Nodal-chain metals

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The band theory of solids is arguably the most successful theory of condensed-matter physics, providing a description of the electronic energy levels in various materials. Electronic wavefunctions obtained from the band theory enable a topological characterization of metals for which the electronic spectrum may host robust, topologically protected, fermionic quasiparticles. Many of these quasiparticles are analogues of the elementary particles of the Standard Model11–18, but others do not have a counterpart in relativistic high-energy theories11–18. A complete list of possible quasiparticles in solids is lacking, even in the non-interacting case. We describe the possible existence of a hitherto unrecognized type of fermionic excitation in metals. This excitation forms a nodal chain—a chain of connected loops in momentum space—along which conduction and valence bands touch. We prove that the nodal chain is topologically distinct from previously reported excitations. We discuss the symmetry requirements for the appearance of this excitation and predict that it is realized in an existing material, iridium tetrafluoride (IrF4), as well as in other compounds of this class of materials. Using IrF4 as an example, we provide a discussion of the topological surface states associated with the nodal chain. We argue that the presence of the nodal-chain fermions will result in anomalous magnetotransport properties, distinct from those of materials exhibiting previously known excitations.

Recently discovered Dirac and Weyl semimetals3–10 host topologically protected degeneracy of four and two electronic bands, respectively, at isolated points in the Brillouin zone close to the Fermi level (E_F). The low-energy excitations in these materials are described by Dirac or Weyl Hamiltonians, as appropriate, of the relativistic quantum field theory, leading to the realization of the chiral anomaly20,21 and topological surface Fermi arcs3,9,10.

Owing to weaker symmetry constraints, condensed matter systems can realize quasiparticles that have no analogues in high-energy theories11–18, hosting new physical phenomena. For example, in the presence of spin–orbit coupling, a valence and a conduction band with different mirror eigenvalues can touch along lines in mirror-invariant planes of the Brillouin zone, forming a so-called accidental nodal loop (ANL). The ANL materials are predicted to host special ‘drumhead’ surface states18, which were argued to provide a route to higher-temperature superconductivity22,23.

The spectrum of a nodal-chain fermion described here is illustrated in Fig. 1. The nodal chain consists of nodal loops, which are distinct from ANLs in that they are guaranteed to appear in the vicinity of the Fermi level (E_F) in certain non-centrosymmetric materials provided that their crystal structure has a non-symmorphic glide-plane symmetry g = [σ t], formed by a reflection σ, followed by a translation t, by a fraction of a primitive lattice vector. For several space groups listed in Fig. 1, such non-symmorphic nodal loops (NSNLs) appear on mutually orthogonal high-symmetry planes, touching each other at isolated points on a high-symmetry axis. Thus, a chain of double degeneracy is formed that goes across the entire Brillouin zone. We first describe the building blocks of nodal chains—NSNLs. For spin–orbit coupled systems, g^2 = −e^−i2k·t, where k is the electron momentum and t is the in-plane component of t; consequently, the possible eigenvalues of g are η±(k) = ±ie−i2k·t which are k-dependent whenever |t| = 0 (ref. 24).

The relation Π1 · t1 = 0 (mod π/2) holds for any of the four in-plane time-reversal invariant momenta (TRIMs) Πi, defined as Πi = −Π1 + Gi, with Gi a reciprocal lattice vector (see Supplementary Information). This definition makes it possible for the two TRIMs Π1,2 to satisfy

\[(Π_1 - Π_2) · t_1 = \frac{π}{2} \mod π \quad (1)\]

so that the glide eigenvalues η±(k) are ±i at k = Π1 and ±1 at k = Π2. Hence, along any in-plane path p that connects Π1 to Π2, the glide eigenvalues η±(k) must smoothly evolve from (+i, −i) to (+1, −1), as illustrated in Fig. 2a. However, in time-reversal-symmetric (Θ-symmetric) systems (see Supplementary Information for a generalization to antiferromagnetic systems), the bands form Kramer's pairs, which are degenerate at TRIMs and carry complex-conjugate eigenvalues. Because the eigenvalues are no longer complex conjugates at Π2, they belong to different Kramer's doublets, meaning that there are several Kramer's pairs that switch partners along p, as shown in Fig. 2b. This argument holds for any in-plane path p, and so there exists a nodal

Figure 1 | Catalogue of nodal-chain metals. A nodal chain appears in metals with the space groups shown whenever there are 4n + 2 electrons per primitive unit cell. The blue and red lines show the nodal loops located in mutually orthogonal planes in the Brillouin zone. The additional double Weyl points are marked with green circles. The high-symmetry lines supporting a twofold degeneracy of valence (conduction) bands are highlighted in orange. In space groups 109 and 122 (shown bottom left), the touching point of the nodal loops is at the point P. The space groups are grouped according to their spectrum degeneracies at the high-symmetry points and lines.

