Photocurrent-driven transient symmetry breaking in the Weyl semimetal TaAs

N. Sirica1,2, P. P. Orth2,3, M. S. Scheurer4, Y. M. Dai5,6, M.-C. Lee7, P. Padmanabhan1, L. T. Mix1, S. W. Teitelbaum6,7, M. Trigo8,9, L. X. Zhao10, G. F. Chen10, B. Xu10, R. Yang10, B. Shen11,12, C. Hu11, C.-C. Lee13, H. Lin14, T. A. Cochran15, S. A. Trugman1, J.-X. Zhu1, M. Z. Hasan5,6, N. Ni11, X. G. Qiu10, A. J. Taylor1, D. A. Yarotski1 and R. P. Prasankumar11,15

Symmetry breaking plays a central role in conventional and topological phases of matter, making the ability to optically drive symmetry changes a critical step in developing future technologies that rely on such control. Topological materials, like topological semimetals, are particularly sensitive to a breaking or restoring of time-reversal and crystalline symmetries, which affect both bulk and surface electronic states. While previous studies have focused on controlling symmetry via coupling to the crystal lattice, we demonstrate here an all-electronic mechanism based on photocurrent generation. Using second harmonic generation spectroscopy as a sensitive probe of symmetry changes, we observe an ultrafast breaking of time-reversal and spatial symmetries following femtosecond optical excitation in the prototypical type-I Weyl semimetal TaAs. Our results show that optically driven photocurrents can be tailored to explicitly break electronic symmetry in a generic fashion, opening up the possibility of driving phase transitions between symmetry-protected states on ultrafast timescales.

Symmetry breaking has long defined the dominant paradigm for describing phase transitions in condensed matter systems. More recently, the discovery of novel topological phases, characterized by topological invariants as opposed to a local order parameter arising from spontaneously broken symmetry, provides an alternative framework for classifying states of matter. Nevertheless, symmetry continues to play a central role in the physics of topological materials, as it underlies topological protection in topological insulators and superconductors, crystalline topological phases and the recently discovered topological semimetals. In Dirac semimetals, symmetry protects the four-fold degeneracy of the Dirac point, while for Weyl semimetals (WSMs), the breaking of time-reversal or inversion symmetry allows for the crossing of two linearly dispersing, non-degenerate bands, giving rise to Weyl points. These points act as monopoles of Berry curvature in momentum (k) space, and their presence leads to several unique experimental manifestations that make these materials appealing for future technological applications.

Conventional probes of symmetry rely on diffractive techniques, like X-ray, neutron and electron scattering, to determine the respective lattice, magnetic and charge ordering in a crystal. Nonlinear optics is also an effective probe of symmetry, as the nonlinear response is described by a third (or higher) rank tensor, allowing for phases hidden to linear probes (for example, in correlated electron systems) to be revealed. In the transition metal monopnictide family of WSMs, the lack of inversion symmetry resulting from a polar ε axis leads to an especially strong nonlinear optical response, with substantial contributions from the generation of helicity-dependent injection and helicity-independent shift photocurrents. Shift currents, resulting from a coherent shift of the electron cloud in real space following photoexcitation, are particularly important, as they play a dominant role in the giant, anisotropic second harmonic response as well as the bulk photovoltaic effect seen in WSMs, and may be traced to a difference in Berry connection between the bands participating in the optical transition. The most common nonlinear optical probe, second harmonic generation (SHG) spectroscopy, is thus sensitive to the asymmetric carrier distribution that accompanies photocurrent generation, making it a powerful tool for measuring the effect of transient photocurrents on material symmetry.

