Coexistence of type-II Dirac semimetallic state and topological nodal lines in $V_3S_4$

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Abstract

Topological semimetals have attracted broad interest in recent years. These exotic phases of matter include type-I/II Dirac/Weyl semimetals as well as topological nodal-line semimetals. However, it is relatively rare for a single condensed matter system to possess two or more topological semimetallic states. Here, using angle-resolved photoemission spectroscopy and density functional theory calculations, we show that the nonmagnetic phase of monoclinic $V_3S_4$ hosts both type-II Dirac quasiparticles and multiple topological nodal lines, protected by a combined symmetry of inversion $P$ and time-reversal $T$. Therefore, $V_3S_4$ serves as a promising platform for studies of exotic transport properties and related applications.
1. Introduction

Topological semimetals (TSMs) received a frenzy of research activity due to the promise of exotic physical phenomena such as Fermi arcs and chiral anomalies [1], and potential applications in low-dissipation transport and quantum computation [2]. Differentiated by the governing equation of low-lying electronic states and the associated quasiparticles, topological semimetals can be classified as (but not limit to) Dirac semimetals where spin-degenerated linear bulk bands touch at discrete points in the momentum space and form bulk Dirac cones [3, 4], Weyl semimetals where the spin degeneracy of the touching bands is lifted [5-7], and nodal-line semimetals in which the bands cross along loops or lines in the momentum space, protected by the combined symmetry of inversion $P$ and time-reversal $T$ [8, 9]. According to the sign of the tilt angles of the cones, Dirac/Weyl semimetals can further be classified as type-I or type-II [10-13]. Distinguished from the type-I semimetals, the type-II semimetals bring about more exotic quasiparticles without a high energy analogue, as a positive product of the group velocities of the two bands directly violates the Lorentz symmetry which is universal in spacetime [10-12]. Experimentally verified type-II Dirac semimetals include $TMX_2 (TM = Pd, Pt; X = Se, Te)$ [14-18], NiTe$_2$ [19], NiTeSe [20], CaAl$_2$Si$_2$ [21] and VAl$_3$ [22], while experimentally confirmed candidates of nodal-line semimetals include InBi [23], $XB_2 (X = Mg, Al)$ [24, 25], $XO_2 (X = Ru, Ir)$ [26, 27], SrAs$_3$ [28], PtSn$_4$ [29], single-layer GdAg$_2$ [30], monolayer Cu$_2$Si [31], ZrSiS family [9,32-37], CaAg$X$ ($X = P, As$) [38-40], XSbTe ($X = La, Gd$) [41, 42], PbTaSe$_2$ [8], TaNiTe$_5$ [43], Co$_2$MnGa [44], Ta$_5$SiTe$_6$ [45], etc. Despite the material abundancy of these topological phases, it is rare that two topological states coexist under the same conditions [46-48]. Such versatile topological semimetals, if realized, would bring about different types of transport anomalies in a single experimental setting, enriching the scope of potential device applications.

Here, we investigate the electronic structure of monoclinic V$_3$S$_4$, and found both theoretically and experimentally that it possesses both type-II Dirac quasiparticles and topological nodal lines that are only slightly gapped due to the presence of spin-orbit coupling (SOC). Previously, the compound of V$_3$S$_4$ is noticed in the literature because it is one of the most promising anode materials in potassium ion batteries, exhibiting a high theoretical capacity and a low reaction potential [49]. In the scope of topological physics, V$_3$S$_4$ is predicted as a topological semimetal via the method of topological quantum chemistry and symmetry indicators [50-53], as well as a Weyl orbital semimetal where symmetry-protected Weyl cones exist in the bulk bands without the need of SOC [54]. However, systematic experimental study of its band structure is still
absent, partly because millimeter-sized single crystals have not been synthesized. Direct reaction and topotactic redox reaction are the mostly-used methods to synthesize $V_3S_4$. However, the end product of direct reaction methods is polycrystalline [55], while the crystals prepared by topotactic redox reaction has a hexagonal unit cell [56], not the monoclinic one we discuss here. Therefore, a new method is needed to synthesize high-quality $V_3S_4$ single crystals, which is suited to perform direct measurements of the electronic structure.

