Quantized Photocurrents in the Chiral Multifold Fermion System RhSi

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The rapid pace of discovery of new classes of Weyl semimetals is driving a search for properties that derive from their unique bandstructure topology. One of the most striking of the predicted properties is the quantized circular photogalvanic effect (QCPGE), whereby excitation of Weyl fermions by helical photons generates a current that is quantized in units of material-independent fundamental constants over a range of photon energies. Although this remarkable result was initially derived for the simplest case of a two-band crossing, it was later shown to apply to more complex multifold fermion band crossings, where the photocurrent is actually enhanced by larger topological charges. Real materials that exhibit this property are difficult to find in practice as the QCPGE requires that Weyl nodes with opposite topological charge, and hence oppositely directed photocurrent, lie at different energies. This condition in turn dictates that the host crystal must break all mirror symmetries and
therefore be chiral. Here we report measurements of photocurrent in the multifold chiral semimetal RhSi that confirm the unique aspects of the predicted multifold fermion response. Specifically, the photocurrent spectrum displays a prominent, mesa-like structure, in which a frequency-independent plateau at low photon energy abruptly falls-off above 0.66 eV, precisely the energy at which the bandstructure indicates the onset of cancelling photocurrent from Weyl nodes of opposite topological charge. The magnitude of photocurrent on this mesa is consistent, within errors arising from indirect estimation of the current relaxation time, with the value expected from quantization, suggesting that RhSi is the first material to support a quantized injection photocurrent of topological origin.

Soon after Dirac discovered his celebrated equation describing a relativistic electron, Hermann Weyl pointed out (1) in 1929 that a massless particle could have a simpler description because the particle’s helicity or handness was a constant, independent of reference frame. Although such Weyl fermions were ruled out as fundamental Standard Model particles after the discovery of neutrino masses, an analogue appears in certain semimetals in which spin-polarized bands cross in momentum space. (2) These crossing points (or Weyl nodes) act as monopoles of Berry curvature and a theorem for periodic systems due to Nielsen and Ninomiya requires the total monopole charge in the Brillouin zone to be zero. (3) As a result of this constraint, Weyl nodes cannot be gapped independently and are thus topologically protected.

In recent years, the existence of Weyl nodes and their associated Fermi arc surface states (4) have been extensively verified by angle-resolved photoemission spectroscopy. (5) The future goal of research in these systems is to understand the role their distinct band-structure topology plays in shaping responses to external perturbations. (6) This requires distinguishing the properties associated directly with topology from those primarily determined by symmetry. The
issue arises because topology and symmetry are inextricably linked in Weyl semimetals, as the existence of Berry curvature requires either inversion or time-reversal symmetry to be broken. The second order optical response, that is a current proportional to the square of an applied ac electric field, is allowed only in media that break inversion symmetry. The photogalvanic effects, which are the subject of this paper, are examples of second-order responses in which light generates a dc current proportional to the intensity of the field. In the circular photogalvanic effect (CPGE) the direction of the induced photocurrent depends on the helicity the electromagnetic wave, whereas the sign of the linear photogalvanic effect (LPGE) depends on the plane of polarization. (7)

While symmetry considerations determine whether a specific transport or optical response is allowed in a material, topology manifests in topological phases such as the quantum Hall effect as quantization of the response in units of fundamental constants, or universality with respect to parameters such as temperature and frequency. The possibility of interesting behavior in the CPGE at linear band crossings was discussed by Hosur (8) in the context of Dirac surface states in 3D topological insulators (TIs). Although the photocurrent was shown to vanish in the inversion symmetric TIs, the theory implies that a non-quantized contribution to the CPGE would arise from each of the band crossings in TIs that break inversion. However, it was subsequently recognized that this direct signature of topology is hidden by mirror symmetries that require nodes of opposite monopole charge to exist at the same energy. As a consequence, the net CPGE from a system of degenerate nodes with perfect Dirac conical dispersion vanishes because of overall Berry charge neutrality. (9)

Despite the cancellation that emerges in the case of Dirac dispersion, CPGE has been observed in inversion breaking, non-chiral Weyl semimetals such as TaAs. (10–13) This nonzero CPGE is a consequence of the departures from symmetric dispersion that occur in real materials, for example curvature or tilting of the Dirac cones. (9) Thus, in such systems the CPGE
Fig. 1. Photocurrents from Weyl semimetals and experimental apparatus. (A) Helical radiation preferentially excites one side of a Weyl cone centered at the Fermi energy, generating a current parallel to the optical wavevector. (B) Schematic band structure showing two nondegenerate Weyl nodes with opposite chirality and hence opposite sense of photocurrent. If one node is well below the Fermi surface, excitation with low energy photons (short arrows) is Pauli blocked and a quantized photocurrent is generated by the other node. Above a threshold energy (long arrows) excitation of both cones becomes allowed, leading to cancellation of the net current. (C) Schematic of the experimental geometry. Variable wavelength pump light is incident on the sample at either normal or $45^\circ$ incidence. Terahertz radiation is collected and focused onto a ZnTe crystal for electro-optic sampling. PD, WP, and WGP refer to photodiode, Wollaston prism, and wire grid polarizer, respectively.
amplitude is not a universal topological property uniquely related to the Berry monopole charge.