In this Article, we show that femtosecond optical excitation transiently lowers the magnetic point symmetry 4mm, with 1 indicating time-reversal symmetry of the type-I WSM TaAs. Time-resolved SHG (TR-SHG) spectroscopy reveals this symmetry change occurs on a picosecond timescale, with no accompanying structural transition, indicating it to be purely electronic in origin. The strong nonlinear optical response exhibited by the transition metal monopnictide WSMs allows us to attribute this reduction in symmetry to changes in the spatial distribution of the electronic polarization that follow from photocurrent generation, supported by our previous terahertz emission experiments. The degree of symmetry breaking is governed by the current direction, which we...
Fig. 1 | Evolution of the second harmonic pattern in TaAs following photocurrent excitation. a–h. Snapshots of SHG patterns (2ω = 3.1 eV) measured along the [1,1,0] (a–d) and [1,1,1] (e–h) axes for various pump delays: Δt = −5.0 ps (a,e), 0 ps (b,f), 1.0 ps (c,g) and 5.0 ps (d,h). The inset in a shows a schematic of the experimental geometry, while insets in b and f show polar plots of the SHG pattern immediately following a linearly polarized pump excitation (hω = 1.55 eV; fluence = 4.34 mJ cm⁻²) aligned nearly along the [1,1,1] axis. Fits of the pattern assuming the magnetic point symmetries of 4mm (a,e) and (d,h)) and 1 (b,f) and (c,g)) are shown as solid purple and blue traces, respectively. Arrows in f and g denote the presence of transient, asymmetric lobes in the photoexcited state, while a small ~2.5° rotation of the SHG pattern along [1,1,1] is evident from the inset in f.

manipulate via the pump polarization. Our results demonstrate that optically driven photocurrents generically break electronic symmetries and can be used to achieve dynamic control of material properties on ultrafast timescales. This control mechanism will have wide-ranging applications, particularly for topological semimetals, where symmetry is intimately tied to topology, opening up an avenue of study rooted in current-induced symmetry breaking.

Prior to pump excitation, Fig. 1a,e shows SHG patterns generated by an optical light pulse with a fundamental frequency, ω, collected along the two in-plane [1,1,0] and [1,1,1] axes of the (112) face that are well described by a nonlinear susceptibility tensor, χ(2)ijk(2ω), obeying the 4mm’ point group symmetry of TaAs (Supplementary Discussion Section X). Here, the emitted second harmonic is dominated by an electric dipole response that is attributed to the polar c axis. This is reflected by a large ratio of χ(2)112/χ(2)111 = 7.4 at hω = 1.55 eV (for z parallel to the crystallographic c axis and h denoting the Planck constant = 4.136 × 10⁻¹⁵ eV·s), as determined from our fits and in agreement with the literature.

Following 1.55 eV photoexcitation, Fig. 1f–h shows pronounced changes in the SHG pattern along [1,1,1] that can be traced to a transient change in symmetry within the material when the pump polarization is nearly aligned along the [1,1,1] axis. With the arrival of the pump pulse in Fig. 1f, the emitted SHG along [1,1,1] is reduced by half and the resultant pattern exhibits a 2.5° rotation with respect to equilibrium (inset of Fig. 1f). In addition, small lobes absent from the static pattern appear at ~90° and ~270° (Fig. 1g), whose asymmetry suggests a reduction of symmetry in the photoexcited state. By contrast, SHG patterns along [1,1,0] grow in amplitude, with no additional rotation or spectral features appearing under pump excitation (Fig. 1b–d). From Fig. 1g, both the rotation and asymmetric lobes in the [1,1,1] TR-SHG pattern follow similar ultrafast dynamics, lasting τ_θ ~ 1.1 ps, where τ_θ denotes the lifetime of these photoinduced spectral features, before symmetry is restored and the intensity of the main lobes at 0° and 180° begins to recover back to its equilibrium value (Fig. 1h).

Coupling of the dynamics for both the rotation and lobe asymmetry in the TR-SHG spectra is further illustrated in Fig. 2, showing photoinduced polarization- and time-dependent changes over the entire [1,1,1] pattern taking for the three probe energies used in our experiments. Figure 2a reveals that both spectral features exhibit an equivalent time dependence, suggesting they originate from the same photoinduced symmetry-breaking transition, while Fig. 2b,c reveals an absence of symmetry breaking under non-resonant probe conditions (discussed further below).