In this work, we report a method synthesizing high quality, large size monoclinic $V_3S_4$ single crystals by combining direct reaction and chemical vapor transport (CVT) techniques [57]. Using angle-resolved photoemission spectroscopy (ARPES) and first-principles density functional theory (DFT) calculations, we identify that the type-II Dirac semimetallic state and the topological nodal line state coexists in the nonmagnetic phase of $V_3S_4$. A pair of tilted bulk Dirac cones locate along the $\Gamma$-$Y$ direction in the Brillouin zone (BZ), and the Dirac point energy is 1.4 eV below the Fermi level, which is protected by the combined $PT$ symmetry. This Dirac cone is found to span an energy region as big as nearly 3 eV and is not surrounded with other topologically-trivial bands, bringing potentially interesting transport properties if we dope the Fermi level to the Dirac point. Furthermore, we observed that several topological nodal lines appear in the BZ near the Fermi level, protected also by $PT$.

2. Results and Discussion

We begin from examining the structural, transport and magnetic properties of $V_3S_4$. The crystal structure and schematic bulk BZ of $V_3S_4$ is shown in Figs. 1(a)-(b). Fig. 1(c) shows the x-ray diffraction data of a $V_3S_4$ single crystal (inset) grown via the chemical vapor transport (CVT) method with I$_2$ as the transport agent (experimental section). The peaks show a perfect match with the reported peak positions for the monoclinic C2/m structure of $V_3S_4$ [ICSD Code 79969], and no impurity phases are observed. The single crystals, sized up to $3 \times 2 \times 0.5$ mm$^3$, show a typical morphology with clear surfaces, which are confirmed to be natural (l00) planes. The single crystals are also finely grounded to measure the powder x-ray diffraction, and the fit of its pattern indicates the lattice parameters of $a = 12.6159(2)$ Å, $b = 3.2862(1)$ Å, $c = 5.8705(1)$ Å and unit cell angles $\alpha = 90^\circ$, $\beta = 115.691^\circ$, $\gamma = 90^\circ$ (Fig. S1). The core-level photoemission spectrum of $V_3S_4$ is shown in Fig. 1(d), from which the characteristic peaks of V and S elements are clearly observed. The peak at 120 eV belongs to the iodine transport agent. Fig. 1(e) depicts the temperature-dependent electrical resistivity of $V_3S_4$ at 0 T and 9 T, showing a metallic
conducting behavior. Temperature-dependent transverse magnetoresistance of V₃S₄ is further depicted in Fig. S2.

