, the electronic spectrum of a three-dimensional electron gas (3DEG) is quantized into Landau levels. When all the charge carriers are confined in the lowest spin-polarised Landau level, the electronic spectrum is quantized into Landau levels. When all the charge carriers are confined in the lowest
Landau level—the so-called quantum limit—the kinetic energy of electrons is quenched in the directions transverse to the field. This favors the emergence of electronic instabilities, either driven by the electron-electron or electron-impurity interactions\cite{1,2,3,4}. So far, the behavior of 3DEGs beyond their quantum limit has been explored in a limited number of low carrier density systems. Yet, different instabilities have been detected, such as a thermodynamic phase transition in graphite\cite{5,6,7,8}, a valley depopulation phase in bismuth\cite{9,10} and a metal-insulator transition (MIT) in narrow-gap doped semi-conductors InSb\cite{11} and InAs\cite{12,13}. The latter occurs when charge carriers are confined in the lowest spin-polarised Landau level – the ultra-quantum limit. This transition is generally attributed to the magnetic freeze-out effect where electrons are frozen on ionized impurities\cite{4,14}.

Lately, low-doped Dirac and Weyl materials with remarkable field-induced properties were discovered\cite{15,16,17,18,19,20}. Of particular interest is the case of ZrTe$_5$. The entrance into its quantum limit regime is marked by quasi quantized Hall resistivity ($\rho_{xy}$)\cite{18} and thermoelectrical Hall conductivity ($\alpha_{xy}$)\cite{20,21}, followed by a higher magnetic field transition\cite{18,22}. This phase transition has initially been attributed to the formation of a charge density wave (CDW)\cite{18,22,23}. Such interpretation has been questioned because of the absence of thermodynamic evidence\cite{24,25}, expected for a CDW transition. Furthermore, ZrTe$_5$ displays a large anomalous Hall effect (AHE), even though it is a non-magnetic material\cite{26,27,28,29,30}.

Here we report electrical, thermo-electrical and optical conductivity measurements over a large range of doping, magnetic field, and temperature in electron-doped ZrTe$_5$. This allows us to track the Fermi surface evolution of ZrTe$_5$ and explain the nature of this phase transition, as well as its links with the observed AHE. We show that the onset of the field-induced transition can be ascribed to the magnetic freeze-out effect. In contrast with usually reported results, we show that the freeze-out regime of ZrTe$_5$ is characterized by a sign change of the Hall and thermoelectric effects, followed by a saturating Hall conductivity. Our results show that the magnetic freeze-out effect differs in this Dirac material as a consequence of the tiny band gap and large $g$-factor of ZrTe$_5$, that favor both an extrinsic and an intrinsic AHE of the spin-polarised charge carriers.

II. Results

A. Fermi surface of ZrTe$_5$

Fig. 1 shows the temperature dependence of the resistivity ($\rho_{xx}$) for four batches, labelled $S_{1-4}$ respectively. Samples from the same batch are labelled by distinct subscript letters (see Supplementary Note 1). At room temperature, $\rho_{xx} \approx 0.7$ $\mu\Omega$.cm. With decreasing temperature, $\rho_{xx}$ peaks at a temperature around which the Hall effect ($\rho_{xy}$) changes sign, which is around 150 K for $S_{3b}$ sample (see Fig. 1). Both shift to lower temperature as the carrier density decreases. These effects have been tracked by laser angle-resolved photoemission spectroscopy and attributed...
to a temperature-induced phase transition where the Fermi energy shifts from the top of the valence band to the bottom of the conduction band as the temperature decreases.32

At low temperature the Fermi energy is located in the conduction band. Figs. 1c)-d) show the quantum oscillations for samples from batches S1, S2 and S3 for a magnetic field (B) parallel to the b-axis of the orthorhombic unit cell. The angular dependence of the quantum oscillation frequency are well fitted by an anisotropic ellipsoid Fermi surface elongated along the b-axis, and in good agreement with previous measurements24,33,34 (see Fig. 1g). Our doping study reveals that the ellipsoid anisotropy increases as the system is less doped, see Fig. 1f). In our lowest doped samples the ratio of the Fermi momentum (kF) along the a and b-axis reach 0.06 implying a mass anisotropy ratio of \( m^*_{b} / m^*_{a} \approx 250 \), where \( m^*_{a,b} \) are the band mass along the a and b axis. This large mass anisotropy ratio is comparable to the one of Dirac electrons of bismuth35. This Fermi surface mapping allows us to accurately determine the Fermi sea carrier densities, \( n_{SdH} \), which agree well with \( n_{H} \) (see Supplementary Note 2). Remarkably S1 samples have a Hall mobility, \( \mu_H \), as large as \( 9.7 \times 10^5 \) V·cm⁻²·s⁻¹ and the last quantum oscillation occurs at a small field of \( B_{QL}(S_1) = 0.3 \) T for \( B \parallel b \). Given the large g-factor, \( g^* \approx 20-30 \), this last oscillation corresponds to the depopulation of the \((0,+)^{th}\) Landau level. Above it the highly mobile electrons are all confined into the lowest spin-polarised \((0,-)^{th}\) Landau level.