Together with separate time-resolved X-ray diffraction experiments (Supplementary Fig. 3), which show no structural dynamics over ultrafast timescales, but only on considerably longer timescales due to laser heating, this suggests an electronic origin of the symmetry-breaking transition. Additionally, Fig. 2, along with symmetry considerations (Supplementary Discussion Section X), excludes the possibility that a dominant surface contribution, arising from a screened bulk response due to a high density of photoexcited carriers (10¹⁴–10¹⁵ cm⁻³), is responsible for the reduced symmetry state, as such an effect would be evident at all probe energies. Hence, the mere generation of a photoexcited charge density is insufficient for lifting 4mm’ symmetry, and it is only when resonantly probing the transiently excited state that symmetry breaking in the SHG pattern is observed.

By reducing symmetry, the constraints imposed in equilibrium are lifted, necessitating that we consider a lower symmetry subgroup of 4mm’ to describe the time-dependent nonlinear susceptibility elements χ(2)ijkl(2ω;Δt), where ω and Δt denote frequency and time delay after pump excitation, respectively. To quantitatively extract information about the behaviour of χ(2)ijkl(2ω;Δt), we simultaneously fit the SHG patterns collected along [1,1,0] and [1,1,1] as a function of pump delay and incident polarization angle, φ (Fig. 1). As compared to equilibrium, the rotation of the pattern along [1,1,1]
and the emergence of asymmetric lobes at 90° and 270° following photoexcitation cannot be accounted for under 4mm′ symmetry, as this requires the lobes to be both symmetric and pinned along the x and y axes. Rather, by considering the different subgroups of 4mm′, we find an optimal fit that captures the aforementioned features of the photoexcited state only in the absence of time-reversal and diagonal mirror, m_{\text{sdz}}, symmetry, described by the magnetic point group 1 (no point symmetries). Using the expression $I_{\text{SHG}}^p(\phi) = \sum_{\alpha=a,b,c} C_{\alpha} \sin^n(\phi) \cos^{4-n}(\phi)$ where $\alpha = \{110\}, \{111\}$ to describe the SHG pattern ($I_{\text{SHG}}(\phi)$) in the 1 symmetry state over a $\Delta t < 2.0$ ps timescale allows us to associate different fit coefficients, $C_{\alpha}^{(110)}$, to specific features in the pattern (Supplementary Discussion Section X). The dynamics of these features are captured by the TR-SHG traces in Fig. 3 ($\Delta I_{\text{SHG}}(\phi)$), plotted as a function of pump delay for select combinations of input and output probe polarizations. Figure 3a captures the time dependence of the largest fit coefficient $C_{\alpha}^{(111)}$, depicting the suppression and subsequent recovery of the dominant lobe in the SHG pattern on a timescale defined by the two fit components $\tau_1$ and $\tau_2$, while Fig. 3b shows the time dependence of $C_{\alpha}^{(111)}$, which illustrates the dynamics of the emergent, asymmetric lobe arising from photoexcitation.

Despite both $C_{\alpha}^{(111)}$ and $C_{\alpha}^{(111)}$ being allowed under 4mm′ symmetry (though $C_{\alpha}^{(111)}$ is small for the static pattern at $h\nu = 1.55$ eV), a reduction to 1 symmetry is captured by the pair of odd fit parameters, $C_{\alpha}^{(111)}$ and $C_{\alpha}^{(111)}$, that quantitatively measure the degree of symmetry breaking imposed by the pump following photoexcitation (Supplementary Discussion Section X). These parameters result from breaking $m_{\text{sdz}}$ and enable fitting of the overall rotation in the pattern. However, as long as time-reversal symmetry remains, relations between the different $C_{\alpha}^{(111)}$ prevent these odd coefficients from capturing the observed asymmetry seen in our data. Rather, an accurate description requires a breaking of time-reversal symmetry to remove the constraints imposed on $C_{\alpha}^{(111)}$, revealing that both $m_{\text{sdz}}$ and time-reversal symmetry must be lifted in order to fully describe our experimental results. This reduction of symmetry from 4mm′ to 1 also allows for the emergence of additional fit parameters in the [1,1,0] pattern, but these remain small and time independent, consistent with the weaker (approximately x100) nonlinear response observed along this axis.

