Electronic band structures dictate the mechanical, optical and electrical properties of crystalline solids. Their experimental determination is therefore crucial for technological applications. Although the spectral distribution in energy bands is routinely measured by various techniques, it is more difficult to access the topological properties of band structures such as the quantized Berry phase, which is a gauge-invariant geometrical phase accumulated by the wavefunction along an adiabatic cycle. In graphene, the quantized Berry phase is accumulated by massless relativistic electrons along cyclotron orbits and is evidenced by the anomalous quantum Hall effect. It is usually thought that measuring the Berry phase requires the application of external electromagnetic fields to force the charged particles along closed trajectories. Contradicting this belief, here we demonstrate that the Berry phase of graphene can be measured in the absence of any external magnetic field. We observe edge dislocations in oscillations of the charge density (Friedel oscillations) that are formed at hydrogen atoms chemisorbed on graphene. Following Nye and Berry in describing these topological defects as phase singularities of complex fields, we show that the number of additional wavefronts in the dislocation is a real-space measure of the Berry phase of graphene. Because the electronic dispersion relation can also be determined from Friedel oscillations, our study establishes the charge density as a powerful observable with which to determine both the dispersion relation and topological properties of wavefunctions. This could have profound consequences for the study of the band-structure topology of relativistic and gapped phases in solids.

Wave–particle duality manifests as an oscillatory structure in the static response of conduction electrons to impurities: Friedel oscillations. These appear in various contexts and can, for example, alter the conductance of two-dimensional electron gases or mediate long-range interactions between magnetic impurities. Because Friedel oscillations intrinsically result from the quantum interference of electronic waves, they necessarily carry information about the crystalline host materials, which impose constraints on the possible wavefunctions. For instance, the wavelength of Friedel oscillations is inversely proportional to the Fermi wavevector and can be used to recover the energy between bright and dark indicates a phase shift of . The FFT images are nm × nm. d, FFT-filtered images of along the three directions of inter-valley scattering. The dotted shape has been added manually to indicate the position of the H atom. The insets show the filters applied in the Fourier space. e, Raw image, with dotted lines highlighting the wavefront for one direction of inter-valley scattering. The red dotted lines correspond to the additional wavefronts. Similar results are obtained in the other directions (see Supplementary Information).
Letter to the Editor

Pseudospin in valley K, The Intra-valley backscattering rotates the pseudospin by $\pi$.

Friedel oscillations in STM images are dominated by backscattering processes along iso-energy contours. At a given tip position, the amplitude of the Friedel oscillation probed by the STM is governed by the interference of the electronic wave pointing towards the H atom and its reflection from the adatom. As a consequence, the angle $\theta_{K}$ that parameterizes the momentum $q$ of the incident electron is directly related to the angle $\theta_{q} = \theta_{K} + \pi$ that indexes the tip orientation at a given position $r$ from the H adatom (see Fig. 2a, c in which the angles are defined with respect to the direction $\Delta K$). In graphene, $\theta_{K}$ also defines the momentum-locked pseudospin of the incident electronic wave in valley K. Intra-valley backscattering involves a rotation of the pseudospin that is always $\pi$, so that the interference is destructive at the leading order ($\Delta K$) from Fig. 2a)15,18,19. In contrast, backscattering from valley K to valley $K'$ involves a rotation of the pseudospin by an angle $-2\theta_{K} = -2\theta_{q}$ (see Fig. 2a, c), which does not lead to destructive interference but instead leads to the peculiar interference pattern we observe. This pattern is linked to the Berry phase of graphene because circling the STM tip around the impurity is equivalent to circling the momentum $q$ of the incident electron on a closed iso-energy contour around the Dirac point in reciprocal space as $\theta_{q}$ is locked on $\theta_{K}$ (see Supplementary Video 1). This is analogous to the trajectory of the momentum on a cyclotron orbit, but with the movement of the STM tip replacing the adiabatic transport of electrons in magneto-transport measurements.

