Higher-order topology in bismuth

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The mathematical field of topology has become a framework in which to describe the low-energy electronic structure of crystalline solids. Typical of a bulk insulating three-dimensional topological crystal are conducting two-dimensional surface states. This constitutes the topological bulk–boundary correspondence. Here, we establish that the electronic structure of bismuth, an element consistently described as bulk topologically trivial, is in fact topological and follows a generalized bulk–boundary correspondence of higher-order: not the surfaces of the crystal, but its hinges host topologically protected conducting modes. These hinge modes are protected against localization by time-reversal symmetry locally, and globally by the three-fold rotational symmetry and inversion symmetry of the bismuth crystal. We support our claim theoretically and experimentally. Our theoretical analysis is based on symmetry arguments, topological indices, first-principles calculations, and the recently introduced framework of topological quantum chemistry. We provide supporting evidence from two complementary experimental techniques. With scanning-tunnelling spectroscopy, we probe the signatures of the rotational symmetry of the one-dimensional states located at the step edges of the crystal surface. With Josephson interferometry, we demonstrate their universal topological contribution to the electronic transport. Our work establishes bismuth as a higher-order topological insulator.
circuit systems, as well as phononic and photonic systems, this work provides a realization of a three-dimensional HOTI in the electronic structure of a crystal.

**Bulk topology.** Fu and Kane gave a simple topological index for a three-dimensional topological insulator in the presence of inversion symmetry $\overline{I}$: One multiplies the inversion eigenvalues (which are $\pm 1$) of all Kramers pairs of occupied bands at all time-reversal symmetric momenta in the Brillouin zone. If this product is $-1$ ($+1$), the insulator is topological (trivial). In the topological case, one says the material has a band inversion. Note that when we evaluate this index for bismuth, we obtain $+1$, in accordance with the well-known result that the band structure of bismuth is topologically trivial from a first-order perspective. A sample of bismuth thus does not have topologically protected gapless surface states. However, this is not because bismuth does not display a band inversion: we will show that there are two band inversions, whose presence is not captured by the first-order index, which is only sensitive to the parity of band inversions. We first extend this index to HOTIs with TRS, $C_3$ rotation, and inversion symmetry $\overline{I}$. We consider a $C_3$ rotational symmetry with axis that is given by the line connecting the time-reversal symmetric momenta $\Gamma$ and $T$ (see Fig. 1a for a representation of the Brillouin zone). For spin-$1/2$ particles, $C_3$ has eigenvalues $-1$ and $\exp(\pm \pi/3)$, where a subspace with $-1$ eigenvalue is closed under TRS, while TRS maps the $\exp(\pm \pi/3)$ subspace to the $\exp(\pm \pi/3)$ one and vice versa. We can thus define a band inversion separately in the occupied band subspaces of an insulator with $C_3$ eigenvalues $-1$ and $\exp(\pm \pi/3)$. To do so, observe that of the eight time-reversal symmetric momenta, two are invariant under $C_3$, ($\Gamma$ and $T$), while two groups of three-time symmetric reciprocal momenta transform into each other under $C_3$ (call them $X_1$ and $L_z$, $l_z = 1, 2, 3$). Denote by $v_i = \prod_y \hat{e}_{i,y}$ the product over all inversion eigenvalues $\xi_i, \xi_i = \pm 1$ of the occupied band’s Kramers pairs at the time-reversal symmetric momenta $Y \in \{ \Gamma, T, X_1, L_z \}$. At $\Gamma$ and $T$ we further define $v^{(+)\Gamma}_Y$ and $v^{(+)\Gamma}_Y$, where the product is restricted to the Kramers pairs with $C_3$ eigenvalues $-1$ and $\exp(\pm \pi/3)$, respectively, such that $v_Y = v^{(+)\Gamma}_Y$ for $Y = \Gamma, T$. By $C_3$ symmetry $v_{X_1} = v_{X_1}, v_{X_2} = v_{X_2}$, and $v_{L_z} = v_{L_z}$ so that the Fu–Kane index is given by $v = v_\Gamma v_\Gamma^* v_{L_z} v_{L_z}^*$. Consider a Kramers pair of states at $X_1$, together with its two degenerate $C_3$ partners at $X_1$ and $X_2$. Out of a linear combination of these states, one can construct one Kramers pair with $C_3$ eigenvalue $-1$, and two Kramers pairs with eigenvalues $\exp(\pm \pi/3)$. This is shown explicitly in the Supplementary Information. When taking the Kramers pair at $X_1$ together with its degenerate partner at $X_2$ and $X_3$ to have negative inversion eigenvalue, these $C_3$ symmetric linear combinations also have negative inversion eigenvalue. Thus, a band inversion at $X_1$ as measured by the Fu–Kane formula induces a single band inversion in the $-1$ subspace, and two (which equals no) band inversions in the $\exp(\pm \pi/3)$ subspace. The same holds for the $L_z$ points. We conclude that the total band inversion in the occupied subspaces with $C_3$ eigenvalues $-1$ and $\exp(\pm \pi/3)$ are given by