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a glide plane. Such systems can accommodate nodal chains formed by a known topological excitations.

The direction of the magnetic field distinguishes NSNLs from all other properties for materials hosting NSNLs when an electric field is aligned. A gapless structure of the Landau levels suggests unusual transport symmetry.

Landau spectrum is gapped for ANLs, it is always gapless for NSNLs. In fact, if inversion-symmetry-breaking terms are smoothly tuned to zero in a NSNL Hamiltonian, then the NSNL shrinks into a Dirac loop (the NSNL) separating the two TRIMs, shown in Fig. 2a. A similar glide-plane argument plays a crucial role in realizing the hour-glass fermions on the surfaces of certain insulators, but here we describe a three-dimensional metallic excitation.

The illustration in Fig. 2b shows that NSNLs appear in materials in which bands come in quadruplets. Therefore, the NSNL is formed between valence and conduction bands whenever the number of electrons per unit cell is

\[ n_{\text{filled}} = 4n + 2, \quad n \in \mathbb{N} \]  

irrespective of all further material details. (Material examples of NSNLs formed by valence or conduction bands, and the ways in which NSNLs can be tuned to \( E_F \) are discussed in Supplementary Information.)

The topological characterization and the existence of the drumhead surface states is similar for ANLs and NSNLs (see Supplementary Information). Despite this similarity, we argue that low-energy excitations produced by ANLs and NSNLs are intrinsically distinct. Unlike ANLs, NSNLs are enforced by the symmetry of the underlying crystal structure. Moreover, NSNLs in \( \Theta \)-symmetric, non-centrosymmetric systems always enclose a TRIM, and so a single nodal loop contains a time-reversed image of each Bloch state in addition to the state itself. In fact, if inversion-symmetry-breaking terms are smoothly tuned to zero in a NSNL Hamiltonian, then the NSNL shrinks into a Dirac point (see Supplementary Information). This feature has immediate consequences in electron transport.

In particular, as outlined in Supplementary Information, application of a magnetic field in the direction orthogonal to the NSNL results in field-driven topological phase transitions. We find that the Landau levels of the conduction and valence bands touch at certain values \( B_c \) of the magnetic field, resulting in pumping of charge (equivalent to e/2 per area covered by a magnetic flux quantum, where \( e \) is the elementary charge) to the surface of the sample that is parallel to the plane of the NSNL. Hence, a step change in the Hall response of the metallic surface state is expected for magnetic field values \( B_c \).

The response of the NSNLs to the mirror-symmetry-breaking, in-plane magnetic field is distinct from that of the ANLs. Although the Landau spectrum is gapped for ANLs, it is always gapless for NSNLs. The crossing of the two Landau levels is protected by the product symmetry \( \Theta \)-g that survives the application of the in-plane field. The gapless structure of the Landau levels suggests unusual transport properties for materials hosting NSNLs when an electric field is aligned with the in-plane magnetic field, similar to case of the chiral anomaly in Weyl and Dirac semimetals. This dependence of the response on the direction of the magnetic field distinguishes NSNLs from all other known topological excitations.

Having established the NSNLs, we can now address systems with two glide planes. Such systems can accommodate nodal chains formed by a pair of touching NSNLs located in mutually orthogonal planes, while the bands at the touching point are still only doubly degenerate.

The criteria for the occurrence of a nodal chain are: (1) the system has to be symmetric under two inequivalent glide planes \( g_{1,2} = [\sigma_x, \{t_1,2\}] \) such that the criterion of equation (1) is fulfilled for the two TRIMs \( \Gamma_{1,2} \), which are located on the intersection of the two glide-invariant planes, for both translation vectors \( t_1,2 \); and (2) the two bands forming the chain must belong to two-dimensional representations at \( \Gamma_{1,2} \), which split into one-dimensional representations on the high-symmetry line connecting \( \Gamma_1 \) and \( \Gamma_2 \).

Out of the 230 space groups, those satisfying the above criteria for two mutually orthogonal glide planes are listed in Fig. 1. The space group number 110 (\( \text{I}4_1/\text{c}d \)) is discussed separately in Supplementary Information. In all the cases shown in Fig. 1, we find that at least one additional point of fourfold degeneracy, formed by two Weyl points of opposite chirality, is present at a high-symmetry point on the boundary of the Brillouin zone.