B. Field induced transition in the ultra-quantum limit of ZrTe5

Fig. 2 shows the field dependence of \( \rho_{xx} \) beyond the ultra-quantum limit of S1, S2 and S3 samples. In the lowest doped samples (S1) \( \rho_{xx} \) increases by more than two orders of magnitude and saturates above \( \approx 7 \) T. This large magnetoresistance vanishes as the temperature increases (see 31), for T>5 K and up to 50 T. A close inspection of the low temperature behavior reveals a light metallic phase above \( B_{QL} \) (see Fig. 2a) which ends at a crossing point at \( B_c = 3.2 \) T above which an insulating state is observed up to 50 T. Following 18 we take this crossing point as the onset of the field induced metal-insulator transition. As the carrier density increases, both the position of \( B_{QL} \) and \( B_c \) increase (see Fig. 2b and c). At the highest doping (samples S3) the amplitude of the magnetoresistance has decreased and the transition is only marked by a modest increase by a factor of two of \( \rho_{xx} \) at \( \approx 30 \) T, indicating that the transition smears with increasing doping (see Fig. 2b). Fig. 2b) shows the doping evolution of \( B_{QL} \) and \( B_c \) which are in good agreement with previous works18,22,24. For an isotropic 3D Dirac material \( B_{QL} = \hbar/e(\sqrt{2})\pi^2 n^{2/3} \) (see i.e.35) with \( n = 3\pi^2 k_F^3 \). In the \( B \parallel b \) configuration \( k_F=\sqrt{k_{F,a}k_{F,c}} \) can be evaluated from the frequency of quantum oscillations. The deduced \( B_{QL} \) is shown by the red line in Fig. 2b) and provides an excellent agreement with the detected \( B_{QL} \). As function of the total carrier density of the ellipsoid (\( n_{SdH} \)) \( B_{QL} = \hbar/e(\sqrt{2A_1A_2}\pi^2 n_{SdH})^{2/3} \) where \( A_1 \) and \( A_2 \) are the anisotropic Fermi momentum ratios between the a and b-axis, and between the c and b-axis.
The doping evolution of $B_c$ is a clue to the nature of this transition. So far it has been attributed to the formation of a charge density wave (CDW) along the magnetic field. Such an instability is favored by the one-dimensional nature of the electronic spectrum along the magnetic field, which provides a suitable $(2k_F)$ nesting vector in the $(0, -)$ Landau level. In this picture, predicted long ago, the transition is of second order and is expected to vanish as the temperature increases. The absence of temperature dependence of $B_c$ and the absence of thermodynamic signature invite us to consider another interpretation.

In the CDW picture, the instability is driven by the electron-electron or electron-phonon interaction and the interaction between electrons and the ionized impurities is neglected. However, in a doped semiconductor, the conduction band electrons are derived from uncompensated donors. Tellurium vacancies have been identified as the main source of impurities in ZrTe$_5$ flux grown samples. According to the Mott criterion, a semiconductor becomes metallic when the density of its carriers, $n$, exceeds a threshold set by its effective Bohr radius, $n/a_B^3 = 0.3$. In presence of a magnetic field the in-plane electronic wave extension shrinks with increasing magnetic field. When $B > B_{QL}$, the in-plane Bohr radius is equal to $a_{B,\perp} = 2\ell_B$ with $\ell_B = \sqrt{\frac{\hbar eB}{4\pi\epsilon m^*}}$. Along the magnetic field direction, the characteristic spatial extension is $a_{B,\parallel} = \frac{a_{B,\parallel}}{\log(\gamma)}$, where $\gamma = \left(\frac{a_B}{\ell_B}\right)^2$ with $a_{B,z}=\frac{\epsilon m_z}{m^* a_{B,0}}$ and $a_{B,c}=\frac{\epsilon m_c}{m^* a_{B,0}}$, where $m_{z,c}$ are the mass along and perpendicular to the magnetic field in units of $m_0$, and $a_{B,0}$ the bare Bohr radius. A MIT transition is thus expected to occur when the overlap between the wave functions of electrons is sufficiently decreased, i.e. when:

