Weyl fermions, Fermi arcs, and minority-spin carriers in ferromagnetic CoS$_2$

Niels B. M. Schröter$^{1,4}$, Iñigo Robredo$^{2,3,4}$, Sebastian Klenz$^5$, Robert J. Kirby$^4$, Jonas A. Krieger$^{1,5,6}$, Ding Pei$^7$, Tianlun Yu$^{1,8}$, Samuel Stolz$^{9,10}$, Thorsten Schmitt$^1$, Pavel Dudin$^{11,*}$, Timur K. Kim$^{11}$, Cephise Cacho$^{11}$, Andreas Schnyder$^{12}$, Aitor Bergea$^{2,3,13}$, Vladimir N. Strocov$^1$, Fernando de Juan$^{2,14}$, Maia G. Vergniory$^{2,14,*}$, Leslie M. Schoop$^{44}$

INTRODUCTION

Since the experimental discovery of topological insulators and topological semimetals, there has been a substantial effort to functionalize topological materials for spintronic applications, most prominently in the family of Bismuth chalcogenides (1–4). However, because of the field of spintronics predates the first prediction of topological insulators (5, 6) and topological semimetals (7), topological phenomena in many well-studied spintronic materials may have been overlooked during initial investigations of their electronic properties. Here, we reveal that CoS$_2$, a material that has been long studied because of its itinerant ferromagnetism and potential for half-metallicity, actually hosts Weyl fermions and Fermi arc surface states in its band structure close to the Fermi level $E_F$, as well as topological nodal lines below the Fermi level. CoS$_2$ is, therefore, a rare example of the recently discovered class of experimentally verified magnetic topological metals (8–10), which have been proposed to realize new mechanisms of spin-to-charge conversion (11), and are of broader interest for fundamental science, for instance, as a platform to realize axion insulators (7), the intrinsic anomalous Hall effect (12), or the anomalous fractional quantum Hall effect (13).

Beyond the discovery of its topological properties, we also clarify the question of whether CoS$_2$ is a true half-metal. Half-metallic ferromagnets, i.e., materials that are metallic in one spin channel but gapped in the other, have been considered as promising materials for spintronic devices, where they could act as sources of highly spin-polarized charge carriers. There has been a longstanding debate on whether CoS$_2$ or the related alloys Co$_{1-x}$Fe$_x$S$_2$ are true half-metals, which has important implications for materials and device engineering. Calculations within the local spin density approximation (LSDA) (14, 15) [see Fig. 1 (A and B)] conclude that Co$_3$S$_2$ hosts a minority-spin electron pocket at the R point that leads to a peak in the minority-spin density of states (DOS), which would make CoS$_2$ a minority-spin conductor. This scenario is supported by magnetotransport experiments that suggest a sign flip in the spin polarization upon hole doping with iron that may turn CoS$_2$ into a half-metal (i.e., vanishing minority-spin DOS at $E_F$) due to the depopulation of a minority-spin electron pocket (16–20). On the other hand, calculations based on the generalized gradient approximation (GGA) (15, 21) [see Fig. 1 (B and C)] conclude that half-metallicity is already obtained in the undoped compound, and quantum oscillation experiments were unable to detect the putative minority-spin electron pocket (21). To resolve the debate about the half-metallicity of CoS$_2$, a direct spectroscopic band structure investigation would be clearly desirable, also because the spin polarization measured with transport probes can be reduced by surface defects (22) and can therefore not entirely rule out intrinsic half-metallicity. It should be noted that finite temperature effects can also reduce the spin polarization of nominally half-metallic ferromagnets (23).

Besides the bulk band structure, electronic surface states also influence the spin polarization at the Fermi level, which becomes particularly important for heterostructure interfaces in spintronic devices where half-metals could function as spin injectors. One important class of surface states are topological Fermi arcs in Weyl semimetals, which are considered to be particularly robust against passivation due to the protection by topological bulk invariants. Our LSDA calculations of CoS$_2$ shown in Fig. 1 (A and B) predict Weyl nodes close to the Fermi level on the $k_x = 0$ and $k_y = 0$ planes...
lished at the time, previous theoretical studies of CoS$_2$ overlooked logical semimetals and Fermi arc surface states was not yet estab-
lished (also see the Supplementary Materials). Since the concept of topo-
disentangle the bulk and surface electronic structure of CoS$_2$. As a
sensitive vacuum ultraviolet ARPES (VUV-ARPES; hv < 120 eV) to
bulk-sensitive soft x-ray ARPES (SX-ARPES; hv > 400 eV) and surface-
whether they are of topological origin.

Unclear whether these surface states are crossing the Fermi level and
26 studies did report the presence of surface states (26), we are able to observe its elusive minority-spin bulk electron pocket at the R point of the Brillouin zone directly, settling the longstanding debate of half-metallicity in CoS$_2$. We also detect a topological line node located at ~150 meV below the Fermi level, as well as a Weyl cone that suggest a Weyl point slightly above the Fermi level, which gives rise to topological Fermi arc surface states that cross the Fermi level. By comparison with ab initio calculations, we find that these Fermi arcs are of majority spin character and there-
fore affect the spin polarization at a heterostructure interface.

