Anomalous Hall effect in ZrTe$_5$

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Research in topological matter has expanded to include the Dirac and Weyl semimetals$^{1-10}$, which feature three-dimensional Dirac states protected by symmetry. Zirconium pentatelluride has been of recent interest as a potential Dirac or Weyl semimetal material. Here, we report the results of experiments performed by in situ three-dimensional double-axis rotation to extract the full 4π solid angular dependence of the transport properties. A clear anomalous Hall effect is detected in every sample studied, with no magnetic ordering observed in the system to the experimental sensitivity of torque magnetometry. Large anomalous Hall signals develop when the magnetic field is rotated in the plane of the stacked quasi-two-dimensional layers, with the values vanishing above about 60 K, where the negative longitudinal magnetoresistance also disappears. This suggests a close relation in their origins, which we attribute to the Berry curvature generated by the Weyl nodes.

Zirconium pentatelluride (ZrTe$_5$) has recently attracted considerable attention, following the observation of negative longitudinal magnetoresistance (LMR)$^{11}$. This negative LMR has been identified with the chiral anomaly$^{12-14}$ that is predicted to occur in Dirac and Weyl semimetals$^{1,2}$ and was recently observed in Na$_3$Bi and Cd$_3$As$_2$ (ref. 18). However, despite the observation of the negative LMR, there are no theoretical predictions showing that ZrTe$_5$ is a three-dimensional (3D) Dirac or Weyl semimetal, in contrast to both Na$_3$Bi (ref. 17) and Cd$_3$As$_2$ (ref. 18). Furthermore, the results of angle-resolved photoemission spectroscopy (ARPES) experiments$^{11,19-23}$ are not yet conclusive.

It is therefore of interest to investigate other unusual transport properties of ZrTe$_5$, especially the Hall response engendered by the Berry curvature. For Dirac and Weyl semimetals in an electric field $\mathbf{E}$, a finite Berry curvature leads to an anomalous velocity $\mathbf{v}_A = \mathbf{E} \times \Omega_k$, which produces the anomalous Hall conductivity

$$\sigma_{xy}^{AHE} = \sum n_{i,k} \Omega_{i,k}$$

where the index $i$ runs over the Weyl nodes, and $n_i$ is the occupation number in node $i$. Depending on the chirality $\chi_i$, $\Omega_{i,k}$ is directed either radially inwards or outwards. Close to the node at $\mathbf{k}_0$, the Berry curvature has a monopole form $\Omega_{i,k} = \chi_i \mathbf{k} / |\mathbf{k}|^3$, where $\Delta k = \mathbf{k} - \mathbf{k}_0$ (ref. 16). The anomalous Hall effect (AHE) arises even for non-magnetic systems. This is because, in $k$-space, the Weyl nodes behave as effective magnetic monopoles, generating strong Berry curvature $\Omega_k$ that acts like an effective magnetic field. To characterize ZrTe$_5$ in more detail, we have obtained the full 4π solid angular dependence of the anomalous Hall signals, that is $\Omega_k$, using in situ 3D double-axis rotation Hall measurements.

ZrTe$_5$ has an orthorhombic layered structure with space group $Cmm\bar{c}$ (inset in Fig. 1a). The ZrTe$_5$ triangular prisms (depicted as the red dashed lines) form one-dimensional chains of ZrTe$_5$, running along the $a$ axis. The chains are connected by additional Te ions, which also form zigzag chains along the $a$ axis and extend along the $c$ axis. As a result, they define quasi-two-dimensional layers that stack along the $b$ axis. As such, it is important to check that the AHE signal is not due to the quantum spin Hall state, while 3D bulk ZrTe$_5$ is predicted to lie near the boundary separating a weak topological insulator and a strong topological insulator$^{25}$. We studied 3D bulk crystals in our experiments.

The transport properties of ZrTe$_5$ were investigated with the current applied along the chain axis $a$. Figure 1a shows that the resistivity $\rho$ in our samples increases with decreasing temperature $T$ down to the lowest $T$, where $\rho$ saturates. Published resistivity curves$^{26,27}$ show resistivity profiles with maxima occurring at a temperature $T_m$ that varies from 135 K (ref. 26) to 65 K (ref. 27). $T_m$ can be systematically decreased by chemical pressure induced by substitution of rare earth elements$^{28}$. For our samples, $T_m \lesssim 5$ K. In ARPES experiments on samples with $T_m = 135$ K, multiple bands were observed at low $T$ (for example 35 K)$^{29}$. At a casual glance, this raises concerns that multiple bands may contribute to the AHE here. However, this is not the case for our samples, for which $T_m \leq 5$ K. The key difference is that while the samples with $T_m = 135$ K show two electron pockets at low $T$ (35 K), in our ZrTe$_5$ samples the ARPES measurements detect only a single hole pocket situated at $\Gamma$ (Fig. 1c).