$$n^{1/3}(a_{B,\perp} a_{B,\parallel})^{1/2} \approx 0.3$$

This MIT is thus a Mott transition assisted by the magnetic field where the metal is turned into an insulator due to the freezing of electrons on the ionized donors by the magnetic field, the so-called magnetic freeze-out effect. According to Eq. 1, $n \propto B_c/\log(B_c)$ and $B_c$ is slightly sublinear in $n$ and evolves almost parallel to $B_{QL}$. In order to test this scenario quantitatively, one has to determine the threshold of the transition from Eq. 1, which requires knowing $\epsilon$ and $m_{z,c}^*$. Temperature dependence of the quantum oscillations gives access to $m_z^* \approx 2m_0$ and $m_c^* \approx 0.02m_0$ for $B \parallel b$, while the optical reflectivity measurements give access to $\epsilon$. Fig. 3 shows $\epsilon$ versus temperature for two samples of batches S$_1$ and S$_3$. $\epsilon$ is as large as $200-400\epsilon_0$ in ZrTe$_5$ (see Supplementary Note 5). The deduced onset from Eq. 1 is shown in dashed black lines in Fig. 2e) for $\epsilon = 200$ and 400, capturing well the doping evolution of $B_c$. We thus attribute the transition detected in the ultra-quantum limit of ZrTe$_5$ to the magnetic freeze-out effect.

It is worth noticing that a large contribution to $\epsilon$ comes from interband electronic transitions resulting in $\epsilon_\infty > 100$, see Supplementary Note 5. This result also clarifies why one can detect highly mobile carriers
even down to densities as low as $10^{13}$ cm$^{-3}$. Due to the light in-plane carrier mass and large dielectric constant, one expects the threshold of the MIT at zero magnetic field to be below $\approx 10^{12}$ cm$^{-3}$.

III. Discussion

A. Magnetic freeze-out in ZrTe$_5$

In InSb ($n_H = 2-5 \times 10^{15}$ cm$^{-3}$), a large drop of the carrier density comes with an activated insulating behavior. In contrast with that usual freeze-out scenario, we find in ZrTe$_5$ a rather soft insulating behavior, where $\rho_{xx}$ saturates at the lowest temperature. Measurements of the Hall effect and thermo-electrical properties at subkelvin temperatures shown in Fig. 4a-c reveal an unexpected field scale, thus confirming that the freeze-out regime of ZrTe$_5$ differs from the usual case. Above 7 T, $\rho_{xy}$ and the Seebeck effect ($S_{xx} = -\frac{E_x}{s_x}$) change signs and saturate from 10 T up to 50 T for $\rho_{xy}$ (see Supplementary Notes 3 and 4). The field induced sign changes of $\rho_{xy}$ and $S_{xx}$ are reminiscent of the sign change in temperature.

The temperature dependence of $S_{xx}/T$ for $B = 0$, 6 and 12 T (shown in Fig. 4d) enables us to quantify the variations of charge carrier density as a function of the magnetic field. At $B = 0$ T, $S_{xx}/T = -5.5 \, \mu V K^{-2}$, which is in quantitative agreement with the expected value for the diffusive response of a degenerate semiconductor: $S_{xx}/T = -\frac{\pi^2}{3} \frac{k_B}{eF} = -5 \, \mu V K^{-2}$ for $T_F \approx 80$ K deduced from quantum oscillation measurements. At $B = 12$ T $S_{xx}/T$ saturates, at low temperature, to $\approx +20 \, \mu V K^{-2}$, a value which is four times larger than at zero magnetic field, pointing to a reduction of the charge carrier density by only a factor of eight. The partial freeze-out of the charge carriers is the source of the saturating $\rho_{xx}$. We now discuss the specificity of ZrTe$_5$ that leads to this peculiar freeze-out regime.

In the $k$-space, the magnetic-freeze out transition corresponds to a transfer of electrons from the lowest Landau level (0,-) to a shallow band, see inset of Fig. 2e), formed by the localized electrons. This theory does not fully apply to ZrTe$_5$ for two reasons. First, it applies to large gap systems with no potential spatial fluctuations, and ZrTe$_5$ has only a band gap of 6 meV, which is fifty times smaller than that of narrow gap semi-conductors such as InSb or InAs. Second, the Fermi surface of ZrTe$_5$ is highly anisotropic. The same critical field is thus reached for a carrier density that is fifty times larger in ZrTe$_5$ than in isotropic Fermi surface materials, like InSb or InAs. The large Bohr radius and the relatively higher density of ZrTe$_5$ will therefore inevitably broaden the density of states, set by: $\Gamma = 2\sqrt{\pi \frac{e^2}{4\pi}} (N_i r_s^3)^{\frac{3}{2}}$ where $r_s \propto \sqrt{\frac{n_0}{N_i}}$ is the screening radius and $N_i$ is an estimate of the impurity concentration. Assuming that $n \approx N_i$, we estimate $\Gamma \approx 6$ meV in $S_1$ samples.