More formally, an isolated H adatom constitutes an atomic scatterer that induces both intra- and inter-valley scattering. It may be modelled by an on-site potential $V_{0}(r)$ (where the amplitude $V_{0} \gg 1$ eV and $\delta(r)$ is the Dirac delta function)20. Elastic scattering of Dirac electrons on dispersion relation from a sequence of energy-resolved scanning tunnelling microscope (STM) images7. This has been used to reconstruct the linear dispersion in graphene13,14. Friedel oscillations have also been used to demonstrate the existence of the pseudospin of graphene, which arises from the sublattice degree of freedom14,15. However, the pseudospin winding, which is directly related to the Berry phase of graphene and characterizes the band structure topology of massless relativistic electrons, has not been retrieved from such STM images.

Figure 1a shows an STM image from our experiments of a H atom chemisorbed on graphene (see Methods and ref. 16 for experimental details). The Fourier transform (Fig. 1b, c) contains signatures of Friedel oscillations associated with the elastic backscattering of massless, relativistic electrons (Dirac electrons) from a given valley K to a nearest-neighbour valley $K'$ (refs 13-15). Figure 1d shows the corresponding oscillation in real space after Fourier-filtering the signal for each direction of inter-valley backscattering. Along with the expected intra-valley backscattering oscillations, with a wavelength of $\lambda_{\Delta K} = \frac{2\pi}{\Delta K} \approx 3.7$ Å (where $\Delta K = K' - K$ connects two adjacent Dirac points), the filtered images present two dislocations in the vicinity of the H adatom (adatom). Trained eyes can track them in raw images (Fig. 1e and Supplementary Information). STM imaging after removing the H atoms16 reveals no structural defects in the graphene, showing that the dislocations appear only in Friedel oscillations. These dislocations allow us to measure the Berry phase, as they are real-space consequences of the pseudospin winding of graphene around the apex of the conical dispersion relation (Dirac cone)—as we will now show.
such a potential has an analytical solution that is non-perturbative in $V_0$ (see Supplementary Information). For an adatom located on sublattice A of the honeycomb lattice of graphene (Fig. 2b) and for a given direction of inter-valley scattering, the elastic scattering yields a modulation of the charge density around the adatom:

$$\Delta \rho(\Delta K, r, V_0) = \Delta \rho_A(r, V_0)\cos(\Delta K \cdot r) + \xi \zeta\Delta \rho_B(r, V_0)\cos(\Delta K \cdot r - (\xi - \zeta')\theta)$$

(1)

Here, the two terms correspond to the charge density modulation on sublattices A and B, respectively, and $V_0$ is the applied STM bias. For intra-valley scattering ($\Delta K = 0$ and the valley index $\xi' = \xi = 1$) the charge modulation is defined entirely by $\Delta \rho_A$ and $\Delta \rho_B$, which describe the universal static response of conduction electrons to impurities—that is, they describe Friedel oscillations$^6$. The Friedel oscillations allow the determination of the spectral properties via their $2p_c$-wavevector dependence$^{13}$ and have an unconventional decay in graphene because of the $\pi$ rotation of the pseudospin in intra-valley backscattering$^{15,18,19}$. Their expressions are given in the Supplementary Information. These oscillations have a long period: $\lambda_{\Delta K}/2\pi = q_0 = 5.2$ nm, for $q_0 = |q_0|$ and $q_0$ fixed by the experimental tunnelling bias $V_0 = 0.4$ V.

Extra oscillations appear in equation (1) for inter-valley scattering ($\Delta K = 0, \xi' = \xi = -1$). In contrast to usual Friedel oscillations, their wavelength $\lambda_{\Delta K}$ is independent of energy, so that they are not smeared by the integration on the STM bias window (see the experimental proof from $dI/dV$ maps in the Supplementary Information). The corresponding modulation of charge density is plotted in Fig. 2e–g for a given direction of inter-valley scattering. Importantly, the angle $-2\theta_q$, which turns out to be the real-space representation of the pseudospin rotation in inter-valley backscattering (see Supplementary Information), appears as an additional phase shift in the density modulation on sublattice B. It encodes the $q$ dependence of the pseudospin and maps its singularity at the Dirac cone apex into a singularity in the real space from which the wavefront dislocation emerges.