The Weyl physics in chiral crystals, in which all mirror symmetries are broken, is qualitatively different from polar, inversion breaking materials such as TaAs. In chiral structures, isolated Weyl nodes can occur at time-reversal invariant momenta. As a result, they can be separated by wavevectors on the order of the full Brillouin zone, allowing for a richer structure of Fermi arc surface states. (14–16) Of more direct relevance to the CPGE, Weyl nodes with opposite topological charge need not be degenerate in energy. Thus, for example, it is possible for one node to be near the Fermi energy, $E_F$, while its oppositely charged partner is below. Transitions near the node below $E_F$ are Pauli blocked at sufficiently low photon energy, and the quantized photocurrent arising from the Weyl node near $E_F$ will dominate.

Recently de Juan et al. (17) predicted that the amplitude of the CPGE in chiral Weyl semimetals is directly proportional to topological charge through the fundamental constants $e$, $\pi$, $h$. In a non-interacting system this result is independent of material-specific properties and the frequency of the excitation light in the region of the spectrum in which Pauli blocking occurs. More precisely, it is the total rate of current generation by circularly polarized light that is quantized, which is described by the equation,

$$\frac{d\vec{j}_i}{dt} = i\pi \frac{e^3}{\hbar^2} C \hat{\beta}_{ij}(\omega) [\hat{\mathbf{E}}(\omega) \times \mathbf{E}^*(\omega)]_j$$

where $\text{Tr} \hat{\beta}_{ij} = 1$ and $C$ is the monopole charge (or Chern number). (17) As we discuss more fully in the summary, the magnitude of the quantized photocurrent is sufficiently large to have potential applications to photodetectors and related photonic devices in the terahertz and far-infrared regions of the spectrum.

Chiral semimetals can host multiple band crossings with monopole charges $C$ larger than one. Despite higher multiplicity and band curvature in these multifold fermion systems, it was show (15, 18) that CPGE quantization continues to hold. Further, the magnitude of the CPGE is
Fig. 2. Symmetry of CPGE and LPGE responses in RhSi. (A) Individual terahertz pulses measured from left- and right-circularly polarized 2000 nm pump light at 45° angle of incidence. Their difference is the photon-helicity-dependent CPGE signal. (B) Measurement of the THz polarization. Orange and green curves show the vertically and horizontal components of the pulse as a function of time. The reconstructed THz pulse (red) curve is then projected onto a plane, showing the direction of linear polarization, θ. (C) Dependence of the angle of LPGE terahertz polarization, θ, on angle of rotation of [111] face about the surface normal, φ, with pump at normal incidence. The relation θ = 3φ predicted by the space group P213 symmetry is confirmed. The CPGE signal is below measurement noise level in this geometry. (D) Same as (C) except 45° incidence. LPGE polarization again varies as θ = 3φ. CPGE is horizontally polarized independent of the crystal orientation confirming that the CPGE current is parallel to the pump wavevector.
enhanced for multifold compared to Weyl fermions because of the greater topological charge.

Figs. 1A and 1B illustrate the mechanism for generation of a photocurrent by circularly polarized light in a Weyl semimetal. Photons with definite helicity selectively induce transitions that flip the direction of electron spin. Because of spin-momentum locking in Weyl bands, the spin-dependent transition rate leads to an asymmetric particle-hole distribution in momentum space that carries a net current in the direction of the helicity vector. This physical picture leads to a relatively simple argument for CPGE quantization. The rate at which electron-hole pairs are created is proportional to $\sigma_1(\omega)E^2/\hbar\omega$, where $\sigma_1$ is the real part of the optical conductivity. This quantity multiplied by $e v_F$ yields the photocurrent generation rate. When the theoretical optical conductivity corresponding to transitions across a Weyl node (19),

$$\sigma_1(\omega) = \frac{e^2}{12\hbar} \frac{\omega}{v_F}$$

is substituted, the factors of $\omega/v_F$ cancel, leading to a frequency-independent and universal rate of photocurrent generation.

RhSi is a structurally chiral material predicted to host multifold fermions and exotic Fermi arcs, (15, 16) predictions that were recently confirmed by ARPES measurements. (20) RhSi is an ideal candidate to search for the QCPGE because the dimensionless anisotropy tensor $\hat{\beta}_{ij}$ reduces to the diagonal matrix with components $(1/3, 1/3, 1/3)$ in its cubic space group $P2_13$ ($\#198$). In order to observe the universal quantized photogeneration rate, the pump photon energies must lie in the Pauli blocking regime, which for RhSi is predicted to onset below about 0.70 eV. (18)

A schematic of the apparatus for generation and detection of the CPGE is shown in Fig. 1C. The excitation source for our measurements was an optical parametric amplifier (OPA) system pumped by an amplified Ti:Sapphire laser, producing wavelength tunable pulses from 1200-2600 nm (0.48-1.0 eV) and duration approximately $\sim$100 fs. Photogalvanic current generated
Fig. 3. **CPGE spectrum and optical conductivity.** (A) CPGE amplitude in units of effective Chern number as a function photon energy showing plateau at low energy and abrupt quenching above photon energy 0.66 eV. Chern number 1 corresponds in engineering units to $\beta = 1.1 \times 10^{-2} \,(\Omega \cdot \text{V} \cdot \text{ps})^{-1}$. Inset shows the theoretical band structure (from Ref. (18)) with Weyl nodes at $\Gamma$ and $R$. The optical transition highlighted by the arrow marks the onset of Pauli blocking. CPGE is predicted to be quantized below this energy. (B) Circles show the real part of the optical conductivity, $\sigma_1$, as measured by laser ellipsometry. Red line is a fit to the theoretical optical conductivity from a Weyl cone with Fermi velocity $v_F = 3.3 \times 10^5 \, \text{m/s}$, multiplied by four to account for the multifold degeneracy of the $\Gamma$ point in RhSi.