We emphasize that in contrast with the spontaneous symmetry breaking seen in conventional photoinduced phase transitions, the symmetry breaking observed here is explicit and originates from the photoexcitation process itself. In this regard, the symmetry resolution gained from nonlinear optical probes like SHG provides a completely generic and robust framework for characterizing light-induced changes in the non-equilibrium state, as no underlying assumptions or reliance on theoretical models is required. While previous studies have reported explicit symmetry breaking from polarization-dependent photoexcitation in Bi and Sb that results from the coupling of phonons to a transiently excited charge density in k-space, we propose an alternative mechanism, which is entirely electronic in origin. Accounting for the fact that optical excitation creates a highly non-equilibrium state, we have carefully considered a number of possibilities, including a spatially inhomogeneous pump volume, anisotropic changes in optical constants and carrier thermalization following photoexcitation, before concluding that the lowering of 4mm′ symmetry to 1 in TaAs most likely arises from photocurrent generation (Supplementary Discussion Section XI).

By having a well-defined, but generic, direction relative to some high-symmetry axis of the crystal, a photocurrent, $J_\nu$, breaks both spatial and time-reversal symmetry through introducing an asymmetry in the non-equilibrium distribution of charge carriers along its direction that must necessarily be odd under time reversal. On the (112) face of TaAs, photocurrents originating from asymmetry in the real (shift) or k-space (projection) carrier density are allowed to flow along the [1,1,1] and [1,1,0] axes. Here, a reduction in symmetry from 4mm′ to 1 occurs when a net current is directed away from either of these two high-symmetry axes, breaking diagonal mirror symmetry (Fig. 4a; Supplementary Discussion Section X). While a polarization-independent photocurrent is always present along [1,1,1] (Fig. 4b), the polarization dependence of the [1,1,0] photocurrent allows us to break symmetry in a controllable manner by exploiting symmetry constraints placed on the shift current following linearly polarized excitation (Fig. 4c and Supplementary Discussion Section IX). As shown in Fig. 4d, varying the linear polarization of the excitation pulse relative to the [1,1,1] axis causes the emergent photoinduced lobes in the transient SHG pattern ($\Delta I \approx 0.1$ ps) to develop a clear polarization-dependent asymmetry, while the pattern itself exhibits a rotation with respect to 0° and 180°. This is fully consistent with a reduction of symmetry brought on by an enhanced shift current response; as the pump polarization is detuned from the [1,1,1] axis, shift currents along [1,1,0] become.

![Fig. 2](image-url) | Isothermal photoinduced change in the second harmonic pattern following optical excitation. Photoinduced polarization- and time-dependent changes in SHG intensity, $\Delta I_{\text{SHG}}(2\omega)$, measured across the entire [1,1,1] pattern after 1.55 eV photoexcitation (fluence = 4.34 mJ cm$^{-2}$) using probe energies of $h\nu = 1.55$ eV (a), $h\nu = 1.03$ eV (b) and $h\nu = 0.89$ eV (c) (Supplementary Fig. 1). Arrows in a denote the recovery of 4mm′ symmetry following the decay of the emergent, asymmetric lobes at ~90° and ~270° (dashed vertical lines), as well as a rotation of the SHG pattern back to equilibrium. Compared to panel a, optical pumping at 1.55 eV does not change the symmetry of the patterns in panels b and c, but suppresses them in a nearly isotropic manner over a $\Delta t < 2.0$ ps timescale (Supplementary Fig. 2).
symmetry allowed, with the largest contribution coming from an equal projection of the pump polarization along the two orthogonal axes of the (112) face (that is, 45°; Supplementary Discussion Section IX). This is reproduced by our data in Fig. 4d and illustrates our ability to exploit symmetry constraints on the photocurrent to tune the degree of symmetry breaking in this material. Similarly, after circularly polarized excitation, symmetry dictates that injection photocurrents can flow only along [1,1,0] (Supplementary Discussion Section XII). The fact that light-induced symmetry breaking in TaAs originates from a dominant helicity-independent shift current whose geometric interpretation is rooted in an asymmetry in the electronic polarization within our experimental resolution (Supplementary Fig. 6). This is unsurprising, since the lack of spectral features at 90° and 270° in the static SHG pattern at 1.55 eV (Fig. 1e) as compared to lower photon energies (Supplementary Fig. 1b,c) makes this probe photon energy optimal for observing photocurrent-induced SHG along the orthogonal [1,1,0] axis, as manifested by the emergent photoinduced lobes in Fig. 1f,g.