In contrast with other narrow-gap semiconductors where $\Gamma \ll E_F \ll \Delta$, the magnetic freeze-
out occurs in ZrTe$_5$ where $\Gamma \approx E_F \approx \Delta$. In this limit, the shallow band of width $\Gamma$ will overlap the LLL of the conduction band, and eventually the valence band giving rise to a finite residual electron and hole charge carriers at low temperature as sketched on Fig. 2c. As a function of doping, $\Gamma$ increases the smearing of the transition (Fig. 2). The convergence of the three energy scales $\Gamma$, $E_F$ and $\Delta$ is one source of the partial reduction of charge carrier density detected in $\rho_{xx}$, $S_{xx}$ and of the sign change of $\rho_{xy}$. This finite residual charge carrier should give rise to a linear Hall effect, contrasting with the saturating $\rho_{xy}$ (and $\sigma_{xy}$), which is typical of an anomalous response. We discuss this anomalous contribution in the last section.

**B. Anomalous Hall Effect in ZrTe$_5$**

Several studies have reported an AHE in ZrTe$_5^{25,29}$. In this case, the Hall conductivity is the sum of two contributions: $\sigma_{xy} = -neB + \sigma_{Axy}$ where the first and second terms are the orbital conductivity and the anomalous Hall conductivity, respectively. At high enough magnetic field, $\sigma_{Axy}$ becomes dominant, setting the amplitude and the sign of $\rho_{xy}$. So far, $\sigma_{Axy}$ has been attributed to the presence of a non-zero Berry curvature—an intrinsic effect—either due to the Weyl nodes in the band structure$^{26}$, or to the spin-split massive Dirac bands with non zero Berry curvature$^{28,29}$. In the latter case, $\sigma_{Axy}$ scales with the carrier density, and its amplitude is expected to be $+1$ ($\Omega$.cm)$^{-1}$ for $n_H = 2 \times 10^{16}$ cm$^{-3}$$^{28}$, which is of the same order of magnitude as our results. Skew and side jump scattering are another source of AHE in non magnetic semiconductors$^{46,47}$. Deep in the freeze-out regime of low doped InSb ($n_H \approx 10^{14}$ cm$^{-3}$), a sign change of the Hall effect has been observed and attributed to skew scattering$^{48}$. In contrast with dilute ferromagnetic alloys, where the asymmetric electron scattering is due to the spin-orbit coupling at the impurity sites, here it is caused by the spin-polarised electron scattering by ionized impurities. Its amplitude is given by $\sigma_{Sxy} = N_S \epsilon g^* \mu_B E_1$ with $\epsilon$ the gap and $\Delta$ the spin-orbit splitting of the valence band. $N_S = N_A + n$ is the density of positively charged scattering centers with $N_A$ the density of acceptors$^{48}$. Note that $\sigma_{Sxy}$ induces a sign change of the Hall conductivity and is only set by intrinsic parameters and by $N_S$. Assuming $N_S \approx n_H (B = 0)$, and taking $g^* \approx 20^{24,15}$ and $E_1 = \epsilon_G = 6$ meV ($\epsilon_G << \Delta$), we find that $\sigma_{Sxy} \approx +1$ ($\Omega$.cm)$^{-1}$, which is similar to the intrinsic contribution. Remarkably, it is four orders of magnitude larger than what has been observed in low doped InSb$^{48}$, due to the tiny gap and a (relatively) larger carrier density in ZrTe$_5$.

Therefore, the AHE contribution can induce a sign change of $\rho_{xy}$ in electron doped ZrTe$_5$. It is accompanied by a peak in $S_{xx}/T$ (see Fig. 4c), $S_{xy}/T$ (see 31) and thus in $\alpha_{xy} = \sigma_{xx} S_{xy} + \sigma_{xy} S_{xx}$ (see Fig. 4d-f)). Our result shows that the thermoelectric Hall plateau$^{20,31}$ observed above 5 K, collapses at low temperature. These peaks can be understood qualitatively through the Mott relation$^{29} \left( \frac{\alpha}{T} = -\frac{2}{3} \frac{\epsilon_G}{e} \frac{d\sigma(e)}{de} |_{e=e_F} \right)$. This is the region where $\rho_{xx}$ and $\rho_{xy}$ (and thus $\sigma_{xx}$ and $\sigma_{xy}$) change the most in field and temperature, so that $S_{xx}$ and $\alpha_{xy}$ are the largest. The increase
occurs in the vicinity of $B_c$, causing a peak in the field dependence of $S_{xx}$ and $\alpha_{xy}$, as it happens across the freeze-out regime of InAs. Whether the Mott relation can quantitatively explain the amplitude of these peaks and the sign change of $S_{xx}$ remains to be determined. This calls to extend theoretical work on the electrical and thermoelectrical response to the freeze-out regime of Dirac materials such as ZrTe$_5$.