V₃S₄ is an itinerant weak antiferromagnet [58]. Previous magnetic susceptibility measurements on V₃S₄ shows no evidence of long range magnetic order, but a Néel temperature of about (8±1) K is determined by a $^{51}$V NMR experiment [59]. A ferromagnetic (FM) ground state below 4.2 K is also suggested, due possibly to an impurity phase [58]. Result of our magnetic susceptibility measurements on a large-size V₃S₄ single crystal is shown in Fig. 1(f). The bifurcation of the zero-field-cooled and the field-cooled magnetization curves below ~8 K signals weak antiferromagnetism. The low magnetization value ($M \sim 10^{-3} \mu_B$/f.u.) implies a small magnetic moment in the crystal.
Figure 2. V₃S₄ being a type-II Dirac semimetal. ARPES data is taken at $T \sim 15$ K (nonmagnetic phase of V₃S₄). (a) Bulk and projected surface BZ, with high-symmetry points indicated. Red dots (labeled as D) mark the positions of the bulk type-II Dirac points. $k_z$ values are defined in units of $k \Gamma - Y$. (b) 3D intensity plot of ARPES spectra measured at $h \nu = 245$ eV ($k_z = 0.52$, close to the bulk D point). (c) DFT band structure of nonmagnetic V₃S₄ without SOC. (d) $h \nu$-dependent ARPES spectra from 60 to 160 eV, appended with the DFT bands along Y-$\Gamma$-Y (dotted lines). (e) DFT band dispersions along an in-plane direction parallel to X-$\Gamma$-X, calculated at different $k_z$ values in the reduced BZ [blue lines in (a)]. (f) ARPES band dispersions along the same directions in (e), taken at $h \nu = 245$ eV ($k_z = 0.52$), 240 eV ($k_z = 0.66$), 235 eV ($k_z = 0.80$), 230 eV ($k_z = 0.95$), and 225 eV ($k_z = 1.09$). The evolution of the band dispersion from a nearly gapless linear Dirac shape (D point) to a gapped Dirac cone (Y point) is seen. Green/yellow lines indicate the bottom of the upper cone / top of the lower cone.
Next we discuss the topological properties of V₃S₄, as revealed by our ARPES measurements and DFT calculations. First, we demonstrate in Figure 2 that nonmagnetic V₃S₄ is a topological Dirac semimetal hosting a pair of bulk, type-II Dirac points along the Y-Γ-Y direction. The bulk BZ and the projected (001) surface BZ are shown in Fig. 2(a) where high-symmetry points, lines and bulk Dirac points (labeled as D) are indicated. Fig. 2(b) shows the band structure of V₃S₄ measured at \( h\nu = 245 \) eV where one of the D points locates. The 3D plot shows clear linear band crossings along both \( k_x \) and \( k_y \) directions at D, confirming its in-plane Dirac-like dispersion. A DFT-derived three-dimensionnal band structure on the \( k_z \)-\( k_z \) plane is shown in Fig. S3, where the tilted Dirac cone can clearly be seen. DFT calculated electronic band structure in the nonmagnetic phase of V₃S₄ without SOC is shown in Fig. 2(c). Three areas between bands are filled with red, green and yellow colors for clarity, of which the green and yellow areas touch each other at the bulk D point. The Dirac point energy is about 1.4 eV below the Fermi level. Along the direction parallel to X-Γ-X [blue lines in Fig. 2(a)] crossing D, the Dirac cone is not tilted [Fig. 2(c)], meaning that the signs of the group velocities of the two crossing bands (slope of the bands) are opposite. Along the Y-Γ-Y direction, however, the Dirac cone is tilted, meaning that the signs of the slope of the bands are the same. This suggests the characteristic feature of the type-II Dirac fermions that violate the Lorentz symmetry [10-12]. Further DFT calculation results with and without SOC along the same direction as Fig. 2(e) are shown in Fig. S4. From our calculations, the Dirac points locate at \( k = \pm (0, 0, 0.49k_{Γ-Y}) \). Fig. 2(d) presents the photon-energy-dependent ARPES spectra along the Y-Γ-Y direction taken with \( h\nu = 60-164 \) eV, overlaid by the corresponding DFT band dispersions. The bulk Γ points correspond to \( h\nu = 83 \) and 134 eV, respectively, while one of the bulk Y points locates at \( h\nu = 107 \) eV. The ARPES \( k_z \)-\( k_z \) maps also match well with the calculated band structures, as detailed in Fig. S5. The calculated in-plane band structures at different \( k_z \)s are shown in Fig. 2(e), where \( k_z = 0 \) and \( k_z = 1 \) define the bulk Γ and Y points, respectively. At \( k_z = 0.49 \), there is a gapless Dirac cone at the zone center marking with “DP”. The ARPES results measured at several representative photon energies are shown in Fig. 2(f). One clearly observes an essentially gapless Dirac cone at \( k_z = 0.52 \) (close to D), situating about 1.4 eV below the Fermi level. The Dirac cone gradually opens a gap when the photon energy decreases, and the largest gap size is about 0.45 eV at 230 eV (\( k_z = 0.95 \)).