Finally, our particular choice of photon energy was based on the giant anisotropic nonlinear response of the static SHG pattern along [1,1,1] at 1.55 eV (refs. 25,26). While degenerate TR-SHG experiments performed at 1.02 eV show some dependence on pump polarization, similar to Fig. 4, the photoinduced change across the entire SHG pattern is dominated by a suppression of the SHG response, with the pattern itself retaining 4mm symmetry within our experimental resolution (Supplementary Fig. 6).

Ab initio calculations for the optical conductivity in TaAs reveal an As–p to Ta–d transition to be the major contribution to the in-plane conductivities, σz and σzz, for 1.55 eV excitation energy, while a Ta–d to Ta–d transition dominates the out-of-plane response, σyy (Supplementary Discussion Section XII). The fact that no symmetry changes are observed under non-degenerate pump excitation for either hωpump > hωprobe (Fig. 2b,c) or hωpump < hωprobe (Supplementary Fig. 5), where ωpump and ωprobe denote the respective frequencies for pump and probe light pulses, can thus be attributed to resonantly probing this initial photoexcited population of carriers. In other words, the transient asymmetry generated under 1.55 eV photoexcitation is lost over an ultrafast timescale due to momentum scattering, consistent with the bandwidth of the emitted terahertz pulses27, and is therefore absent as photoexcited carriers relax to the lower lying, non-degenerate energy states probed at 0.89–1.03 eV (Fig. 2b,c). Further support is provided by band-resolved imaging of the photocurrent response in the topological insulator Bi2Se3, which reveals that the transient asymmetry due to optically excited photocurrents is lost within ~165 fs (ref. 41). Hence, by using degenerate pump and probe energies, we ensured that only those states responsible for generating the photocurrent following pump excitation are probed; we note that any contribution arising from sum frequency generation can be discounted, since symmetry breaking in the TR-SHG pattern exists on timescales much longer than the temporal overlap of the pump and probe pulses.

In conclusion, by performing TR-SHG spectroscopy on the (112) surface of the WSM TaAs, we reveal a transient breaking of all magnetic point group symmetries following optical excitation, reducing the symmetry from 4mm to 1. Both the prompt recovery of equilibrium symmetry, as well as the absence of an ultrafast structural transition following optical excitation, suggest that light-induced symmetry breaking in TaAs originates from transient photocurrent generation. Specifically, the presence of a polar c axis in the transition metal monopnictide WSMs leads to a dominant helicity-independent shift current whose geometric interpretation is rooted in an asymmetry in the electronic polarization introduced by optical excitation25. In this regard, our TR-SHG study reflects time-dependent changes to the polarization distribution that fail to respect both spatial and time-reversal symmetries, and whose relaxation is governed by a polarization-independent recovery, τnet, describing the return of the electronic polarization back to equilibrium.