Since our interest is in the AHE arising from $\Omega_k$ produced by Weyl nodes, it is important to check that the AHE signal is not associated with conventional ferromagnetism. For this purpose, we have performed torque magnetometry measurements. The results are shown in Fig. 1b for selected samples. No magnetic ordering is observed, confirming that the AHE in ZrTe$_5$, shown in Figs. 2–4, does not come from magnetism. This is as expected, since ZrTe$_5$ does not contain magnetic elements.

The first clue for a large Berry curvature in ZrTe$_5$ came from Hall measurements in sample Z2 with the magnetic field $\mathbf{H}$ lying in the
obtained from $6\theta$. However, plotted as a function of $H$ (the ordinary Hall term) from the curves in Fig. 2, $\theta$ lies within the $ab$ plane at selected $H$. Variations of $\theta$ angular dependence of the MR and Hall signals in sample Z2.

Fig. 1 | Resistivity, magnetization and ARPES spectrum of $\text{ZrTe}_5$. a, $\rho$ versus $T$ for $\text{ZrTe}_5$ (samples Z2, Z5 and ZQ3). As $T$ decreases from 200 K, $\rho(T)$ increases monotonically but approaches saturation below 20 K. The inset shows the crystal structure of $\text{ZrTe}_5$. b, Torque signal $r$ versus $H$ measured at 2.5 K (samples Z10, ZQ3 and ZQ4). The inset shows magnetization $r-H$. The quadratic behaviour of $r$ versus $H$ implies that the dominant contribution is either a paramagnetic or diamagnetic response. The absence of any anomaly in $r-H$ at weak $H$ rules out magnetic ordering in samples Z10 and ZQ3. In sample ZQ4 a weak anomaly is resolved, but it occurs below 0.3 T, whereas the AHE signal onsets above ~1 T. From the accumulated data in all samples, we conclude that the AHE signal and torque anomaly in ZQ4 are unrelated (all samples investigated show the AHE signal but ZQ4 is the only one to display a torque anomaly). c, ARPES data along a momentum cut parallel to the chain axis $a$, measured from the Fermi energy $E_F$, for sample ZA1 measured at $T=17$ K with incident photon energy of 6 eV. The ARPES spectrum reveals a single hole band.

$ab$ plane (Fig. 2). The resistivity $\rho_{xx}$ versus $H$ (Fig. 2a) displays a negative LMR in a narrow range of $\theta \leq 1^\circ$, where $\theta$ is the angle between $H$ and $a$. This confirms the results reported in ref. 11. Interestingly, the Hall resistivity $\rho_{yx}$ shows a very unusual zigzag profile, suggestive of an anomalous contribution (Fig. 2b). By subtraction of the high-field, linear positive background (the ordinary Hall signal of
When carefully aligned using a double-axis rotator, the out-of-plane (ab-plane) field. The evidence strongly supports a large Berry curvature arising from Weyl nodes.

To understand the in-plane Hall contribution, we made detailed measurements using a double-axis rotator to acquire the AHE signal in sample ZQ3 as a function of the angular variation of the Hall vector (r, θ, φ) where r is proportional to the angle between the ab-plane and the AHE signal, or effectively Ω⊥. When carefully aligned using the double-axis rotator, the out-of-plane (ab-plane) AHE signals are antisymmetric with respect to both H and φ (see Fig. 3a–c).

Next, we focus on the contribution from the in-plane component of H (in the ac plane). With H in plane and at an angle φ to a, we observe remarkably large AHE signals at each value of φ except when H∥a (φ = 0) (see Fig. 3d–f). The AHE contribution is much less sensitive to tilt angle, compared with the ab-plane experiment—its amplitude saturates rather gradually with increasing φ. We remark that this ‘true’ planar Hall signal is anomalous. It is rigorously antisymmetric in H as well as in φ. Obviously, the conventional Lorentz force cannot produce a Hall signal with H in plane. However, the experimental results show that there is a large contribution of the AHE, comparable to or even larger than that from out-of-plane (ab-plane) field. The evidence strongly supports a large Berry curvature arising from Weyl nodes.