In summary, we show that the doping evolution of the onset transition detected in the ultra-quantum limit of ZrTe$_5$ can be ascribed to the magnetic freeze-out, where electrons become bound to donors. In contrast to the usual case, the freeze-out regime of ZrTe$_5$ is marked by a modest reduction of the charge carrier density due to the convergence of three tiny energy scales in this Dirac material: the band gap, the slowly varying potential fluctuations and the Fermi energy. Deep in the freeze-out regime, the Hall conductivity changes sign and becomes anomalous with a relatively large amplitude for this low carrier density and non-magnetic material. This AHE could thus have an extrinsic origin due to skew-scattering of the spin-polarised electrons by ionized impurities. Distinguishing and tuning both intrinsic and extrinsic contributions by varying the charge compensation or strain is an appealing perspective for future research. To date, the AHE of the spin-polarised electrons in the ultra-quantum limit has been detected in a limited number of cases. Many Dirac materials with small gaps and large $g$-factors remain to be studied, in particular at higher doping where the intrinsic and extrinsic AHE are both expected to be larger.

**Methods**

Two sets of ZrTe$_5$ samples have been used in this study. The first ones, grown by flux method where iodine served as a transport agent for the constituents, have the lowest carrier density. The second ones, grown by Chemical Vapor Transport (CVT), have the highest density. Electrical and thermal transport measurements have been measured using four point contacts. Contact resistance of a less 1 kΩ has been achieved by an Argon etching, follow by the deposit of 10 nm Ti buffer layer and of 150 nm Pd layer. High magnetic field measurement has been done at LNCMI-Toulouse. Thermoelectrical and thermal transport measurements has been done using a standard two-thermoemeters one-heater set up similar to one used in. Further experimental details can be found.

**IV. Data availability**

All data supporting the findings of this study are available from the corresponding author B.F. upon request.
V. Acknowledgments

We thank K. Behnia, J-H Chu, A. Jaoui, B. Skinner and B. Yan for useful discussions. We acknowledge the support of the LNCMI-CNRS, member of the European Magnetic Field Laboratory (EMFL). This work was supported by JEIP-Collège de France, by the Agence Nationale de la Recherche (ANR-18-CE92-0020-01; ANR-19-CE30-0014-04), by a grant attributed by the Ile de France regional council and from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (Grant Agreement No. 636744). A.A. acknowledges funding from the Swiss National Science Foundation through project PP00P2_170544. The work at Brookhaven National Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Contract No. DESC0012704.

Ethics declarations

Competing interests: the authors declare no competing financial or non-financial interests.

Author contributions

B.F and A.G conducted the electrical, thermo-electrical and thermal conductivity measurements up to \( B = 17 \)T. High-field measurements have been conducted by M.L, M.M, D.V and C.P at LNCMI-Toulouse. Optical measurements have been conducted by A.A and C.C.H and analyzed by R.L and A.A. Samples have been grown by Q.L and G. Gu. Electrical contacts on the samples have been prepared by J.L.S and B.F. B.F wrote the manuscript.
FIG. 1. Doping evolution of the Fermi surface of ZrTe$_5$: a) Temperature dependence of $\rho_{xx}$ for the four different batches studied, labelled respectively $S_{1a}, S_{2b}, S_{3a}$. Samples from the same batch are labelled by distinct subscript letters. $n_{SdH}$ is the carrier density deduced from quantum oscillations (see [11]). b) $\rho_{XX}$ vs B for $S_{3b}$ ($n_{S3b} = 6.7 \times 10^{17}$ cm$^{-3}$). The dashed line indicates the zero value of $\rho_{XX}$. c)–e) Shubnikov-de Haas quantum oscillations measured in the three samples $S_{1a}, S_{2b}, S_{3a}$ at $T = 2$ K for $B // b$. g) Angular dependence of the frequency of quantum oscillations (F) in open circles as function of $\theta_1, \theta_2$, the angles between the $b$-axis and the magnetic field rotating in the (b,a) and (b,c) planes, respectively. The dotted lines are the frequency, $F$, for an ellipsoid Fermi surface of anisotropy $A_i$ ($F = F_0(1 + (1/A_i^2 - 1)\cos^2(\theta))/2$). For the two planes of rotations, $A_i$ is given by $k_{F,x}/k_{F,b}$ and $k_{F,y}/k_{F,b}$, labelled $A_1$ and $A_2$ respectively. Their doping evolution is shown in f) and agrees well with the literature.