$$
\begin{align*}
L^{(-)}_i &= v^{(-)}_i v^{(-)}_i^* v_{i,L_z} v_{i,L_z}^*, \\
L^{(+)\Gamma}_i &= v^{(+)\Gamma}_i v^{(+)\Gamma}_i^* v_{i,L_z} v_{i,L_z}^*,
\end{align*}
$$

(1)

respectively. We then distinguish three cases: (i) $v^{(+)\Gamma}_i = v^{(+)\Gamma}_i = 1$ for a trivial insulator, (ii) $v^{(+)\Gamma}_i = v^{(-)}_i = -1$ for a $\mathbb{Z}_2$ topological insulator, and (iii) $v^{(+)\Gamma}_i = v^{(+)\Gamma}_i = -1$ for a HOTI.

Thus far, our considerations apply to all crystals with TRS, $C_3$ and $\overline{I}$. We now evaluate the above topological index for elementary bismuth, crystallizing in space group $R\overline{3}m$, number 166, which possesses these symmetries (see Fig. 1b). Even though bismuth is not an insulator, there exists a direct bandgap separating valence bands from conduction bands (see Fig. 1c). This allows us to evaluate the indices $v^{(+)\Gamma}$ and $v^{(+)\Gamma}$ for the valence bands. We do so with the group characters obtained from first-principles calculations (see Methods). The result is $v^{(+)\Gamma} = v^{(+)\Gamma} = -1$, which derives from $v^{(+)\Gamma}_i = v^{(+)\Gamma}_i = -1$, that is, there is a $C_3$-graded double band inversion at the $T$ point. Hence, bismuth is a HOTI according to the topological index defined above (if we neglect the fact that it has a small electron and hole pocket).