The concept of topological defects in waves was introduced by Nye and Berry, who showed that the dislocations in radio waves echoing off ice sheets in Antarctica resulted from phase singularities in the complex scalar field that describes the wave propagation$^6$. Such topological defects in waves are ubiquitous in physics from fluids$^{21,22}$ to singular optics$^{23,24}$ and condensed matter$^{25-27}$. We follow Nye and Berry in defining the complex scalar field $\Delta \rho_A(r) = |\Delta \rho_A(r)|e^{i\Delta \phi}$, the real part of which describes the Friedel oscillation on sublattice B (the second term in equation (1)). The phase, $\Delta \phi(r) = \Delta K \cdot r - 2\theta_q$, is singular at $r = 0$. It can be regarded as a potential for which the gradient is the sum of a uniform field and a vortex$^2$. In our case, the uniform field represents the standing electronic wave associated with inter-valley backscattering, and the vortex represents the perturbation of the wave by the pseudospin rotation. The circulation of this field is the phase accumulated along a closed path C. It is necessarily quantized to a topological number $2\pi N$ (for an integer $N$), because $\Delta \phi(r)$ is a single-valued function and must return to the same observable charge density after circulating along the closed circuit. In singular optics $N$ is called the ‘charge’ of the phase singularity. It represents the number of additional wavefronts necessary to accommodate for the phase accumulated along C. It is obviously 0 if the closed path does not enclose the phase singularity. For a path enclosing the singularity (Fig. 2f), the gradient circulation of $\Delta \phi(r)$ is equal to the winding of $-2\theta_q$ and hence to that of $-2\theta_q$. Because the Berry phase in graphene, $\gamma = \pi$, is given by half the winding of $\theta_q$ (see Supplementary Information) it follows that $2\pi N = 4\gamma$ for a clockwise-oriented contour. The $N = 2$ additional wavefronts seen in Fig. 2f are therefore a signature of the Berry phase in graphene and prove the existence of Dirac cones. We note that, given the quality of the STM image, the winding $4\gamma = 4\pi$ can also be directly retrieved from the phase of the Fourier transform$^{19}$ as shown in Figs. 1c and 2d.

The contribution from sublattice A to the total electron density modulation alters only the shape of the dislocation, which is a robust topological feature (see Supplementary Information). The dislocations are shifted from $r = 0$ in the direction $\Delta K$, in agreement with experiments (Fig. 1d, e, and g).

The H atom can be placed on a different sublattice, as inferred from the different orientations of the tripod shape$^{16}$ of the H signal in Fig. 3a. For a given direction of closed path around the impurity, the sign of $N$ is opposite for the two orientations (Fig. 3b). This is because the two configurations relate to one another via inversion symmetry with respect to the centre of a C–C bond. Because the underlying lattice of graphene is bipartite, this further means that this single-particle topological signature of the sublattice imbalance also relates, via Lieb’s theorem$^{28}$, to the spontaneous magnetic moments induced by the electron interactions at half filling$^{16}$. In contrast to this many-body effect, the dislocations in Friedel oscillations are independent of doping (see Supplementary Information).
Information). Figure 3c, d shows that if two H atoms are placed on neighbouring carbon atoms there is no dislocation in the inter-valley scattering signal. This results from the annihilation of dislocations of opposite N and illustrates that disorder must break sublattice symmetry (see Supplementary Information).

In quantum mechanics, wavefront dislocations have been predicted for scalar wavefunctions such as the Aharonov–Bohm wavefunction, but were thought to be unobservable owing to the U(1) gauge invariance of the density. We have demonstrated that dislocations appear in the charge density of vectorial wavefunctions, the components of which can interfere with each other by scattering between distant time-reversed valleys. Because wavefront dislocations arise from phase singularities that relate to the topological properties of band structures for vectorial wavefunctions, wavefront dislocations in Friedel oscillations can lead to the identification of relativistic and topological phases, as already established theoretically for rhombohedral graphite and one-dimensional insulators. This method of determining the topological properties of band structures is complementary to transport measurements under a strong magnetic field. However, in contrast to transport measurements, where it destroys quantum Hall measurements, disorder turns out to be an asset here, as long as an area of 100–500 nm² with a point-like scatterer is available on the surface.