at the surface of the RhSi crystal radiates a THz pulse into free space that is collected and collimated by an off-axis parabolic (OAP) mirror and then focused onto a ZnTe crystal for time-resolved electro-optic sampling of the THz transient. This all-optical technique avoids artifacts from asymmetric electrical contacts and laser-induced heating, and enables precise determination the direction of the current through measurement of the THz polarization.

The selection rules and polarization properties of photogalvanic currents in RhSi under linear and circular polarized excitation are summarized in Fig. 2. Panel 2A shows the sign reversal of the THz transient that occurs when the helicity of the light is reversed, which is the signature of the CPGE. To test that the directions of LPGE and CPGE currents are consistent with the RhSi space group, we measured THz emission from the [111] surface as a function of angle of
rotation, $\phi$, of the sample about the surface normal. Measurements were performed at normal and 45° angle of incidence. At normal incidence, THz emission was observed when the pump was linearly polarized, but was undetectable for circularly polarized pump light. However, at 45° angle of incidence THz emission appeared under circularly polarized excitation as well.

To fully characterize the polarization state of the THz radiation we used a linear polarizer placed before the ZnTe detector in order to measure the horizontal and vertical components of the electric field. Fig. 2B shows a typical result of the THz electric field resolved into its two orthogonal components. Using this method, we found that the LPGE emission is linearly polarized and its amplitude is independent of $\phi$. The direction of the LPGE electric field, $\theta$, rotates such that $\theta = 3\phi$, consistent with the 3-fold rotational symmetry of the [111] surface and in agreement with theoretical prediction based on the second-order susceptibility tensor for space group $P2_13$ (Fig. 2C and 2D).

The CPGE emission observed at 45° incidence is also linearly polarized, but its plane of polarization is locked to the plane of incidence as the sample is rotated (Fig. 2D), in contrast to the LPGE emission. However, this result is also consistent with symmetry because, as mentioned above, $\hat{\beta}_{ij}$ defined in Eq. 1 is diagonal and proportional to the unit tensor in $P2_13$ structures. Thus the CPGE current is proportional to a single scalar coefficient and directed parallel to the photon helicity, obeying the relation, $j \propto \beta(E \times E^*)$ regardless of crystal orientation. The observation of zero CPGE at normal incidence follows because $j$ is now perpendicular to the surface, and the electric dipole radiation does not escape the RhSi crystal. By contrast, excitation at oblique incidence generates a component of $j$ parallel to the surface that can couple to free space, and whose plane of polarization is parallel to the plane of incidence regardless of crystal orientation.

Having confirmed that the polarization selection rules are consistent with crystal symmetry, we turn to spectral properties of the multifold fermion system related to Weyl semimetal topl-
Fig. 3A shows that the dependence of the CPGE amplitude on pump photon energy is in striking agreement with the theoretical prediction. The amplitude increases rapidly, by a factor of 150, as the photon energy decreases from 1.1 to 0.66 eV. It then abruptly reaches a plateau that persists to the lowest energy of the measurement range, 0.5 eV. The inset shows the calculated bandstructure for RhSi (15, 18), highlighting that the photon energy where the CPGE from the Weyl node at $\Gamma$ is quenched (0.66 eV) matches the energy at which Pauli blocking no longer inhibits excitation of the Weyl node at $R$.

Above, we have demonstrated that the direction, polarization, and spectrum of the CPGE in RhSi are in agreement with the theoretical nonlinear response of a Weyl node in a chiral semimetal. Next, we turn to a comparison of the CPGE amplitude with the predictions of universality and quantization. As we discuss below, we find that the amplitude of the CPGE in RhSi is consistent with theory, but it is not at present possible to demonstrate quantization with the precision achieved in the quantum Hall effects, for example. The primary reason is that quantization does not apply directly to the photocurrent, but instead the rate of photocurrent generation, $dj/dt$. As a result, $j$ depends on the momentum relaxation time, $\tau$, as well as the quantized prefactor. Although in principle $\tau$ can be determined from the time-dependence of the photocurrent transient, in practice this requires that $\tau$ exceeds the excitation pulse width, $T$. However, carrier dynamics in RhSi are in the opposite regime, $\tau \ll T$. The evidence for this comes first from the fact that the CPGE waveform is identical to that of LPGE, which is instantaneous on the scale of the 100 fs laser pulse. (21) Furthermore, $\tau \ll T$ is independently confirmed by dc conductivity and Hall effect measurements, which yield $\tau = 2.6$ fs (see supplementary materials for details).