As a second approach, we employ the formalism of elementary band representations to demonstrate the nontrivial topology. Since there is always an energy separation between valence and conduction bands, we restrict our consideration to the three doubly-degenerate valence bands shown in red in Fig. 1e. In particular, we checked explicitly that the set of all bands at lower energy than these is topologically trivial. At time-reversal symmetric momenta the eigenvalues of all symmetry operators have been computed (see Methods). Referring to the character tables in the Bilbao Crystallographic Server, we assign to all the bands their corresponding irreducible representations. The results of the eigenvalue calculations are listed in Supplementary Information section C. They show that the valence bands cannot be decomposed into any linear combination of physical elementary band representations, which are elementary band representations that respect TRS. It is the main result of ref. 19, that if such a decomposition is not possible, the electronic band structure of bismuth has to be topological and without a description in terms of exponentially localized Wannier states, in contraposition to the conclusion drawn from Fu–Kane’s parity criterion. To understand which symmetry protects this topological phase, we repeated the symmetry eigenvalue calculation with an artificially lowered symmetry. The representative elements of point group $3m$ are $C_3$, around the $z$ axis (denoted 3 in the space group names), $I$ (denoted by overbar), two-fold rotational symmetry about the $y$ axis (denoted 2), and mirror symmetry with respect to the $x$–$z$ plane (denoted $m$). After lowering the space group $R\overline{3}m$ (166) to $R\overline{3}m$ (160) or $R\overline{3}2$ (155), a similar elementary band representation analysis within the symmetry-reduced space groups shows that the valence bands can be decomposed into physical elementary band representations in this case, indicating that they are topologically trivial. Therefore, neither two-fold rotation nor mirror symmetry protects the nontrivial topology of bismuth. In contrast, as long as $I$ is preserved, lowering it to space group $R\overline{3}$ (148), the valence bands are still topological in the sense that they cannot be decomposed into physical elementary band representations in space group 148. We conclude that the nontrivial topology is protected by $I$ (in combination with the three-fold rotation). Notice that the rhombohedral lattice always respects the three-fold rotational symmetry. Since we learned from topological quantum chemistry that the bulk bands have no Wannier description, we expect the presence of special flow in Bi, and hence protected gapless modes on its boundaries. Since we know the surfaces of bismuth to be non-topological, these gapless boundaries must be hinges. This is compatible with previous works showing that Bi (111) bilayers (possibly on a substrate) host one-dimensional edge channels.

When we change the parameters of the tight-binding model of bismuth slightly, it undergoes a transition from a second-order to a first-order topological insulator. However, we confirmed the higher-order character of bismuth that is suggested by the original tight-binding model parameters independently by performing first-principles calculations, as well as an analysis in the framework of topological quantum chemistry. In particular, we took into account all occupied bands of bismuth up to its momentum-dependent energy gap. This is important since it has been shown that bands far away from this gap still contribute significantly to measurable effects, such as the unusually large $g$-factor of holes.

**Bulk–boundary correspondence.** We present a direct calculation which allows us to conclude that a TRS system with $v^{(+)\Gamma} = v^{(+)\Gamma} = -1$ has to have hinge modes for terminations of the crystal that globally respect inversion symmetry or further symmetries. We consider...
a crystal of hexagonal shape (see Fig. 1c) that preserves $C_3$ rotational and inversion symmetry. The steps outlined here in words are explicitly demonstrated using a Dirac model in Supplementary Information section A. We think of the insulator with $\psi^{(x)} = \psi^{(x/3)} = -1$ as a superposition of two topological insulators, one in each of the independent $C_3$ subspaces. Consider adiabatically turning off any coupling between these two subspaces, while preserving the bulk gap. The resulting system has two Dirac cones (a Dirac theory represented by $4 \times 4$ matrices) on all surfaces of the crystal. Next, we seek to gap these surface Dirac cones by weakly coupling the two $C_3$ subspaces. We want to do so while preserving TRS, as well as the symmetries $C_3$ and $\bar{I}$ of the crystal. Of these, TRS is the only constraint that acts locally on a given surface. From the representation theory of the two-dimensional Dirac equation, we find that for a TRS that squares to $-1$, as required for spinful electrons, there exists a unique mass term $m$ that gaps the two Dirac cones in a time-reversal symmetric way. It remains to study how this mass term transforms under $C_3$ and $\bar{I}$ to determine its relative sign between different surfaces of the crystal. Relative to the kinetic part of the surface Dirac theory, $m \to -m$ under inversion and $m \to +m$ under $C_3$ (see Supplementary Information section A for details). As a result, the sign of the mass term alternates between adjacent lateral surfaces of the hexagonal crystal (see Fig. 1c). Each change of sign in the mass term is a domain wall in the Dirac theory and binds a Kramers pair of modes propagating along it. These are the one-dimensional hinge modes of the HOTI. The sign of the mass term on the top and bottom surface is not universally determined so that both patterns of hinge modes shown in Fig. 1c are compatible with the bulk topology of $\psi^{(x)} = \psi^{(x/3)} = -1$ (in a real system, the particular electronic structure determines which pattern has lower energy). Apart from this ambiguity, the argument presented here rests solely on the nontrivial bulk topology and is independent of the exact form of the surface electronic structure, as long as the surface is gapped while preserving the respective symmetries. This constitutes the generalized topological bulk–boundary correspondence characteristic of a HOTI, where the existence of one-dimensional hinge modes directly follows from the three-dimensional bulk topology. The HOTI's bulk–boundary correspondence requires that these hinge modes are locally stable.
The hinge modes in the electronic structure plots we present here. It does not have metallic bulk and surface states that would obscure the topological character of the phase: the minimal TRS surface manipulations of large systems feasible.