Online content
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1. Sólyom, J. Methods for calculating and measuring the band structure. In Fundamentals of the Physics of Solids Vol. 2 (ed. Sólyom J.) 151–194 (Springer, 2009).
2. Berry, M. V. Quantal phase factors accompanying adiabatic changes. Proc. R. Soc. Lond. A 392, 45–57 (1984).
3. Xiao, D., Chang, M.-C., Niu, D. Berry phase effects on electronic properties. Rev. Mod. Phys. 82, 1959–2007 (2010).
4. Novoselov, K. S. et al. Two-dimensional gas of massless Dirac fermions in graphene. Nature 438, 197–200 (2005).
5. Zhang, T., Tan, Y.-W., Stormer, H. L. & Kim, P. Experimental observation of the quantum Hall effect and Berry’s phase in graphene. Nature 438, 201–204 (2005).
6. Nye, J. F. & Berry, M. V. Dislocations in wave trains. Proc. R. Soc. Lond. A 336, 165–190 (1974).
7. Crommie, M. F., Lutz, C. P. & Eigler, D. M. Imaging standing waves in a two-dimensional electron gas. Nature 363, 524–527 (1993).
8. Friedel, J. The distribution of electrons round impurities in monovalent metals. Philos. Mag. 43, 153–189 (1952).
9. Zala, G., Narozhny, B. N. & Aleiner, I. L. Interaction corrections at intermediate temperatures: longitudinal conductivity and kinetic equation. Phys. Rev. B 64, 214204 (2001).
10. Ruderman, M. A. & Kittel, C. Indirect exchange coupling of nuclear magnetic moments by conduction electrons. Phys. Rev. 96, 99–102 (1954).
11. Kasuya, T. Theory of metallic ferro- and antiferromagnetism on Zener’s model. Prog. Theor. Phys. 16, 45–57 (1956).
12. Yoshida, K. Magnetic properties of Cu-Mn alloys. Phys. Rev. 106, 893–898 (1957).
13. Rüter, G. M. et al. Scattering and interference in epitaxial graphene. Science 317, 219–222 (2007).
14. Mallet, P. et al. Role of pseudospin in quasiparticle interferences in epitaxial graphene probed by high-resolution scanning tunnelling microscopy. Phys. Rev. B 86, 045444 (2012).
15. Brihuega, I. et al. Quasiparticle chirality in epitaxial graphene probed at the nanometer scale. Phys. Rev. Lett. 101, 206802 (2008).
16. González-Herrero, H. et al. Atomic-scale control of graphene magnetism by using hydrogen atoms. Science 352, 437–441 (2016).
17. Springer, P. T., Petersen, L., Plummer, E. W., Lægsgaard, E. & Besenbacher, F. Giant Friedel oscillations on the beryllium(0001) surface. Nature 275, 1764–1767 (1977).
18. Cheianov, V. V. & Fal’ko, V. I. Friedel oscillations, impurity scattering, and temperature dependence of resistivity in graphene. Phys. Rev. Lett. 97, 226801 (2006).
19. Dutreix, C. & Katsnelson, M. I. Friedel oscillations at the surfaces of rhombohedral N-layer graphene. Phys. Rev. B 93, 035413 (2016).
20. Katsnelson, M. I. Graphene: Carbon in Two Dimensions (Cambridge Univ. Press, 2012).
21. Berry, M. V., Chambers, R. G., Large, M. D., Upstill, C. & Walsmsley, J. C. Wavefront dislocations in the Aharonov–Bohm effect and its water wave analogue. Eur. J. Phys. 1, 154–162 (1980).
22. Berry, M. V. Making waves in physics. Nature 438, 21 (2000).
23. Dennis, M. R., O’Holleran, K. & Padgett, M. J. Singular optics: optical vortices and polarization singularities. In Progress in Optics Vol. 53 (ed. Wolf, E.) 293–363 (Elsevier, 2009).
24. Rafayelyan, M. & Brasselet, E. Bragg–Berry mirrors: reflective broadband plates. Opt. Lett. 41, 3972–3975 (2016).
25. Kösteritz, J. M. & Thouless, D. J. Ordering, metastability and phase transitions in two-dimensional systems. J. Phys. C 6, 1181–1203 (1973).
26. Feynman, R. P. Application of quantum mechanics to liquid helium. In Progress in Low Temperature Physics Vol. 1 (ed. Gorter, C. J.) 17–53 (Elsevier, 1955).
27. Abrikosov, A. A. On the magnetic properties of superconductors of the second group. Sov. Phys. JETP 5, 1174–1182 (1957).
28. Lieb, E. H. Two theorems on the Hubbard model. Phys. Rev. Lett. 62, 1201–1204 (1989).
29. Dutreix, C. & Delplace, P. Geometrical phase shift in Friedel oscillations. Phys. Rev. B 96, 195207 (2017).