The effect we report in this study originates from the fact that symmetry imposes general constraints on material properties and thus can have important consequences for topological...
materials, where topology is closely related to symmetry. Since symmetry constrains the total number of Weyl nodes in TaAs, a reduction in symmetry brought on by photocurrent generation is expected to shift these nodes in both energy and momentum. This will alter the Fermi arc surface states, suggesting future time- and angle-resolved photoemission spectroscopy experiments to directly measure the impact of transient photocurrents on the electronic band topology. More generally, our findings can be applied to any material system where either an optically generated or externally applied current breaks electronic symmetries. While generic, these results have important implications for topological semimetals; as the ability to alter symmetry on ultrafast timescales in these materials can lead to the potential realization of topological field effect transistors.

Online content
Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41563-021-01126-9.

Received: 19 May 2020; Accepted: 8 September 2021; Published online: 8 November 2021

References

1.  Wen, X.-G. Topological orders and edge excitations in fractional quantum Hall states. Adv. Phys. 44, 405 (1995).
2.  Sachdev, S. Topological order, emergent gauge fields, and Fermi surface reconstruction. Rep. Prog. Phys. 82, 014001 (2019).
3.  Hasan, M. Z. & Kane, C. L. Colloquium: topological insulators. Rev. Mod. Phys. 82, 3045 (2010).
4.  Ando, Y. & Fu, L. Topological crystalline insulators and topological superconductors: from concepts to materials. Annu. Rev. Condens. Matter Phys. 6, 361 (2015).
5.  Gao, H., Venderbos, J. W., Kim, Y. & Rappe, A. M. Topological semimetals from first principles. Annu. Rev. Mater. Res. 49, 153 (2019).
6.  Armitage, N. P., Mele, E. J. & Vishwanath, A. Weyl and Dirac semimetals in three-dimensional solids. Rev. Mod. Phys. 90, 015001 (2018).
7.  Young, S. M. et al. Dirac semimetal in three dimensions. Phys. Rev. Lett. 108, 140405 (2012).
8.  Wan, X., Turner, A. M., Vishwanath, A. & Savrasov, S. Y. Topological semimetal and Fermi-arc surface states in the electronic structure of pyrochlore iridates. Phys. Rev. B 83, 205101 (2011).
9.  Xu, S.-Y. et al. Discovery of a Weyl fermion semimetal and topological Fermi arcs. Science 349, 613 (2015).
10. Yang, L. X. et al. Weyl semimetal phase in the non-centrosymmetric compound TaAs. Nat. Phys. 11, 728 (2015).
11. Liu, Z. K. et al. Evolution of the Fermi surface of Weyl semimetal in the transition metal pnictide family. Nat. Mater. 15, 27 (2015).
12. Jia, S., Xu, S.-Y. & Hasan, M. Z. Weyl semimetals, Fermi arcs and chiral anomalies. Nat. Mater. 15, 1140 (2016).
13. Parameswaran, S. A., Grover, T., Abanin, D. A., Pesin, D. A. & Vishwanath, A. Probing the chiral anomaly with nonlocal transport in three-dimensional topological semimetals. Phys. Rev. X 4, 031035 (2014).
14. Huang, X. et al. Observation of the chiral-anomaly-induced negative magneto-resistance in 3D Weyl semimetal TaAs. Phys. Rev. X 5, 031023 (2015).
15. Torczynsky, D. H. & Hsieh, D. In Magnetic Characterization Techniques for Nanomaterials (ed. Kumar, C. S.) 1–49 (Springer, 2017).
16. Zhao, L., Torczynsky, D., Harter, J., de la Torre, A. & Hsieh, D. In Encyclopedia of Modern Optics 2nd edn (eds Guenther, B. D. & Steel, D. G.) 207–226 (Elsevier, 2018).
17. Zhao, L. Evidence of an odd-parity hidden order in a spin–orbit coupled correlated iridate. Nat. Phys. 12, 32 (2016).