Although we cannot perform a precise test of quantization, we have determined that the steady-state current, $\tau(dj/dt)$, is consistent with theory. The factors that enter the conversion of photocurrent generated in RhSi to the amplitude of the electro-optic signal are described in
detail in supplementary materials. The calibration takes into account the impedance mismatch for THz radiation between RhSi and free space, the Fresnel coefficients at the pump wavelength, the collection and focusing efficiency of the OAP mirrors, and the electro-optic coefficient of the ZnTe detection crystal. To determine the Fresnel coefficients we used laser ellipsometry to measure the complex linear optical conductivity. The real part, $\sigma_1$, plotted in Fig. 3B, agrees with the theoretical prediction for photoexcitation across a Weyl node.

The vertical scale on Fig. 3A indicates the CPGE amplitude converted to effective Chern number, based on the above factors and $\tau = 2.6$ fs. The value at the plateau is seen to correspond to $C \approx 3.5$, which is quite close to the predicted value of 4. (15, 18) However, as standard propagation of errors analysis shows that the calibration is reliable only to within a factor of two, this result should be taken as a demonstration of consistency with, rather than confirmation of quantization. It is nevertheless striking that the scale of the CPGE amplitude in RhSi is given by the simple combination of fundamental constants $e^3/h^2$.

Finally, the experimental demonstration of a CPGE amplitude consistent with theory is potentially important for photodetection and sensing applications. As a benchmark, we consider a unity gain photodetector, in which one electron is collected in the external circuit for each photon absorbed. The gain of a CPGE photodetector relative to this benchmark is given by $\alpha C \omega \tau / 3$, where $\alpha$ is the fine structure constant. Clearly, maximizing $\tau$, the only relevant material parameter, is crucial to the potential performance of devices based on CPGE. Our results suggest that broadband, unity gain photodetectors in the THz and infrared range can be realized values if momentum lifetimes greater than 1 ps can be achieved through crystal purification and cooling below room temperature.
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Supplementary Materials

Crystal Growth and Structure Refinement

Single crystals of RhSi were grown from a melt using the vertical Bridgman crystal growth technique. Here the crystal growth was performed with an off-stoichiometric composition with slightly excess Si. First, a polycrystalline ingot was prepared using the arc melt technique with the stoichiometric mixture of Rh and Si metal pieces of 99.99 % purity. Then the crushed powder was filled in a custom-designed sharp-edged alumina tube and finally sealed inside a tantalum tube with argon atmosphere. The temperature profile for the crystal growth was controlled with a thermocouple attached at the bottom of the tantalum ampoule containing the sample. The sample was heated to 1500°C and then slowly cooled to cold zone with a rate of 0.8 mm/h. Single crystals with average dimension of ∼15 mm length and ∼6 mm diameter were obtained. A picture of the grown crystal is shown in the inset of Fig. S1. The crystals were analyzed with a white beam backscattering Laue X-ray diffraction technique at room temperature. The samples show very sharp spots that can be indexed by a single pattern, revealing excellent quality of the grown crystals without any twinning or domains. A Laue diffraction pattern of the oriented RhSi single crystal superposed with a theoretically simulated pattern is presented in Fig. S1. The structural parameters were determined using a Rigaku AFC7 four-circle diffractometer with a Saturn 724+ CCD-detector applying graphite-monochromatized Mo-Kα radiation. The crystal structure was refined to be cubic P2₁3 (#198) with lattice parameter, a=4.6858(9) Å.

Material Symmetries

1. Nonlinear Tensor in the [111] basis

The second-order optical nonlinearity generates currents at both the sum and difference frequencies of the applied electric field. LPGE and CPGE correspond to the current generated at
Fig. S1. Crystal Growth and Diffraction. Laue diffraction pattern of a [111] oriented RhSi single crystal superposed with a theoretically simulated pattern. Inset shows picture of the grown RhSi single crystal.

the difference frequency,

$$j_i \propto \sigma_{ijk} E_j E_k^*$$  \hspace{1cm} (3)

For cubic space group $P2_13$ the only nonvanishing elements of $\sigma_{ijk}$ have indices $xyz$ and permutations. The elements with even permutations of $xyz$ are equal to $\sigma_{xyz}$ and odd permutations are equal to $\sigma_{x'yz'}$. If we write $\sigma_{xyz} = \alpha + i\gamma$ where $\alpha$ and $\gamma$ are both real, the structure of the third rank tensor can be displayed in the form,

$$\sigma^{(2)}_{xyz} = \begin{pmatrix}
  0 & 0 & 0 \\
  0 & \alpha - i\gamma & \alpha + i\gamma \\
  0 & \alpha + i\gamma & \alpha - i\gamma \\
\end{pmatrix}$$

(4)
where the element $\sigma_{ijk}$ is the $k$th element of the column vector in the $i$th row and $j$th column of the matrix.

2. Transformation properties of the CPGE

The circular photogalvanic current can be written in terms of the photon helicity,

$$j_i = \beta_{ij}(E \times E^*)_j.$$  \hspace{1cm} (5)

The second rank CPGE tensor is contracted from the third-rank conductivity tensor according to the relation,

$$\beta_{ij} = \sigma_{ikl} \epsilon_{jkl},$$ \hspace{1cm} (6)

where $\epsilon_{jkl}$ is the unit antisymmetric tensor. Substitution of the conductivity tensor for the RhSi space group (Eq. 2) yields,

$$\beta_{ij} = i \beta \delta_{ij},$$ \hspace{1cm} (7)

where $\delta_{ij}$ is the Kronecker delta. Substitution into Eq. 3 yields,

$$j = i \beta E \times E^*,$$ \hspace{1cm} (8)

which shows that for the case of space group $P2_13$ the CPGE current is always directed parallel to the helicity vector, regardless of its direction with respect to the crystal axes.
3. LPGE sample rotation dependence