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**Methods**

**Sample preparation.** Graphene was grown on silicon carbide (6H-SiC(0001)) by thermal annealing following the procedure described previously\(^{30}\). This leads to the growth of graphene layers, the low-energy physics of which is that of single-layer graphene owing to the decoupling by rotational disorder\(^{31}\). The doping of the top graphene layer could be controlled by the number of underlying layers, which is governed by the annealing temperature and time\(^{16}\). The results presented in the main text were obtained on a thick multilayer sample (more than five graphene layers) in which the substrate is too far away to dope the layers by charge transfer (see also Supplementary Information). A thinner sample (2–4 graphene layers) was prepared to investigate the effect of doping (see Supplementary Information). Hydrogen atoms were deposited on the surface of the graphene on the SiC substrate by thermal dissociation of H\(_2\) in a custom-made H-atom beam source under ultrahigh vacuum conditions\(^{32}\). A molecular H\(_2\) beam was passed through a hot tungsten filament held at 1,900 K. The pristine graphene substrate was placed 10 cm away from the filament, held at room temperature of around 25 °C during atomic H deposition and subsequently cooled down to 5 K, the temperature at which we carried out all STM and scanning tunnelling spectroscopy experiments presented here. H\(_2\) pressure was regulated by a leak valve and fixed to 3 × 10\(^{-7}\) torr as measured in the preparation chamber for the present experiments. The atomic H coverage was adjusted by varying the deposition times between 200 s and 60 s, corresponding to final coverages between 0.10 and 0.03 H atoms per nm\(^2\).

**STM measurements.** The STM measurements were performed in situ using a custom-made low-temperature STM operating at 5 K under ultrahigh vacuum. Figures 1a and 3a, c were obtained in constant current mode. Conductance spectra and images presented in the Supplementary Information were taken using a lock-in technique, with an a.c. voltage (with a frequency of 830 Hz and amplitude of 1–2 mV root mean square) added to the d.c. sample bias.

**Data availability**

The datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.

30. Varchon, F., Mallet, P., Magaud, L. & Veuillen, J.-Y. Rotational disorder in few-layer graphene films on 6H-SiC(0001): a scanning tunneling microscopy study. *Phys. Rev. B* **77**, 165415 (2008).

31. Hass, J. et al. Why multilayer graphene on 4H-SiC(0001) behaves like a single sheet of graphene. *Phys. Rev. Lett.* **62**, 1201–1204 (2008).

32. Hornøe, L. et al. Clustering of chemisorbed H(G) atoms on the graphite (0001) surface due to preferential sticking. *Phys. Rev. Lett.* **97**, 186102 (2006).

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**Author contributions** H.G.-H. and I.B. performed the experiments. V.T.R. discovered the dislocations, which were explained with the theory derived by C.D. M.I.K. and C.C. gave technical support and conceptual advice. C.D. and V.T.R. wrote the manuscript with the input of all authors. V.T.R. coordinated the collaboration.

**Competing interests** The authors declare no competing interests.

**Additional information**

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