The DFT electronic structure presented in Fig. 2 was calculated in the nonmagnetic phase without SOC, so each band, either the valence band or the conduction band, is doubly degenerated. Wannier-numbered Band 12 and Band 13 [Fig. 2(c)] touch each other at the Dirac
point D along Γ-Y, forming a pair of fourfold degenerate Dirac points at the BZ. The dispersion around the Dirac point is tilted along Γ-Y but not the two other orthogonal k directions, signaling the existence of Lorentz-violating type-II Dirac fermions. From the representation analysis, this band crossing is found unavoidable, because the two bands belong to different representations (Δ₁ and Δ₂), respectively, as distinguished by the σ₉ mirror symmetry in the Z-Γ-Y plane. Although the Δ₁ and Δ₂ representations are one-dimensional, such that the degeneracy is an accidental one, the difference of the representations do allow the bands

Figure 3. Multiple nodal lines in V₃S₄. (a) k-space location of the I-Z plane (purple), corresponding to the measured constant energy contour in (i) (hν = 245 eV). (b) DFT band structure along I-Z-I without SOC. The three nodal line intersections are marked as N₁, N₂ and N₃. (c)-(h) k-space span of the nodal lines viewed along k₂ [(c), (e), (g)] and kₓ [(d), (f), (h)]. (i) ARPES constant energy contour at binding energy E_B = 2.0 eV at 15 K. Dotted lines indicate the BZ boundaries. (j) ARPES band dispersion along I-Z-I [red line in (i)]. (k) Zoomed-in image of the red box in (j), appended by DFT band dispersions. N₁-N₃ are found to be consistent with gapless band intersections.
crossing at a single nodal point. Since the atomic numbers of V and S are relatively small, SOC is expected to have little effect on the overall band structure. We presented DFT band calculations with SOC in Fig. S6. We found that, when SOC is included, the SU(2) symmetry is broken, a finite but small energy gap will open at the type-II Dirac points along Γ-Y.

Second, we demonstrate in Figure 3 that nonmagnetic V₃S₄ is a topological nodal-line semimetal hosting multiple topological nodal lines close to the Fermi level. The 3D BZ and the I-Z plane ($k_z = 0.5$) is depicted in Fig. 3(a), highlighting the location of the measured constant energy contour in Fig. 3(i) ($h\nu = 245$ eV, $k_z = 0.52$). More DFT and ARPES constant energy contours are shown in Fig. S7 and Fig. S8. The DFT band structure along the I-Z-I direction is shown in Fig. 3(b); the ARPES band dispersion along I-Z-I [red line in Fig. 3(i)] is shown in Fig. 3(j), and the zoomed-in image of the red box is shown in Fig. 3(k). By comparison of the DFT band structure and the ARPES spectrum, we identify three band touching points near the Fermi level, labeled $N_1$, $N_2$, and $N_3$ [Fig. 3(b)]. It is seen in Fig. 3(k) that no resolvable energy gap is formed at these nodal points. DFT calculations shown in Figs. 3(c)-3(h) further verified that the $N_1$-$N_3$ points belong to three different topological nodal lines that intersect with the I-Z-I segment. The $k$-space span of the $N_1$-$N_3$ nodal lines viewed along $k_z$ ($k_x$) are shown in Figs. 3(c), 3(e) and 3(g) [Figs. 3(d), 3(f) and 3(h)]. According to the orbital character analysis, the $N_1$, $N_2$ and $N_3$ points are provided by the $d$ orbitals of the two different V atoms in the unit cell, preserving the time-reversal symmetry $T$. The point group of the V₃S₄ structure is $C_{2h}$, preserving the space inversion $P$. Therefore, The three nodal lines are protected by the combined symmetry $PT$ in the absence of SOC.