[1] Celli, V. & Mermin, N. D. Ground state of an electron gas in a magnetic field. Phys. Rev. 140, A839 (1965). [2] Halperin, B. I. Possible states for a three-dimensional electron gas in a strong magnetic field. Japanese Journal of Applied Physics 26, 1913 (1987).
[3] MacDonald, A. H. & Bryant, G. W. Strong-magnetic-field states of the pure electron plasma. Phys. Rev. Lett. 58, 515 (1987).
[4] Yafet, Y., Keyes, R. & Adams, E. Hydrogen atom in a strong magnetic field. Journal of Physics and Chemistry of Solids 1, 137 – 142 (1956).
[5] Fauqué, B. et al. Two phase transitions induced by a magnetic field in graphite. Phys. Rev. Lett. 110, 266601 (2013).
FIG. 2. Doping evolution of the transition detected in the ultra-quantum regime of ZrTe$_5$ for $B \parallel b$: a) $\rho_{xx}$ vs magnetic field for samples $S_{1b}$. Inset: same as a) up to 1 T. b) Same as a) with a zoom on the crossing point in $\rho_{xx}$. c, d) Same as a) for samples $S_{2c}$ and $S_{3b}$. At low doping the onset of the transition is marked by a crossing point. At the highest doping it evolves into a step in $\rho_{xx}$. The width of the step has been taken as the error bar of $B_c$. e) Doping evolution of the position of the last quantum oscillation, $B_{QL}$ (yellow closed circles) and the onset of the transition, $B_c$ (yellow closed squares) as determined in $\rho_{xx}$ which agrees well with results from the literature. The dashed red line in Fig. 2e) is the value of $B_{QL}$ for an anisotropic ellipsoid (see text). The dashed black lines are the onset of the magnetic freeze-out transition according to Eq. 1 with $\epsilon = 200$ and 400. Inset: sketch of the density of state of n-type ZrTe$_5$ for $B > B_c$: the (0,-) Landau level of the conduction and valence band are plotted in blue and red while the shallow band is in green. The broadened density of states ($\Gamma$) derived from Eq. 4. The freez-out transition in ZrTe$_5$ occurs in the peculiar regime where $\Gamma \approx \Delta \approx E_F$.

FIG. 3. Temperature dependence of the dielectric constant $\epsilon$ in units of $\epsilon_0$ for two samples from batch $S_4$ ($n_{SdH}=3.6 \times 10^{16}$ cm$^{-3}$) and $S_3$ ($n_{SdH}=6.7 \times 10^{17}$ cm$^{-3}$) for $E \parallel a$ and $E \parallel c$ (red point) of ZrTe$_5$. 
FIG. 4. Electrical and thermoelectrical properties for S_{xy} for B \parallel xy. a) \rho_{xy} vs B. b) Hall conductivity, \sigma_{xy} vs B. \sigma_{xy} = \rho_{xy} / \rho_{xx}. We assumed here that \rho_{xx} = p_{yy} (see Supplementary Note 4). Inset of b) zoom of \sigma_{xy} from 5 to 16 T. c) Seebeck (S_{xy}) effect divided by the temperature vs B from T = 0.7 K up to 4.6 K. d) Thermo-electrical Hall conductivity, \alpha_{xy}, divided by T vs B (see Supplementary Note 4). e) Temperature dependence of \frac{S_{xy}}{T} at B = 0, 6 and 12 T. f) Temperature dependence of \sigma_{xy} and \frac{\alpha_{xy}}{T} at B = 12 T. The sign change of \sigma_{xy} is accompanied by a peak in \frac{\alpha_{xy}}{T}.