We use Rodrigues’ formula to transform this tensor into the basis where $z'$ is parallel to the [111] direction in the crystal basis, which yields

$$
\sigma^{(2)} \propto \left[ \begin{array}{ccc}
-\alpha \sqrt{2} & 0 & -\alpha \\
0 & \alpha \sqrt{2} & -i \gamma \sqrt{3} \\
-1 & i \gamma \sqrt{3} & 0 \\
\end{array} \right] \left[ \begin{array}{ccc}
-\alpha & 0 & -\alpha \\
0 & \alpha \sqrt{2} & 0 \\
-1 & 0 & \sqrt{3} a \\
\end{array} \right] \left[ \begin{array}{ccc}
-i \gamma \sqrt{3} & 0 & 0 \\
0 & 0 & 0 \\
-i \gamma \sqrt{3} & 0 & 0 \\
\end{array} \right] \left[ \begin{array}{ccc}
\alpha \sqrt{2} & 0 & \alpha \\
0 & \alpha \sqrt{2} & 0 \\
0 & 0 & 2 \alpha \\
\end{array} \right].
$$

Using this tensor we can calculate the LPGE response for fixed linear pump polarization as the crystal is rotated about the $z'$ (or [111]) axis. The crystal rotation corresponds to the transformation $\sigma'_{\alpha \beta \gamma} = R_{\alpha i} R_{\beta j}(\phi) R_{\gamma k}(\phi) \sigma_{ijk}$, where,

$$
R(\phi) = \left[ \begin{array}{ccc}
\cos(\phi) & \sin(\phi) & 0 \\
-\sin(\phi) & \cos(\phi) & 0 \\
0 & 0 & 1 \\
\end{array} \right].
$$

If, for example, the pump polarization is fixed in the $x'$ direction, then the LPGE current depends only on the tensor elements $\sigma'_{xxx}$ and $\sigma'_{yxx}$ and from Eqs. 7 and 8 we have,

$$
\sigma'_{xxx} = R^3_{xx} \sigma_{xxx} + R_{xx} R^2_{xy} \sigma_{xyy} + R_{xy} R_{xx} \sigma_{yxy} + R^2_{xy} R_{xx} \sigma_{yyx} \\
\propto \left( -\sqrt{2} \cos^3(\phi) + 3 \sqrt{2} \cos \phi \sin^2 \phi \right) = -\sqrt{2} \cos(3\phi)
$$

and

$$
\sigma'_{yxx} = R_{yx} R^2_{xx} \sigma_{yxx} + R_{yx} R^2_{xy} \sigma_{xyy} + R_{yy} R_{xx} \sigma_{yxy} + R_{yy} R_{xy} R_{xx} \sigma_{yyx} \\
\propto \left( -3 \sqrt{2} \cos^2 \phi \sin \phi - \sqrt{2} \sin^3 \phi \right) = \sqrt{2} \sin(3\phi).
$$

From Eqs. 9 and 10 we obtain the dependence of the LPGE current on crystal rotation angle,

$$
j(\phi) \propto \cos(3\phi) \hat{x}' - \sin(3\phi) \hat{y}'.
$$
Eq. 11 implies that the angle, $\theta$, of the LPGE current relative to the $x'$ axis is given by $\theta = 3\phi$. This is consistent with what is observed and shown in Fig. 2 C and D in the main text.

**Material Properties**

1. **Scattering time ($\tau$)**

We performed resistivity and Hall measurements on RhSi at room temperature, obtaining the dc conductivity $\sigma = 3.6 \times 10^3 \ \Omega^{-1} \mathrm{cm}^{-1}$ and carrier density $n = 1.62 \times 10^{21} \ \mathrm{cm}^{-3}$. Assuming Weyl dispersion, these measurements can be combined to yield a value for $v_F \tau$, the product of the Fermi velocity and the momentum lifetime, respectively. The conductivity is given by,

$$\sigma = N_F e^2 D = \frac{4\pi}{3\hbar} e^2 k_F^2 v_F \tau,$$

(14)

and the carrier density is,

$$n = \frac{4\pi}{3} k_F^3.$$

(15)

Solving for $v_F \tau$ we have

$$v_F \tau = \left( \frac{3}{4\pi n^2} \right)^{1/3} \frac{\sigma}{e^2/\hbar}.$$

(16)

Based on the band structure reported in Flicker et al. (18) we estimate the Fermi velocity to be $v_F = 2.5 \times 10^5 \ \mathrm{m/s}$. Substituting this value into Eq. 14 yields $\tau = 2.6 \ \mathrm{fs}$.