In our calculation, The gapless nature of the $N_1$-$N_3$ nodal lines is found by first identifying all the $k$ points with zero energy gap within the first BZ using the WANNIERTOOLS package [60]. The topological protection of these nodal lines can then be inferred from calculating the topological number of the form $\gamma = \oint C A(k) \cdot dk$, where $A(k) = -i \sum_{n \in \text{occ}} \langle u_n(k) \vert \partial_k \vert u_n(k) \rangle$ is the Berry connection of the occupied states, $C$ is a closed loop in the momentum space. If $C$ is pierced by a nodal line, one has $\gamma = \pi$, otherwise $\gamma = 0$. We calculated the Berry phase with a loop around each nodal line, and always obtain $\gamma \neq \pi$. Therefore, the nodal lines presented in Figs. 3(c)-(h) are topologically nontrivial. When SOC is absent, they are protected by $PT$. When SOC is included, the SU(2) symmetry will be broken, so these bands will in general be gapped, leaving numerous discrete nodal points in the BZ (Fig. S9).
For completeness of our discussion, we also performed DFT band calculations of V$_3$S$_4$ in the FM state in the Supporting Information, in which each V atom has a magnetic moment of about 2.1 $\mu_B$. Our results showed that it is a magnetic Weyl semimetal [61]. In the FM state, the spin-down part is an insulator with a large direct band gap near the Fermi surface in the whole BZ, while the spin-up part forms a Weyl point along the I-Z direction (Fig. S10). The bands near the Weyl point are basically provided by the $d$ orbitals of the two unequal V atoms. The Weyl point appears at the Fermi level due to the number of electrons occupied, as we can see in the electronic structure (Fig. S11). It is noted, however, that although the ground state energy of the FM state is calculated to be lower than that of the nonmagnetic state, this FM ground state is not observed in our transport and magnetic measurements (Fig. 1).

3. Conclusion

In summary, we demonstrate the growth of millimeter-sized high-quality single crystals of V$_3$S$_4$ using the chemical vapor transfer method. We systematically study the electronic band structure of V$_3$S$_4$ via ARPES measurements and DFT calculations, and demonstrate that the nonmagnetic phase of V$_3$S$_4$ hosts both a type-II Dirac semimetallic state and a nodal-line semimetallic state, with a pair of tilted Dirac cones at the $\Gamma$-Y direction and several prolonged nodal lines near the Fermi level. We conclude that the Dirac cone and the nodal lines are protected by a combination of $P$ and $T$ symmetries in the absence of SOC. The small atomic numbers of the elements and a good fitting to our ARPES measurements justified our usage of an SOC-free calculation model. The coexistence of type-II Dirac quasiparticles and topological nodal lines in V$_3$S$_4$ makes it a promising platform for exploration of novel topological properties.

4. Methods

*Material Synthesis:* Single crystals of V$_3$S$_4$ were grown by the chemical vapor transport (CVT) method using high-purity V$_3$S$_4$ powder as the starting material with I$_2$ as the transport agent.

Synthesis of powder. – Polycrystalline V$_3$S$_4$ is produced by a solid state reaction method. V powder (99.9%) and S powder (99.99%) were finely grounded and mixed with a ratio of 44:56 [62]. The mixture was then pressed into a pellet of approximately 12 MPa, which was put into a SiO$_2$ ampoule, evacuated to at least 10 mTorr and backfilled with 1/5 partial atmosphere of Ar. The sealed ampoule was placed in a tube furnace, heated to 450°C and held for 5 hours, then heated to 1150°C and held for an additional 5 hours (heating ramp 14°C/h). Finally, it was cooled down to room temperature.
Single crystal growth by chemical vapor transport. – Single crystals of V₃S₄ were grown by the chemical vapor transport (CVT) with I₂ as a transporting agent. 1 g of the abovementioned finely grounded polycrystalline V₃S₄, checked with XRD, was sealed in an evacuated quartz ampoule (22 mm in diameter and about 250 mm long) after the addition of 8 mg/ml of I₂. The sealed ampoule was heated in a two-zone furnace to a low temperature \( T_L = 800 \, ^\circ \text{C} \) and a high temperature \( T_H = 900 \, ^\circ \text{C} \) in 60 hours. After maintaining at this condition for two months, the sealed ampoule was cooled down to room temperature. Using this procedure, shiny single crystals of sizes up to \( 3 \times 2 \times 0.5 \, \text{mm}^3 \) were obtained, as shown in the inset of Fig. 1(c).

**PPMS Measurements:** Resistivity measurements were performed at temperatures between 2 K and 300 K, and magnetic fields between -14 T to 14 T, in a Quantum Design Physical Properties Measurement System (PPMS) by a standard four-probe technique, with a drive current of 4 mA.