18. Harter, J. W., Zhao, Z. Y., Yan, J.-Q., Mandrus, D. G. & Hsieh, D. A parity-breaking electronic nematic phase transition in the spin-orbit coupled metal CaReO3. Science 356, 295 (2017).
19. van Aken, B. B., Rivera, J.-P., Schindel, M. & Fiebig, M. Observation of ferrotoroidic domains. Nature 449, 702 (2007).
20. Jin, W. et al. Observation of a ferro-rotational order coupled with second-order nonlinear optical fields. Nat. Phys. 16, 42 (2020).
21. Ma, Q. et al. Direct optical detection of Weyl fermion chirality in a topological semimetal. Nat. Phys. 13, 842 (2017).
22. Sirica, N. et al. Tracking ultrafast photocurrents in the Weyl semimetal TaAs using THz emission spectroscopy. Phys. Rev. Lett. 122, 197401 (2019).
23. Gao, Y. et al. Chiral terahertz wave emission from the Weyl semimetal TaAs. Nat. Commun. 11, 720 (2020).
24. Wu, L. et al. Giant anisotropic nonlinear optical response in transition metal monopnicdite Weyl semimetals. Nat. Phys. 13, 350 (2016).
25. Patankar, S. et al. Resonance-enhanced optical nonlinearity in the Weyl semimetal TaAs. Phys. Rev. B 98, 165113 (2018).
26. Osterhoudt, G. B. et al. Colossal photovoltaic effect driven by the singular Berry curvature in a Weyl semimetal. Nat. Mater. 18, 471 (2019).
27. Ma, J. et al. Nonlinear photoresponse of type-II Weyl semimetals. Nat. Mater. 18, 476 (2019).
28. Sipe, J. E. & Shkrebtii, A. I. Second-order optical response in semiconductors. Phys. Rev. B 61, 5337 (2000).
29. Li, Z. et al. Second harmonic generation in the Weyl semimetal TaAs from a quantum kinetic equation. Phys. Rev. B 97, 085201 (2018).
30. Morimoto, T. & Nagaosa, N. Topological nature of nonlinear optical effects in solids. Sci. Adv. 2, 1501524 (2016).
31. Sotome, M. et al. Spectral dynamics of shift current in ferroelectric semiconductor SbSi. Proc. Natl Acad. Sci. USA 116, 1929 (2019).
32. Parker, D. E., Morimoto, T., Orenstein, J. & Moore, J. E. Diagrammatic approach to nonlinear optical response with application to Weyl semimetals. Phys. Rev. B 99, 045121 (2019).
33. Weber, C. P. Ultrafast investigation and control of Dirac and Weyl semimetals. J. Appl. Phys. 129, 070901 (2021).
34. Khurgin, J. B. Current induced second harmonic generation in semiconductors. Appl. Phys. Lett. 67, 1113 (1995).
35. Ruzicka, B. A. et al. Second-harmonic generation induced by electric currents in GaAs. Phys. Rev. Lett. 108, 077403 (2012).
36. Zong, A. et al. Evidence for topological defects in a photoinduced phase transition. Nat. Phys. 15, 27 (2019).
37. Zong, A. et al. Dynamical slowing-down in an ultrafast photoinduced phase transition. Phys. Rev. Lett. 123, 097601 (2019).
38. Li, J. J., Chen, J., Reis, D. A., Fahy, S. & Merlin, R. Optical probing of ultrafast electronic decay in Bi and Sb with slow phonons. Phys. Rev. Lett. 110, 047401 (2013).
39. Murray, E. D. & Fahy, S. First-principles calculation of femtosecond symmetry-breaking atomic forces in photoexcited bismuth. Phys. Rev. Lett. 105, 055502 (2010).
40. O’Mahony, S. M. et al. Ultrafast relaxation of symmetry-breaking photo-induced atomic forces. Phys. Rev. Lett. 123, 087401 (2019).
41. Soifer, H. et al. Band-resolved imaging of photocurrent driven by the singular Berry curvature in a Weyl semimetal. Nat. Phys. 15, 27 (2019).
42. Takasan, K., Morimoto, T., Orenstein, J. & Moore, J. E. Current-induced second harmonic generation in inversion-symmetric Dirac and Weyl semimetals. Preprint at arXiv https://arxiv.org/abs/2007.08887 (2020).