2. **Terahertz index of refraction**

The complex index of refraction at THz frequencies determines the impedance mismatch between RhSi and free space. We can obtain an accurate estimate of $\tilde{n}$ from the dc conductivity. Given the value of $\tau$ determined in the previous section, the THz emission lies in the low frequency limit of the optical conductivity, where $\omega \tau \ll 1$ and $\sigma(\omega) \rightarrow \sigma_{dc}$. In this regime, the complex permittivity at low frequency is

$$\tilde{\epsilon}(\omega) = -\frac{\tilde{\sigma}(\omega)}{i\omega} = \frac{i\sigma_{dc}}{\omega},$$

(17)
The complex index of refraction is then given as,

\[ \tilde{n} \equiv n + i\kappa = \sqrt{\frac{\tilde{\varepsilon}(\omega)}{\epsilon_0}} = (1 + i)\sqrt{\frac{\sigma_{dc}}{2\epsilon_0\omega}} = 57(1 + i). \]  \hspace{1cm} (18)

3. Near infrared optical conductivity

We used laser ellipsometry to measure \( n \) and \( k \) at several frequencies. Using the formula

\[ \frac{\sigma_1}{\omega\epsilon_0} = 2n\kappa. \]  \hspace{1cm} (19)

we determined the real part of the optical conductivity of RhSi at the wavelengths used to excite the photogalvanic currents. We then compare that data to the theoretical prediction for a Weyl cone, \( \sigma(\omega) = g \frac{e^2}{12\hbar v_F} \omega \) where \( g \) is the degeneracy of the bands. In the absence of a general formula for multifold fermions, this is a useful prediction to compare with our measurements.

Relating the detected electro-optic signal to current density in the sample

1. Introduction

In this section we describe the system calibration function, which allows us to convert from THz current generated in the RhSi crystal to signal from the electro-optic detector. The analysis requires the following:

1. Determination of the electric field at the surface of the sample that arises from a photogenerated surface current.

2. The frequency-dependent transfer function of the collection optics that quantifies the propagation of the field from the sample surface to the ZnTe detection crystal.

3. Conversion of the electric field at the ZnTe surface crystal to signal at the output of the biased photodetector scheme.
In step 1 we calculate the electric field at the surface of the RhSi as function of time, which is dependent on laser parameters such as power and focal width, and the CPGE factor $\beta$. In step 2 we Fourier transform this pulse and multiply the resulting spectrum by $\mathcal{F}_{\text{corr}}(\nu)$ and $\mathcal{F}_{\text{coll}}(\nu)$. The product of these filter functions describes the collection, collimation, and refocusing of the THz emission onto the ZnTe detection crystal. In step 3, we first calculate an inverse Fourier transform to yield the electric field arriving at the ZnTe as a function of time. Finally, we use the linear and electro-optic coefficients of ZnTe to convert this electric field to the detected signal, $\Delta V/V$, based on our biased photodetector scheme. By calibrating our detection system as described above, we can reverse the steps to convert the measured $\Delta V/V$ signal to a value for $\beta$ in RhSi. As reported in the main text, based on the theoretical prediction that $\beta = \frac{\pi}{3} \frac{e^3}{h^2} C$, we find a best fit estimate $C = 3.5$.

2. Surface electric field

In the near-field the electric field at the sample surface is determined from the boundary conditions. We assume a current density that decays exponentially with depth below the sample surface, $z$, according to $J(z) = J_0 e^{-\alpha z}$, where $\alpha$ is the (power) attenuation coefficient at the pump wavelength. The contribution to the electric field from a slab of thickness $dz$ is given by

$$E^{THz}(z) = \frac{Z_0}{Z_{THz}} J_0 e^{-\alpha z} dz.$$  (20)

In escaping the sample and reaching the vacuum above, the electric field propagates a distance $z$ and crosses the interface. The propagation factor can be neglected because $\alpha^{-1}$ is much less than both the wavelength and the attenuation length of THz radiation. Taking into account the Fresnel transmission coefficient for THz waves at the interface and integrating over the depth yields the THz field just above the sample surface,
\[ E_{0}^{\text{THz}} = \frac{Z_{0}J_{0}/\alpha}{\bar{n}_{\text{THz}}(\bar{n}_{\text{THz}} + 1)}. \] (21)

We note that this result is equivalent to the Bloembergen-Pershan formula for second-harmonic generation in reflection, adapted to THz generation.

To compare theory and experiment, we compute the value of \( J_{0} \) expected from the prediction of a quantized circular photogalvanic effect (QCPGE). We start with the rate equation for CPGE,

\[ \frac{dJ}{dt} = \beta E^{2} - \frac{J}{\tau}, \] (22)

where \( 1/\tau \) is the momentum scattering rate, \( \beta \) is the CPGE coefficient, and \( E \) is the electric field of the pump laser. For a cubic crystal the theoretical prediction is,

\[ \beta = \frac{\pi e^{3}}{3 h^{2} C}. \] (23)

where \( C \) is the Berry monopole charge.

At normal incidence the electric field of the pump laser at the surface of the sample is given by

\[ E(r, t) = E_{0}e^{-r^{2}/r_{0}^{2}}e^{-t^{2}/T^{2}} \] (24)

where \( T \) is the pulse duration and \( r_{0} \) is radius of the pump beam at the focus. The next step is to express \( E_{0} \) in terms of the measured laser parameters: average power \( P \), repetition rate \( f \), \( r_{0} \), and \( T \). Integrating the laser intensity over space and time yields the relation

\[ E_{0}^{2} = \frac{2PZ_{0}}{\pi \sqrt{\pi f T r_{0}^{2}}}, \] (25)

where we include a factor of 1/2 to account for 45° angle of incidence. As the momentum scattering lifetime \( \tau \) is much shorter than the laser pulse duration, the CPGE current is given by the steady-state limit of Eq. 22, or