A nodal chain represents a new topological excitation, distinct from a collection of NSNLs. To see this, first note that the two NSNLs that form a nodal chain cannot be separated. The argument provided above for the appearance of the NSNL guarantees that there must be an odd number of band crossings along the high-symmetry line connecting \( \Gamma_1 \) and \( \Gamma_2 \).

The non-trivial transport properties of the nodal chain can be inferred from the above analysis of NSNLs in magnetic fields (a detailed study of the transport properties will be reported elsewhere (T.B., Q.S.W., A.A.S., manuscript in preparation)), suggesting several distinct scenarios for the Landau-level spectrum. Here we proceed with the analysis of the topological surface states of nodal chains that we illustrate using a particular real material example.

We found the nodal-chain state in iridium tetrafluoride (\( \text{IrF}_4 \)). The orthorhombic crystal structure of this compound belongs to space group number 43 (\( \text{Fdd}2 \)). The primitive unit cell contains two formula units so that the number of electrons satisfies equation (2). Each iridium site is surrounded by an octahedron of six fluorine atoms, four of which are shared with the neighbouring octahedra. The octahedra form a bipartite lattice as shown in Fig. 3a, b (see Supplementary Information for a detailed description of the crystal structure). The space group contains two mutually orthogonal glide planes: \( g_1 \) and \( g_2 \), formed by a reflection about the (100) and (010) plane, respectively, followed by a translation of (1/4, 1/4, 1/4) in the reduced coordinates.

Possible antiferromagnetic ordering with a Néel temperature of less than about 100 K was reported for \( \text{IrF}_4 \) in magnetic susceptibility measurements. A paramagnetic phase is expected to occur at temperatures below the Néel temperature, which are still accessible for angle-resolved photoemission spectroscopy (ARPES). We first discuss the paramagnetic phase, in which the crystal symmetries and band filling guarantee the presence of a nodal chain corresponding to the bottom left scenario in Fig. 1.

To study paramagnetic \( \text{IrF}_4 \) we performed first-principles calculations as detailed in Supplementary Information. The obtained band structure is shown in Fig. 3c. We indeed find a nodal chain, plotted in Fig. 4a, consisting of two NSNLs in the (100) and (010) planes. Both NSNLs cross the chemical potential four times, resulting in topologically protected touching points between electron and hole pockets (arrows in Fig. 3d). Similartouchings of carrier pockets, although of different topological origin, were predicted for type-II Weyl semimetals and ANLs. These Fermi-surface touching points can be probed using soft X-ray ARPES, and have been argued to be important for potential higher-temperature superconducting phases.

The nodal chain produces non-trivial topological surface states on the (100) surface of \( \text{IrF}_4 \), as shown in Fig. 3e, f. The projection of the (010) NSNL (100) NSNL onto the surface Brillouin zone is a line (oval), shown dashed in Fig. 3f. Fermi arcs arise from the touching points of the Fermi pockets. For the projection of the (100) NSNL (region 1 in Fig. 3h), a single such arc produced by the drumhead state

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**Figure 2** | Non-symmorphic nodal loop. a, Any path \( p \) connecting a pair of time-reversal-invariant momenta \( \Gamma_{1,2} \) in a glide-invariant plane (blue) that fulfil the criterion of equation (1) must have a gap closing point, which belongs to a non-symmorphic nodal loop (red). b, Two Kramers pairs shown along any path \( p \) connecting \( \Gamma_{1,2} \). The evolution of the glide eigenvalues along the path is shown in colour for all bands.
The crystal structure of IrF$_4$. Corner-sharing octahedra of fluorine atoms enclose iridium atoms. The colour indicates the two sublattices related by an approximate chiral symmetry. The same structure viewed along the [001] axis.

Band structure of paramagnetic IrF$_4$. Bands determined from first-principles (density functional theory, DFT; solid red lines) and from a tight-binding model with chiral symmetry (dotted green lines) are shown. The Fermi surface of IrF$_4$ consists of electron pockets (cyan) and hole pockets (red/dark blue when viewed from the outside/inside of the sheet), which touch (orange arrows) along the nodal rings. The density of states of the (100) surface shown along the high-symmetry lines of the surface Brillouin zone. Topological surface states are clearly visible. The density of states at the Fermi energy (dashed horizontal line in e), plotted in the (100) surface Brillouin zone. The end points of the surface Fermi arcs coincide with the projections of the bulk touching points of the electron and hole pockets. The dashed black line is the projection of the nodal chain into the surface Brillouin zone. The magenta line is the projection of a plane used to calculate the bulk $Z_2$ invariant. Analogues of e and f, but for a tight-binding model with chiral symmetry. The numbers in h indicate the number of topological surface bands in that region; the green lines correspond to the projection of the additional nodal loop imposed by chiral symmetry into the surface Brillouin zone. The colours in e–h indicate the density of states, with blue corresponding to zero, white to intermediate and red to high density of states.