**ARPES Measurements:** ARPES measurements were performed at Beamline 03U of the Shanghai Synchrotron Radiation Facility (SSRF) [63, 64], Shanghai, China. The energy and angular resolutions were set to 10 meV and 0.1°, respectively. The samples were cleaved in situ along the (100) plane and measured at \( T \sim 15 \, \text{K} \) (nonmagnetic phase of V₃S₄) in a working vacuum better than \( 5 \times 10^{-11} \, \text{Torr} \). Additional ARPES data (not shown) was also collected at Beamline 09U (Dreamline) of SSRF. The ARPES images obtained in rapid scanning modes are corrected using a Fourier-based method to remove artifacts from the grid [65].

**First-Principles Calculation:** The electronic structure calculations were done using the DFT method encoded in the Vienna Ab-initio Simulation Package (VASP) [66, 67]. The core electrons were described by the projector-augmented wave (PAW) pseudo-potentials [68]. The Perdew-Burke-Ernzerhof (PBE) approximation is used for the exchange-correlation function [69]. The DFT-D3 method was also used to include the van-der-Waals correction [70, 71]. Plane waves with a kinetic energy cutoff of 520 eV were used as the basis set. The \( k \)-points sampling is \( 11 \times 11 \times 6 \) with the \( \Gamma \) scheme. Both cell parameters and atomic positions are fully relaxed until the forces on each atom are smaller than \( 10^{-3} \, \text{eV} \, \text{Å}^{-1} \), and the total energy convergence criterion is set to be \( 10^{-7} \, \text{eV} \, \text{Å}^{-1} \). GGA+\( U \) correction is applied to the V 3\( d \) orbitals, and \( U \) is set to be 3 eV. The five V \( d \) orbitals and three S \( p \) orbitals are used to construct the maximally localized Wannier functions [72]. The nodal lines were calculated using the WANNIERTOOLS package, where the gap threshold was set as \( 10^{-4} \, \text{eV} \) when searching for the gapless points [60]. The representation analysis was carried out with the Irvsp code together
with the VASP package [73]. The WannSymm package was used to add crystal symmetries to the Wannier fitted orbits [74].

Supplementary Information

Supporting Information is available from the Wiley Online Library or from the author.

Data Availability

Data are available from the corresponding author upon reasonable request.
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Author Contributions

C.L. conceived and designed the research project. Y.-J.H. and X.-M.M. grew and characterized the single crystals. Y.-J.H., X.-M.M. and R.L. performed the transport and magnetic measurements with help from T.S. Y.-J.H., X.-M.M., C.Z., H.R., X.-R.L., Y.Z., M.Z., R.L., T.S., X.L., C.C., and C.L. performed the ARPES measurements with onsite support from Q.J., Y.Y., Z.J., Z.L., M.Y., and D.S. M.-Y.Z. performed the DFT calculations with help from H.X. Y.-J.H., M.-Y.Z., and C.L. analyzed the data and wrote the paper.

Competing Interest

The authors declare no competing financial or non-financial interests.
Supporting Information

Coexistence of type-II Dirac semimetallic state and topological nodal lines in V₃S₄

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Figure S1. Powder x-ray diffraction pattern of V₃S₄. Open circles: XRD data; red line: fit to the data; blue line: background of data; green line: difference between the data and the fit; pink vertical bars: XRD peak positions of V₃S₄ from the ICSD database. The refined lattice parameters are \( a = 12.6159(2) \) Å, \( b = 3.2862(1) \) Å, \( c = 5.8705(1) \) Å; unit cell angles \( \alpha = 90^\circ \), \( \beta = 115.691(1)^\circ \), \( \gamma = 90^\circ \).

Figure S2. Temperature-dependent transverse magnetoresistance of V₃S₄. The transverse magnetoresistance is defined as \( MR = [\rho(B) - \rho(0)]/\rho(0) \times 100\% \). \( MR \) exhibits a non-saturating \( -B^2 \) dependence reaching 25\% at 2 K and 14 T and decreases with increasing temperature.
Figure S3. DFT-derived Type-II Dirac points in V₃S₄. Figure shows the three-dimensional band structure of the two relevant bands near one of the Dirac points on the $k_x$-$k_z$ plane. $k_z$ values are defined in units of $k_{\Gamma-Y}$. The tilted Dirac cone can clearly be seen.