\[ J_{0} = \beta E_{0}^{2} \tau_{s} t_{p} \sin \theta_{in}, \] (26)
where $t_p$ and $t_s$ are the Fresnel transmission coefficients for $s$ and $p$ polarized fields, respectively, at the pump wavelength. These coefficients are functions of the complex index of refraction, which is determined from laser ellipsometry measurements described earlier. The sine of the angle of propagation in the medium, $\theta_{\text{in}}$, appears because the radiated electric field is proportional only to the component of $\mathbf{J}$ that is tangential to the surface. Substituting Eq. 26 into Eq. 21 yields

$$E_{0}^{\text{THz}} = \frac{Z_0 E_0^2 \beta t_s t_p \sin \theta_{\text{in}}}{\alpha \tilde{n}_{\text{THz}} (\tilde{n}_{\text{THz}} + 1)},$$

which using Eq. 25 gives the THz electric field amplitude as a function of pump laser power,

$$E_{0}^{\text{THz}} = \frac{2P Z_0^2 \beta t_s t_p \sin \theta_{\text{in}}}{\pi \sqrt{\pi} \alpha f \tau_0^2 \tilde{n}_{\text{THz}} (\tilde{n}_{\text{THz}} + 1)}.$$

3. Radiation from the photoexcited region

The THz radiation emitted by the sample is collected by a $45^\circ$ OAP which collimates the beam. A second OAP then focuses it onto a ZnTe electro-optic sampling (EOS) crystal. Longer wavelengths radiated from the sample diverge more strongly and focus less tightly than shorter ones.
The resulting wavelength (or frequency) dependent transfer function, $F_{\text{coll}}(\nu)$ relating EOS signal detector to the THz radiation was shown by Côté et al. (22) to be

$$F_{\text{coll}}(\nu) = \text{erf}^2 \left( \frac{2\pi \nu L r_0}{f_1 c} \right),$$

(29)

where $\nu$ is frequency, $L = 25.4$ mm and $f_1 = 101.6$ mm are the radius and focal length of the OAPs, respectively. A plot of $F_{\text{coll}}(\nu)$ for the parameters our setup is shown in Fig. S2.

The treatment of Ref. (22) assumes that the first OAP is centered on the axis defined by the surface normal. In our experimental configuration, the radiation propagates at $45^\circ$ relative to this OAP, which allows longer wavelengths, which are more strongly diffracted, to be collected preferentially. The geometry of the dipole radiation is shown in Fig. S3. Below we describe a calculation of the resulting correction factor $F_{\text{corr}}(\nu)$.

We begin with the relation for the vector potential $A$ in terms of the current density $J$ in the limit that the distance from the current source to the observation point, $r$, is much larger than the dimensions of the source,

$$\lim_{kr \to \infty} A(x) = \frac{\mu_0}{4\pi} \frac{e^{ikr}}{r} \int J(x') e^{-i kn \cdot x'} d^3 x'$$

(30)

with $k = 2\pi/\lambda$, $\lambda$ the THz wavelength, $n$ a unit vector in the direction from the current source to observation point.

We assume that photoexcitation by a Gaussian focal point generates a CPGE current density parallel to the surface of form,

$$J(x') = I \exp \left[ -\left( \rho'/\rho_a \right)^2 \right] \delta(z') \hat{c}$$

(31)

where $I$ is the surface current density and $\delta(z)$ is the Dirac delta function. The integral of the Gaussian distribution can be performed analytically, with the result,
Fig. S3. Calculation geometry. Schematic geometry used to calculate the integral in Eq. (30)

\[
\begin{align*}
A(x) &= I \frac{\mu_0}{4\pi} e^{ikr} \int_0^\infty d\rho' e^{-(\rho'/\rho_a)^2} \int_0^{2\pi} d\phi' \int_{-\infty}^{\infty} d\zeta' e^{-ik\rho' \sin(\theta)(\cos(\phi') \cos(\phi)+\sin(\phi) \sin(\phi'))} \delta(\zeta') \hat{x} \\
&= I \frac{\mu_0}{4\pi} e^{ikr} \exp \left[- \left( \frac{k\rho_a \sin(\theta)}{2} \right)^2 \right] \hat{x},
\end{align*}
\]

where \( I = I \pi \rho_a^2 \) is the current.

The fields are given through the usual relations

\[
\begin{align*}
B &= \frac{1}{\mu_0} \nabla \times A \\
E &= \frac{iZ_0}{k} \nabla \times B.
\end{align*}
\]

Thus, the magnetic field is

\[
B = \frac{I}{8\pi} \frac{e^{ikr}}{r^2} \exp \left[- \left( \frac{k\rho_a \sin(\theta)}{2} \right)^2 \right] \left\{ \cos(\theta) \left( k^2 \rho_a^2 \sin^2(\theta) + 2ikr - 2 \right) \hat{y} + \sin(\theta) \sin(\phi) \left( k^2 \rho_a^2 \cos^2(\theta) - 2ikr + 2 \right) \hat{z} \right\}.
\]