We now turn to experimental data that support our higher-order bulk–boundary correspondence in bismuth. Even though bismuth is metallic in the bulk and on the surface, only its topological hinge states are protected against scattering by weak disorder as compared to trivial surface states, for example. We expect hinge states between (i) the top surface, which is denoted (111) in the primitive unit vectors, and three of the six lateral surfaces and (ii) between adjacent lateral surfaces. The geometry of the samples was more amenable to the study of the hinge states of type (i), as we outline below.

STM experiment. With an STM, we studied the electronic structure of step edges on the (111) surface of bismuth. Owing to the buckled honeycomb structure of the bismuth bilayer along the [111] trigonal direction, STM topographic images of the (111) plane of bismuth show bilayer steps with two different types of bisectrix edges: type A and type B (marked as red and blue lines in Fig. 2a). We highlight two structures of triangular and nearly hexagonal shape (Fig. 2a,c). In particular the step edge in Fig. 2c can be seen as (the negative of) a one bilayer tall version of the crystal shapes shown in Fig. 1c. We thus expect hinge states at either the type A or the type B edges owing to the higher-order topology. (All A type and all B type edges are mutually equivalent owing to the $C_3$ rotational symmetry of the bismuth (111) surface.) Indeed, we observe strongly localized edge states only at type A edges in Fig. 2b,d, which display the differential conductance map overlaid on top of the topographic data to illuminate the edge states at the van Hove singularity energy of the bismuth edge states. A previous experimental study showed a one-dimensional
van Hove singularity of the edge states ($E = 183 \text{ meV}$) and quasiparticle interference of the spin-orbit locked edge states. The same study demonstrated the absence of $k \rightarrow -k$ scattering for these states. These experimental observations and model calculations strongly suggest that the edge states are living in the momentum-dependent energy gap of the bismuth (111) surface states. Every other edge of a hexagonal pit exhibits localized edge states and these edge states are discontinued at the corner where type A and type B edge meet (Fig. 2c,d). This feature remarkably reproduces the hinge modes calculated for the hexagonal nanowire, as shown in Fig. 1d.