To understand why both Fermi arcs of the (010) NSNL appear on a linear projection of the (010) NSNL produce two Fermi arcs, consistent with the fact that there are two such Fermi pocket touchings that project onto the same point in the surface Brillouin zone.

The arcs originating on different NSNLs are connected either directly or through a carrier pocket. Moreover, the $Z_2$ invariant computed along the gapped, $\Theta$-symmetric plane projected onto the magenta path in Fig. 3f is non-trivial. Hence, the path corresponds to an edge of a two-dimensional topological insulator, and has to host an odd number of Kramers pairs of edge states. In accord with the observed connectivity of Fermi arcs, there is a single Kramers pair of such edge states. To understand why both Fermi arcs of the (010) NSNL appear on the same side of its projection onto the (100) surface, we need to expose the approximate chiral symmetry that is present in the material. We constructed a tight-binding model for the pseudospin-1/2 orbitals located on the iridium sites that represent the two sublattices of the IrF$_4$ structure, and fitted the parameters to reproduce the first-principles results (see Supplementary Information). We found that the avoided crossing along the $Z$–$\Gamma$ line in Fig. 3c originates from the hoppings within the sublattices. The amplitudes of these hoppings are more than three times smaller than those of the inter-sublattice hoppings, meaning that there exists a weakly broken chiral symmetry in IrF$_4$, relating the two sublattices of the crystal structure. The chiral symmetry can be restored in the model by setting the intra-sublattice hoppings to zero. The corresponding band structure is shown in Fig. 3c, and it can be seen that the gap along the $Z$–$\Gamma$ line now vanishes, and an additional nodal loop appears. It connects to the nodal chain, thus creating a nodal loop located in the visible (front and top) faces of the box and the dashed lines indicate nodal lines located in the hidden (bottom and back) faces of the box. In c, all lines are solid to highlight the net structure.
net, shown in Fig. 4. The projection of the additional nodal loop onto the (100) surface is shown in green in Fig. 3h.

Endowed with the chiral symmetry, the Hamiltonian allows for an additional topological classification (see Supplementary Information), which predicts two/one/zero surface modes to exist in the regions labelled 2/1/0 in Fig. 3h. In the presence of the chiral symmetry, all these regions are topologically distinct and separated by nodal loops. When the chiral symmetry is weakly broken in real IrF₄, only the parity of the number of surface states remains topologically protected and the additional nodal loop becomes gapped. However, because the breaking of the chiral symmetry is weak, the location of surface modes in the surface Brillouin zone of IrF₄ is inherited from the chiral-symmetric structure.

The possible antiferromagnetic ordering in IrF₄ at low temperatures preserves the nodal-chain structure if the magnetic moment is aligned with the [001] axis. In fact, the nodal chain survives weak breaking of time-reversal symmetry, but not the breaking of glide planes.

We also looked for other possible nodal chain candidates. Several reports²⁷,³⁰ of stable XY₄ crystals (X = Ir, Ta, Re; Y = F, Cl, Br, I) with lattices formed of octahedra, similar to the IrF₄ lattice, exist, but with only fragmentary crystallographic data. Assuming these compounds crystallize in the same space group as IrF₄, we carried out an exhaustive first-principles study and found nodal chains in each of them (see Supplementary Information). We find that the particular shape of the chain and its position relative to the Fermi level depend on the lattice constants of the unit cell, suggesting the possibility of fine tuning with uniaxial or hydrostatic strains.

The prediction of the new nodal-chain state of matter in the IrF₄ class of materials opens up avenues for further study of novel physical properties associated with these compounds. The presence of both strongly and weakly correlated compounds in this family enables the interplay between the nodal-chain topology and electron–electron interactions, as well as magnetism, to be studied. The application of strains that break one of the glide planes in these compounds provides a route for a similar study of the NSNL phase, as well as for experimental probing of the anomalous magnetoelectric response predicted here for NSNLs.

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Supplementary Information is available in the online version of the paper.

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