Figure S4. DFT band dispersions along an in-plane direction parallel to X-$\Gamma$-X without/with SOC. Bands are calculated at different $k_z$ values in the reduced BZ. $k_z$ values are defined in units of $k_{\Gamma-Y}$. 


Figure S5. Electronic structure in the \( k_x-k_z \) plane. (a) Left panel: ARPES intensity maps in the \( k_x-k_z \) plane taken at \( E_B = 0.2 \) eV. The photon energies used were from 60 to 164 eV. Red curves indicate the momentum locations for \( h\nu = 83, 107 \) and 134 eV, respectively. The inner potential is estimated to be 38 eV. Right panel: corresponding constant energy contours obtained with DFT calculations. (b) Same as (a) but at \( E_B = -1.3 \) eV – the binding energy near the bottom of conduction band along the \( \Gamma \)-\( Y \)-\( \Gamma \) direction. Red dashed lines represent the BZ boundary. (c) Schematic crystal structure with lattice constants and angles. \( a' = a \sin \beta = 11.37 \) Å is the projection of \( a \) along \( k_z \).

Figure S6. DFT bulk band structure of \( \text{V}_3\text{S}_4 \) without/with SOC. The type-II Dirac cone along \( \Gamma \)-\( Y \) opens a small gap when SOC is included.
Figure S7. Constant-energy contours of multiple BZs calculated by DFT. (a) The BZ boundaries viewed along $k_z$. The high symmetry points $\Gamma$-Y-$\Gamma$-$\Gamma$-$\Gamma$ in the vertical direction are linearly arranged along $k_z$. However, the high symmetry points $\Gamma$-$\Gamma$-$\cdots$-$\Gamma$-$\Gamma$ in the horizontal direction are not arranged along the $k_y$ direction, until the 12th $\Gamma$ point which approximately coincides with the $k_z = 0$ line. (b), (c) The constant-energy contours at $E_B = 0.0$ and 2.0 eV viewed along $k_z$ (at the $k_z = 0$ plane) calculated by DFT. Red lines indicate the BZ boundaries. The 12th BZ constant energy contours almost repeat the first BZ constant energy contours.
Figure S8. ARPES in-plane constant-energy contours at different binding energies ($E_B = 0.0$, 1.0, 1.5, and 2.0 eV). $k_z$ values are defined in units of $k_{\Gamma}-Y$. (a)-(d), (i)-(l), (q)-(t) are the constant-energy contours calculated by DFT at $k_z = 0$, 0.5, and 1, respectively. (e)-(h), (m)-(p), (u)-(x) are constant energy contours for 135 eV ($k_z = 0.04$), 245 eV ($k_z = 0.52$), 230 eV ($k_z = 0.95$) photons. Red dashed lines represent the BZ boundary.
Figure S9. \( k \)-space distributions of the nodal points viewed along \( k_z \) (top) and \( k_x \) (bottom). When SOC is included, the SU(2) symmetry be broken; the nodal lines crossing \( N_1 \), \( N_2 \) and \( N_3 \) in Fig. 3 of the main text change to discrete nodal points, which are defined as \( k \) positions where the DFT gap is smaller than 0.1 meV.

Figure S10. Bulk band structure of \( \text{V}_3\text{S}_4 \) calculated in the ferromagnetic state without SOC. Left panel: the spin-up part of the bands. A Weyl point along the I-Z direction is present. Right panel: the spin-down part of the bands. This spin component shows an insulating behavior with a large direct band gap near the Fermi surface in the whole BZ.
**Figure S11. Orbital-resolved band structure of ferromagnetic V₃S₄ (spin up + spin down).**

(a) Primitive cell of V₃S₄, with definitions of the V₁ and V₂ atoms. (b) Left/right panels: V₁ d \ /V₂ d orbital projections, indicating that the orbital components of the Weyl point near the Fermi level are basically provided by the d orbitals of the two unequal V atoms.