Transport experiment. We exploited proximity-induced superconductivity to reveal ballistic hinge states along monocrystalline bismuth nanowires. When these (non-superconducting) nanowires are connected to superconducting contacts (implementing a superconductor/bismuth nanowire/superconductor or S/Bi/S Josephson junction), a supercurrent runs through them at low temperature. Our experiments unambiguously demonstrate that the supercurrent flows via extremely few narrow one-dimensional channels, rather than via the entire surface or bulk of the nanowire. The experimental indications are as follows. (i) Periodic oscillations of the critical current through the nanowires caused by a magnetic field, with a period corresponding to one magnetic flux quantum through the wire section perpendicular to the field. Such oscillations indicate interference between two supercurrent-carrying paths located at the nanowire edges (see also the Supplementary Information), since a uniform current density in such a long narrow wire would produce instead a monotonously decaying critical current. (ii) The supercurrent flowing through the nanowire persists to extremely high magnetic fields, up to several Tesla in some samples. Since the orbital dephasing due to a magnetic flux through the supercurrent-carrying channel area destroys the induced supercurrent, this indicates that the channels are extremely narrow spatially. (iii) Finally, we have recently provided a direct signature of ballistic transport along those one-dimensional channels, by measuring the supercurrent-versus-phase relation (also called current–phase relation) of the S/Bi/S junction. This was done by inserting the bismuth nanowires into an asymmetric superconducting quantum interference device (SQUID) configuration. Whereas tunneling or diffusive transport give rise to the usual nearly sinusoidal current–phase relation of superconductor/normal metal/superconductor Josephson junctions, the sharp sawtooth-shaped current–phase relation that we found instead demonstrates that transport occurs ballistically across the wire. The scattering probability $p$ was estimated to be 0.1 along the 1 $\mu$m long bismuth wire from the harmonics content of this current–phase relation (where the $n$th harmonic decays like $(1-p)^n/n$). This leads to a lower bound of the elastic mean free path $l_e$ along these edges equal to 10, much larger than the value $l_e = 0.1$ determined for the surface states. This surprising result is explained by the dominant contribution of the topologically protected hinge states to the supercurrent. Indeed, the supercurrent carried by a diffusive channel is $(L/l_e)^2 \approx 100$ times smaller than the supercurrent carried by a ballistic channel ($L$ is the wire length). The position of the edge states can be deduced from the periodicity of the SQUID oscillations, which is inversely proportional to the area enclosing the flux. In a sample of parallelogrammatically cross-section whose geometry and orientation was precisely determined, we detected a beating of two paths enclosing different fluxes $\Phi$ and $\Phi'$ (see Fig. 3a). This demonstrated that the edge states are located along the two acute edges of the (111) facets. Those edges coincide with the expected hinge states perpendicular to the trigonal [111] axis (see Fig. 3b). The contribution of each path was extracted and is shown in Fig. 3d,e. The supercurrents carried by the two hinges differ by a factor of four. This can be explained by a difference in the quality of the contact to these hinge states: the top hinges of the nanowire have been more severely etched than the bottom ones during the deposition of the superconducting electrodes (see Fig. 3a). This strong etching reduces the coupling of edge states to the superconducting contacts and the supercurrent is decreased even though the ballistic nature is unaffected.

**Fig. 3 | Evidence for hinge states from Josephson-interference experiments.** a. Single-crystal bismuth nanowire (coloured brown) connected to superconducting electrodes (coloured blue). The wire has a parallelogrammatic cross-section. Its orientation along one of the bisectrix axes of bismuth was determined by electron diffraction, showing evidence of (111) facets parallel to the substrate. The 1.4 $\mu$m long, rightmost section of the wire, in parallel with a superconducting weak link, forms an asymmetric SQUID. b. Schematic representation of the investigated bismuth nanowire of parallelogrammatic cross-section described above, indicating (red lines) the position of the experimentally identified topological hinge states in relation to the hinge states determined theoretically in a bismuth sample of hexagonal symmetry oriented along the trigonal [111] axis. c. The magnetic field $B$ dependence of the critical current $I_c$, shown by the current–phase relation of the bismuth Josephson junction (whose critical current is much lower than the superconducting weak link). d,e. The current–phase relation in c can be decomposed into the sum of two sawtooth waves of different periods, corresponding respectively to the internal and external area of the SQUID $\Phi$ and $\Phi'$ shown in a.
Comparing Figs. 3d and 1c, we note that one of the two hinges on top of the nanowire must be of A type and the other one of B type (the same is true for the bottom two hinges). Our observation of a ballistic channel at one of these hinges at the top, and one at the bottom of the nanowire, is thus in line with the theoretical expectation from the higher-order topology of bismuth.

Summary. The bismuth–antimony alloy, Bi$_x$Sb$_{1-x}$, was the first material realization of a three-dimensional topological insulator$^{1,4}$. The composition x was used to interpolate between bismuth, without band inversion, and the band-inverted antimony. In this work, we have demonstrated theoretically that the allegedly trivial end of this interpolation, bismuth, has in fact a three-dimensional topological band structure as well. It is a HOTI with helical hinge states. We have presented two complementary pieces of experimental evidence supporting this result, using STM and Josephson-interferometry measurements. The type of hinge states discussed here may be used for lossless electronic transport owing to their local protection from backscattering by TRS disorder. Further applications include spintronics, owing to their spin–momentum locking, and—when proximitized with superconductivity—topological quantum computation. For the latter, a nanowire with hexagonal cross-section may provide a particularly convenient way of building a hexon: a group of six Majorana states, one at each hinge. Hexons have been proposed as building blocks for a measurement-only quantum computer$^{16}$.