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
Methods

Crystal growth. TaAs single crystals were grown from polycrystalline samples by chemical vapour transport using iodine (2 mg cm⁻²) as the transporting agent. Large polyhedral crystals with dimensions up to 1.5 mm were obtained in a temperature field of ΔT = 1,150–1,000 °C following three weeks of growth; temperature in an evacuated quartz ampoule. The as-grown three-dimensional crystals exhibit multiple surface facets, with the (112) face being identified by X-ray diffraction measurements.

TR-SHG. TR-SHG experiments were performed on the (112) surface of different as-grown TaAs single crystals, sourced from entirely different batches, using an amplified Ti/sapphire laser system operating at a 250 kHz repetition rate. SHG from-grown TaAs single crystals, sourced from entirely different batches, using an amplified Ti/sapphire laser system operating at a 250 kHz repetition rate. SHG

Δ

in a temperature field of

agent. Large polyhedral crystals with dimensions up to 1.5 mm were obtained amplified Ti/sapphire laser system operating at a 250 kHz repetition rate. SHG

as-grown TaAs single crystals, sourced from entirely different batches, using an amplified Ti/sapphire laser system operating at a 250 kHz repetition rate. SHG

anomalously Hall conductivity in bcc Fe. Phys. Rev. B 98, 115115 (2018).

Acknowledgements

This work was performed at the Center for Integrated Nanotechnologies at Los Alamos National Laboratory, a US Department of Energy, Office of Basic Energy Sciences user facility, under user proposal nos 2017BC00864 and 2019AU0167. Use of the Linac Coherent Light Source, SLAC National Accelerator Laboratory, is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under contract no. DE-AC02-76SF00515. N.S. and R.P.P gratefully acknowledge the support of the US Department of Energy through the Los Alamos National Laboratory LDRD programme. P.P.O, J.-X.Z. and D.A.Y are supported by the Center for Advancement of Topological Semimetals, an Energy Frontier Research Center funded by the US Department of Energy Office of Science, Office of Basic Energy Sciences, through the Ames Laboratory under contract no. DE-AC02-07CH11358. T.A.C. and M.Z.H. acknowledge support from the US Department of Energy under grant DE-FG-02-05ER46200. Work at University of California, Los Angeles was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under award no. DE-SC002117 for single-crystal growth and characterization. C.H. thanks the support of the Julian Schwinger Fellowship at University of California, Los Angeles. M.S.S. acknowledges support from the National Science Foundation under grant no. DMR-1664842. C.-C.L. acknowledges the Ministry of Science and Technology of Taiwan for financial support under contract no. MOST 108-2112-M-032-105-MY2. T.A.C. was supported by the National Science Foundation Graduate Research Fellowship Program under grant no. DGE-1656466. M.T. and S.W.T. were supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences through the Division of Materials Sciences and Engineering under contract no. DE-AC02-76SF00515. We thank Y.-M. Sheu for the helpful discussion.

Author contributions

TaAs single crystals were grown and characterized by L.X.Z, G.F.C., B.X., R.Y., B.S., C.H., N.N., and X.G.Q., with additional sample characterization and physical insights provided by T.A.C. and M.Z.H.; N.S. and Y.M.D. performed the TR-SHG experiments with help from M.-C.L., P.P. and L.T.M.; N.S., S.W.T., M.T. and R.P.P. performed the time-resolved X-ray diffraction experiments with help from Linac Coherent Light Source staff. The data were analysed by N.S., P.P.O. and M.S.S. with a detailed symmetry analysis performed by P.P.O. and M.S.S. Ab initio calculations were carried out by C.-C.L. and H.L. with additional insight provided by J.-X.Z. The manuscript was written by N.S., R.P.P. and P.P.O. with added contributions from S.A.T., A.T. and D.A.Y.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41563-021-01126-9.

Correspondence and requests for materials should be addressed to N. Sirica or R. P. Prasankumar.

Peer review information Nature Materials thanks Liuyan Zhao and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permissions information is available at www.nature.com/reprints.