24
and to leading order in $1/r$, the electric field is given by

$$E \approx \frac{ikZ_0 I}{8\pi} \frac{e^{ikr}}{r} \exp \left[ -\left( \frac{k \rho_a \sin(\theta)}{2} \right)^2 \right] \left\{ \left( \cos^2(\theta) \cos^2(\phi) + \sin^2(\phi) \right) \mathbf{\hat{x}} - \left( \sin^2(\theta) \cos(\phi) \sin(\phi) \right) \mathbf{\hat{y}} - \left( \sin(\theta) \cos(\theta) \cos(\phi) \right) \mathbf{\hat{z}} \right\}. \quad (37)$$

The experimental setup comprised 101.6 mm focal length OAPs of 50.4 mm circular cross-sectional diameter, thus the half-angle subtended by the parabola is $\alpha = \tan^{-1}(0.25)$ in both $\theta$ and $\phi$. The expression for the field Eq. (37) is integrated over this subtended solid angle $\Omega$ and divided by the total integrated field to determine the fraction $F_{\text{corr}}(\nu)$ of the emitted field collected by the first parabola as a function of frequency, i.e.,

$$F_{\text{corr}}(\nu) = \frac{\int_{\Omega \in \text{OAP}} E(\nu, \Omega) d\Omega}{\int_{\Omega = 4\pi} E(\nu, \Omega) d\Omega}. \quad (38)$$

Numerical evaluation of this ratio is shown in Fig. S4 for the $E_x$ component of Eq. (37). In this geometry, the higher frequency spectral components of the emitted THz more preferentially radiate in the normal direction of the sample surface, i.e., at $45^\circ$ relative to the collection OAP, effectively low-pass filtering the detected THz field.
**Fig. S5. Predicted and measured pulses.** Comparison of measured signal with calculation based on dispersionless THz propagation through the ZnTe electro-optic crystal.

4. Electro-optic detection using ZnTe

The last step in the calibration is the conversion of the electric field at the surface of the ZnTe crystal to the signal at the output of the biased photodetector scheme. Detection of the THz field is performed through electro-optic sampling (EOS) in ZnTe (110). In this technique the THz electric field introduces transient birefringence, $\Delta n$, in the ZnTe, which is detected by a co-propagating probe beam at 800 nm. Our analysis is based on the detailed studies of the EOS in technique presented in Refs. (23, 24). For THz frequencies below 3 THz we neglect dispersion in ZnTe and assume a real index $n = 2.85$. (25) The transient birefringence generates a polarization rotation in the probe beam. We measure the rotation using an optical bias scheme (26, 27) that yields a gain factor of 88 as compared with the conventional balanced detector measurement. In the conventional scheme, the fractional change in the balanced output is given by,

$$\frac{\Delta V(\tau)}{V} = \frac{\omega n^3 r_{41}}{2c} \int_0^L dz \int_{-\infty}^{\infty} dt E_{THz}(z,t) I_0(z,t-\tau)$$

(39)

where $\omega$ is the angular frequency of the probe pulse, $c$ is the speed of light, $L$ is the propagation distance through the crystal, $E_{THz}$ is the THz field strength, $r_{41} = 4$ pm/V is the electro-optic constant, $I_0(z,t-\tau)$ is the intensity of the probe beam, and $\Delta V(\tau)$ is the change in output voltage.

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coefficient of ZnTe at 800 nm, \( n = 2.85 \) is the index of refraction of ZnTe and

\[
I_0(z, t - \tau) = I_0 \exp\{-[z - v_g(t - \tau)]^2/(v_g T_{pr})^2\} \tag{40}
\]

is the normalized intensity of the 800 nm probe beam with pulse duration, \( T_{pr} \), which propagates with group velocity \( v_g \).

THz transients with bandwidth less than 3 THz, Eq. 39 simplifies to,

\[
\frac{\Delta V(\tau)}{V} = \frac{\omega n^3 r_{41} L}{2c} \int_{-\infty}^{\infty} dt E_{THz}(t) I_0(t - \tau). \tag{41}
\]

Because the duration of the probe pulse is approximately 35 fs, much less that the time scale of the THz transient, we make the approximatin that \( I_0(t - \tau) \to \delta(t - \tau) \) to obtain

\[
\frac{\Delta V(\tau)}{V} = \frac{\omega n^3 r_{41} L}{2c} E_{THz}(\tau). \tag{42}
\]

Fig. S5 demonstrates excellent agreement between the detected EOS transient and the calculation using Eq. 42. Based on this calculation, and the calibration factors discussed above, we determine that the amplitude of the THz emission from RhSi corresponds to a Chern number of 3.5, as referenced in the main text.

Finally, we present typical amplitudes of the currents and electric fields that are generated as the pulse propagates from RhSi to the ZnTe detector. According to Eq. 25 a pump pulse train with average power 100 mW generates an electric field at the RhSi surface of approximately \( 10^9 \) V/m. Assuming for the moment that \( C = 1 \), Eq. 26 the yields a current density parallel to the surface of \( 1.5 \times 10^{12} \) A/m\(^2\) in a layer of thickness \( \approx 10^{-7} \) m, which using Eq. 28 generates an electric field \( \approx 10^4 \) V/m just above the surface. Given the collection efficiency factors, the field reaching the surface of the ZnTe detector is approximately \( 1.5 \times 10^2 \) V/m. Substituting this electric field into Eq. 40 and including a gain factor of 80 from the biased detector scheme yields a signal \( \Delta V/V \approx 10^{-3} \). The measured signal \( \Delta V/V \approx 3 \times 10^{-3} \) corresponds to a Chern number of approximately 3.
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