Methods. Methods, including statements of data availability and any associated accession codes and references, are available at https://doi.org/10.1038/s41567-018-0224-7.

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Author contributions

F.S., A.M.C., B.A.B. and T.N. carried out the theoretical analysis and model calculations. Z.W. and M.G.V. performed the first-principles calculations and topological quantum chemistry analysis. A.M., S.S., A.Y.K., R.D., H.B., and S.G. conceived and carried out the transport experiments including crystal growth. S.J., I.D. and A.Y. conceived and carried out the STM/STS experiments.

Competing Interests

The authors declare no competing interests.

Additional information

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Methods
First-principles calculations. We employed density functional theory as implemented in the Vienna Ab Initio Simulation Package (VASP)\(^{64–69}\). The exchange correlation term is described according to the Perdew–Burke–Ernzerhof prescription, together with projected augmented-wave pseudopotentials\(^{68,69}\) and the spin–orbit interaction included. For the self-consistent calculations we used a $12 \times 12 \times 12$ $k$-point mesh for the bulk band-structure calculations. The eigenvalues of the symmetry transformations were deduced from the matrix representations of the respective symmetry operation calculated using the Bloch eigenstates from VASP.

STM experiment. Bismuth crystals were cleaved at room temperature under ultrahigh vacuum conditions and the cleaved samples were cooled down to 4 K, at which temperature STM and STS measurements were carried out. The cleaved bismuth crystal exhibits a (111) plane of the bismuth rhombohedral structure (which is the (001) plane of the bismuth hexagonal structure). For STM measurements, a mechanically sharpened platinum–iridium tip was used, and electronic properties of the probe tip were characterized before the experiments on bismuth by checking a reference sample. Differential conductance maps (Fig. 2b,d) were taken simultaneously with topographic data at the van Hove singularity energy ($V = 183$ meV) of the bismuth edge states using a lock-in amplifier with an oscillation of 3 meV and current $I = 3.5$ nA. The data shown in this work is reproduced on many step edges of Bi (111) with atomically different tips. All of the islands on the Bi (111) surface show the expected step height of 4 Å for bismuth bilayers and all of the extended edges are identified as zigzag structures of either A type or B type. A type and B type edges are equivalent in the hexagonal nanowire geometry as described in the main text (Fig. 1c); however, the existence of the Bi (111) surface under the bismuth bilayer breaks the inversion symmetry, and A as well as B type edges can be identified in STM measurements. Only A type edges show the spectroscopic feature of a sharp peak at 183 meV, which is the van Hove singularity energy of the one-dimensional edge state. Quasi-particle interference measurements reveal that this edge state is continuously dispersing down to the Fermi level and starts to merge with the surface states at the momentum where the surface gap closes\(^{14}\). This spectroscopic feature of geometric confinement only at A type edges resembles the topological hinge modes expected for the hexagonal nanowire, as discussed in the main text.

Transport experiment. The nanowires grew during slow sputtering deposition of high-purity bismuth on a slightly heated silicon substrate. High-resolution transmission electron microscopy indicates high-quality single crystals of hexagonal or rhombohedral cross-sections, with clear facets. The facet widths are typically 50 nm to 300 nm wide. Resistance measurements show that transport in the normal state (when contacts to the nanowires are not superconducting) occurs predominantly due to surface states, with an elastic mean free path of the order of 100 nm.

Data availability. The data that support the plots in Figs. 1, 2 and 3 within this paper and other findings of this study are available from the corresponding author upon reasonable request. The information on elementary band representations is available on the Bilbao crystallographic server\(^{63}\).

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