We emphasize that the planar Hall signal described here is very different from the so-called ‘planar Hall effect’ Vθ, observed using transverse voltage probes in conventional, planar angular magnetoresistance (AMR) experiments on thin films of a ferromagnet or any high-mobility semimetal as H is rotated in the plane. In such AMR experiments, Vθ is strictly symmetric in H and hence is not a true Hall signal obeying Onsager’s theorem for the Hall conductivity σxy(H) = −σyx(−H). For clarity, we refer to the transverse voltage in AMR experiments as the ‘off-diagonal AMR’ signal.

Recent studies proposed the ‘planar Hall effect’ in Weyl systems. At first glance, their predictions seem relevant to our Hall results. However, this is not the case. The planar signal in refs 19,30 is strictly symmetric in H, and hence an example of an off-diagonal AMR signal, whereas the in-plane AHE signal uncovered in ZrTe5 is strictly antisymmetric in both H and φ.
The negative LMR and AHE in sample ZQ4. c, d. The AHE $\rho_{\text{AHE}}$ curves and Nernst $\Delta S_c$ curves, respectively, for sample Z5 at selected $\theta$ measured at 2.5 K (c) and 8 K (d). The variations of the AHE and Nernst signals versus $\theta$ are shown in the insets. The close similarities suggest that the two signals have the same origin.

Finally, the $T$ dependence of the AHE provides further evidence for the Weyl node origin (see Fig. 4). As shown in Fig. 4a, the negative LMR, suggestive of the chiral anomaly originating from the Weyl nodes, starts to become prominent below about 60 K. The AHE signal shows a similar onset—it is first resolved at 60 K, and then increases strongly as $T$ decreases to 2.5 K (Fig. 4b). The close correlation between the negative LMR and the AHE further supports the Weyl node origin of the AHE.

We briefly discuss the results of the anomalous Nernst effect (ANE) shown in Fig. 4c,d. Since the AHE is observed for ZrTe$_5$, it is natural to expect that the system also shows an ANE. The Nernst effect is often more sensitive to transverse currents than is the Hall signal. Figure 4c,d shows the angular dependence of the AHE and ANE for sample Z5. The close relation implies the same origin for the AHE and the ANE. For recent ANE work on Mn$_3$Sn, we refer the reader to ref. 16.

One potential scenario for Weyl nodes appearing in ZrTe$_5$ is that, since the energy gap $\Delta$ at the $\Gamma$ point is small, Weyl nodes can be induced when the time-reversal symmetry is broken by a large Zeeman energy under an applied magnetic field with strength $B$, which splits the bands at the $\Gamma$ point. When $\Delta = (g_v + g_c)\mu_B B/2$ is satisfied, the gap closes and the Weyl nodes appear. Here, $g_v$, $g_c$ are the $g$ factors for the valence and conduction bands, respectively. The other possibility is that, since ZrTe$_5$ is located near the boundary of a weak topological insulator and a strong topological insulator, if the inversion symmetry is broken in the system and there is a slight change in lattice parameter, the system automatically falls into a Weyl semimetallic phase, according to the general phase diagram proposed in earlier studies. The fact that the anomaly of the resistivity occurs at $T_c \leq 5$ K for our ZrTe$_5$ samples is suggestive of a subtle difference in doping or lattice constant in our samples compared with samples with $T_c = 135$ K. Because the inversion-symmetry-broken Weyl states contain at least four Weyl nodes, or two kinds of Weyl pair, it would be interesting to investigate how they respond to an applied magnetic field. Our results indicate that exploring whether the inversion symmetry is broken in ZrTe$_5$ and how the Weyl nodes appear would be interesting directions to pursue in future research.

Methods
Methods, including statements of data availability and any associated accession codes and references, are available at https://doi.org/10.1038/s41567-018-0078-z.
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Methods

Three-dimensional full 4π solid-angular-dependent transport measurements were made using a standard six-contact method with a home-made double-axis rotator installed on a commercial Physical Property Measurement System (PPMS, manufactured by Quantum Design, Inc.). In the main text, we take axis $a$, $c$, and $b$. The high-momentum-resolution laser-ARPES measurements were carried out using a Scienta R4000 electron analyser and 6.0 eV ultraviolet light generated from a Ti:sapphire oscillator with photon energy quadrupling through two stages of second-harmonic generation. The energy, angular and momentum resolutions for this set-up are 10 meV, 0.3° and 0.004 Å$^{-1}$, respectively. Samples were cleaved in situ at a base pressure lower than $5 \times 10^{-11}$ torr. ARPES measurements at beamline 5-4 at the Stanford Synchrotron Radiation Lightsource (SSRL) in the Stanford Linear Accelerator Center were made with 9 eV incident photon energy. Samples were cleaved in situ between 10 and 20 K at a chamber pressure lower than $5 \times 10^{-10}$ torr.

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.