6LeBoeuf, D. et al. Thermodynamic signatures of the field-induced states of graphite. Nature communications 8, 1337 (2017). URL [https://www.nature.com/articles/s41467-017-01394-7]
7Zhu, Z. et al. Graphite in 90 t: evidence for strong-coupling excitonic pairing. Phys. Rev. X 9, 011058 (2019). URL [https://journals.aps.org/prx/abstract/10.1103/PhysRevX.9.011058]
8Marcenat, C. et al. Wide critical fluctuations of the field-induced phase transition in graphite. Phys. Rev. Lett. 126, 106801 (2021). URL [https://link.aps.org/doi/10.1103/PhysRevLett.126.106801]
9Zhu, Z. et al. Emptying dirac valleys in bismuth using high magnetic fields. Nature Communications 8, 15297 (2017). URL [https://doi.org/10.1038/ncomms15297]
10Iwasa, A. et al. Thermodynamic evidence of magnetic-field-induced complete valley polarization in bismuth. Scientific Reports 9, 1672 (2019). URL [https://doi.org/10.1038/s41598-018-38206-x]
11Shayegan, M., Goldman, V. J. & Drew, H. D. Magnetic-field-induced localization in narrow-gap semiconductors Hg_{1-x}Cd_{x}Te and InSb. Phys. Rev. B 38, 5585–5602 (1988).
12Kaufman, L. A. & Neuringer, L. J. Magnetic freezeout and band tailing in n-InAs. Phys. Rev. B 2, 1840–1846 (1970).
13Jaoui, A. et al. Giant seebeck effect across the field-induced metal-insulator transition of inas. npj Quantum Materials 5, 94 (2020). URL [https://doi.org/10.1038/s41535-020-00296-0]
14Aronzon, B. A. & Tsidilkovskii, I. M. Magnetic-field-induced localization of electrons in fluctuation potential wells of impurities. Physica Status Solidi (b) 157, 17–59 (1990).
15Moll, P. J. W. et al. Magnetic torque anomaly in the quantum limit of weyl semimetals. Nature Communications 7, 12492 (2016). URL [https://www.nature.com/articles/ncomms12492]
16Ramshaw, B. et al. Quantum limit transport and destruction of the weyl nodes in TaAs. Nature communications 9, 2217 (2018). URL [https://www.nature.com/articles/s41467-018-04542-9https://www.]
24 Galeski, S. et al. | "Origin of the quasi-quantized hall effect in ZrTe\textsubscript{5}" | Nature Communications 12, 3197 (2021). URL | https://doi.org/10.1038/s41467-021-23435-y

25 Tian, Y. et al. | "Gap-opening transition in dirac semimetal zrte\textsubscript{5}" | Phys. Rev. Lett. 126, 236401 (2021). URL | https://link.aps.org/doi/10.1103/PhysRevLett.126.236401

26 Liang, T. et al. | "Anomalous hall effect in ZrTe\textsubscript{5}" | Nature Physics 14, 451–455 (2018). URL | https://doi.org/10.1038/s41567-018-0078-z

27 Sun, Z. et al. | "Large zeeman splitting induced anomalous hall effect in zrte5. npj Quantum Materials 5, 36 (2020). URL | https://doi.org/10.1038/s41556-018-0078-z

28 Liu, Y. et al. | "Induced anomalous hall effect of massive dirac fermions in ZrTe\textsubscript{5} and HfTe\textsubscript{5} thin flakes. Phys. Rev. B 103, L201110 (2021). URL | https://link.aps.org/doi/10.1103/PhysRevB.103.L201110

29 Mutch, J. et al. | "Abrupt switching of the anomalous hall effect by field-rotation in nonmagnetic zrte\textsubscript{5} (2021). 2101.02681." | URL | https://arxiv.org/abs/2112.15227 arXiv2112.15227.

30 Lozano, P. M. et al. | "Anomalous hall effect at the lifshitz transition in ZrTe\textsubscript{5} (2021)." | URL | https://arxiv.org/abs/2112.15227

31 See Supplemental Material for more details on the samples, the comparison of quantum oscillations results, the thermal conductivity measurement, additional electrical thermoelectrical data sets and the determination of the dielectric constant.

32 Zhang, Y. et al. | "Electronic evidence of temperature-induced lifshitz transition and topological nature in zrte5. Nature Communications 8, 15512 (2017)." | URL | https://doi.org/10.1038/ncomms15512

33 Kamm, G. N., Gillespie, D. J., Ehrlich, A. C., Wieting, T. J. & Levy, F. | "Fermi surface, effective masses, and dingle temperatures of ZrTe\textsubscript{5} as derived from the shubnikov–de haas effect. Phys. Rev. B 31, 7617–7623 (1985)." | URL | https://link.aps.org/doi/10.1103/PhysRevB.31.7617

34 Izumii, M. et al. | "Shubnikov-de haas oscillations and fermi surfaces in transition-metal pentatellurides ZrTe5and HfTe5. Journal of Physics C: Solid State Physics 20, 3691–3705 (1987)." | URL | https://doi.org/10.1088/0022-3719/20/24/011

35 Zhu, Z., Faqu"c, B., Fuseya, Y. & Behnia, K. | "Angle-resolved landau spectrum of electrons and holes in bismuth. Phys. Rev. B 84, 115137 (2011)." | URL | https://journals.aps.org/prb/abstract/10.1103/PhysRevB.84.115137

36 Wang, J. et al. | "Vanishing quantum oscillations in dirac semimetal ZrTe\textsubscript{5}. Proceedings of the National Academy of Sciences 115, 9145–9150 (2018)." | URL | https://www.pnas.org/content/115/37/9145.full.pdf

37 Liang, T. et al. | "Evidence for massive bulk Dirac fermions in Pb\textsubscript{1−x}Sn\textsubscript{x}Se from Nernst and thermopower experiments. Nature communications 4, 2696 (2013)." | URL | https://www.nature.com/articles/ncomms3696

Publisher’s Note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
38. Mermin, N. D. & Wagner, H. Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic heisenberg models. *Phys. Rev. Lett.* 17, 1133–1136 (1966). URL https://link.aps.org/doi/10.1103/PhysRevLett.17.1133

39. Shahi, P. et al. Bipolar conduction as the possible origin of the electronic transition in pentatellurides: Metallic vs semi-conducting behavior. *Phys. Rev. X* 8, 021055 (2018). URL https://link.aps.org/doi/10.1103/PhysRevX.8.021055

40. Salzmann, B. et al. Nature of native atomic defects in ZrTe$_5$ and their impact on the low-energy electronic structure. *Phys. Rev. Materials* 4, 114201 (2020). URL https://link.aps.org/doi/10.1103/PhysRevMaterials.4.114201

41. Mott, N. F. & Davis, E. *Electronic Processes in Non-Crystalline Materials* (Oxford: Clarendon Press, 1971).

42. Mott, N. F. *Metal-insulator transitions* (Taylor & Francis, London, 1990), 2nd edition edn.

43. Shklovskii, B. I. & Efros, A. L. *Electronic properties of doped semiconductors* (Springer-Verlag, New York, 1984).

44. Martino, E. et al. Two-dimensional conical dispersion in ZrTe$_5$ evidenced by optical spectroscopy. *Phys. Rev. Lett.* 122, 217402 (2019). URL https://link.aps.org/doi/10.1103/PhysRevLett.122.217402

45. Dyakonov, M., Efros, A. & Mitchell, D. Magnetic freeze-out of electrons in extrinsic semiconductors. *Phys. Rev.* 180, 813–818 (1969). URL https://journals.aps.org/pr/abstract/10.1103/PhysRev.180.813

46. Chazalviel, J. N. & Solomon, I. Experimental evidence of the anomalous hall effect in a nonmagnetic semiconductor. *Phys. Rev. Lett.* 29, 1676–1679 (1972). URL https://link.aps.org/doi/10.1103/PhysRevLett.29.1676

47. Nozières, P. & Lewiner, C. A simple theory of the anomalous hall effect in semiconductors. *J. Phys. France* 34, 901–915 (1973). URL https://doi.org/10.1051/jphys:019730034010090100

48. Biernat, H. & Kriechbaum, M. Anomalous hall effect of n-InSb at high magnetic fields. *Physica Status Solidi (b)* 78, 653–657 (1976).

49. Behnia, K. *Fundamentals of thermoelectricity* (Oxford University Press, Oxford, 2015).

50. Skinner, B. & Fu, L. Large, nonsaturating thermopower in a quantizing magnetic field. *Science advances* 4, 2621 (2018). URL https://www.science.org/doi/10.1126/sciadv.aat2621

51. Fu, B., Wang, H.-W. & Shen, S.-Q. Dirac polarons and resistivity anomaly in ZrTe$_5$ and HfTe$_5$. *Phys. Rev. Lett.* 125, 256601 (2020). URL https://link.aps.org/doi/10.1103/PhysRevLett.125.256601

52. Wang, C. Thermodynamically induced transport anomaly in dilute metals ZrTe$_5$ and HfTe$_5$. *Phys. Rev. Lett.* 126, 126601 (2021). URL https://link.aps.org/doi/10.1103/PhysRevLett.126.126601

53. Mutch, J. et al. Evidence for a strain-tuned topological phase transition in ZrTe$_{5+y}$ Science Advances 5, eaav9771 (2019). URL https://www.science.org/doi/abs/10.1126/sciadv.aav9771

54. Zheng, G. et al. Transport evidence for the three-dimensional dirac semi metal phase in ZrTe$_5$. *Phys. Rev. B* 93, 115414 (2016). URL https://link.aps.org/doi/10.1103/PhysRevB.93.115414

55. Zhang, J. L. et al. Anomalous thermoelectric effects of ZrTe$_5$ and beyond the quantum limit. *Phys. Rev. Lett.* 123, 196602 (2019). URL https://link.aps.org/doi/10.1103/PhysRevLett.123.196602