RESULTS
Our samples were synthesized using chemical vapor transport. We studied their elemental composition with core-level spectroscopy and energy-dispersive x-ray spectroscopy, which confirmed the expected stoichiometry (see Fig. 1E). Powder x-ray diffraction con-


cirmed the previously reported cubic space group 205 and a lattice
constant of a = 5.5287 Å (5) (see Materials and Methods and the Sup-
plementary Materials for more details about synthesis and charac-
terization). We measured a Curie temperature of $T_c$ = 124 K and a
saturation magnetization of 0.91 $\mu_B$/Co at 9 T (which becomes
linear at 0.2 T and 0.89 $\mu_B$), in good agreement with the literature
values (28) (see Fig. 1F for magnetization curves). The coercivity in
our data is small, about 10 to 15 Oe, which agrees also with the
literature values (16).

When cleaving CoS$_2$ for ARPES experiments, we obtained two
distinct cleavage planes with the surface normal pointing along the
(111) and (100) directions. We performed photon energy–dependent
ARPES measurements with soft x-ray photons (hv = 350 to 800 eV)
to locate the high-symmetry planes along the $k_z$ direction normal to
the sample surface (see the Supplementary Materials). The band
structure in the $k_z$ = π plane containing the R point is for the (111)
surface displayed in Fig. 2 (see fig. S9 for a definition of the
high-symmetry planes). We can clearly identify circular Fermi sur-
face pockets at the R point in the corner of the Brillouin zone in
Fig. 2A. Our calculated Fermi surface (Fig. 2B; using the LSDA) is in
good qualitative agreement with the experimental data, confirming the
existence of Fermi surface pockets at the R point. When inspect-
ing the experimental band dispersion along the R-Γ-R direction
(Fig. 2C), we see that the circular pockets at the R point are electron-
like and are related to another parabolic band with a minimum at
around ~0.65 eV by the exchange splitting. The magnitude of the
exchange splitting extracted from the energy distribution curve at
the R point (Fig. 2D) is $\Delta E$ = 0.60 eV (3). Our LSDA calculations of
the band dispersion shown in Fig. 2E are in good qualitative agree-
ment with the experimental data and indicate that the observed
electron pocket is of minority-spin character, which implies that
CoS$_2$ is not a true half-metal. However, the experimentally observed
exchange splitting is ~250 meV smaller than in the LSDA calcula-
tions, such that the majority spin bands are located closer to the
Fermi level in the experiment than expected from the calculations.
The data measured on the (100) surface also show electron pockets
at the R point and are displayed in the Supplementary Materials.

To search for the topological nodal line and Weyl nodes in CoS$_2$, we
also probed the bulk band structure in the $k_z$ = 0 plane, contain-
ing the Γ point, as illustrated in Fig. 3. Figure 3 (A to D) displays the
experimental and calculated Fermi surfaces for the (111) and (100)
cleavage planes, which are in good qualitative agreement. Figure 3E
shows the band dispersion along the M-Γ direction (black arrow in

parallel to the magnetization direction (see Fig. 1D), which should
give rise to topological Fermi arc surface states. In addition, we find
topological nodal lines a few hundreds of milli–electron volts below
the Fermi level, which are protected by a $\{m_z, \frac{1}{2} 0 \frac{1}{2}\}$ glide operation
(also see the Supplementary Materials). Since the concept of topo-
logical semimetals and Fermi arc surface states was not yet estab-
lished at the time, previous theoretical studies of CoS$_2$ overlooked
these important features in its band structure, which can have a de-

cisive influence on spin transport properties.

Previous angle-resolved photoelectron spectroscopy (ARPES) ex-
periments (24–26) on CoS$_2$ were performed with photon energies
between hv = 20 to 120 eV where the inelastic mean free path of the
photoelectrons can be expected to be close to its minimum ~0.5 to
1 nm, resulting in very surface sensitive probes. This implies that
the signal from bulk bands is substantially broadened along the mo-

dentum direction $k_z$ perpendicular to the sample surface (27),
which makes the identification of any bulk band dispersion in these
experiments challenging, and no minority-spin bulk electron pocket
in the vicinity of the R point could be resolved. While previous
studies did report the presence of surface states (26), it remained
unclear whether these surface states are crossing the Fermi level and
whether they are of topological origin.

Here, we overcome these limitations by using complementary
bulk-sensitive soft x-ray ARPES (SX-ARPES; hv > 400 eV) and surface-
sensitive vacuum ultraviolet ARPES (VUV-ARPES; hv < 120 eV) to
disentangle the bulk and surface electronic structure of CoS$_2$. As a

Fig. 1. Electronic structure and characterization of CoS$_2$ samples. (A) Band
structure obtained from LSDA. (B) Comparison of DOS from both spin channels for
LSDA and GGA. The red solid area shows the majority spin, and the blue solid area
shows the minority spins. (C) Band structure obtained from GGA. (D) Illustration of the
Weyl points in the bulk Brillouin zone, which are located on the high symmetry
planes $k_z$ = 0 and $k_z$ = 0 parallel to the magnetization direction M. Red dots indicate
Weyl points with positive Chern number C; blue dots indicate Weyl points with
negative Chern number. (E) Core-level spectroscopy measured with photon energy
hv = 602 eV; arrows indicate elemental core levels and valence band (VB). Inset shows
energy-dispersive x-ray spectroscopy (EDX) curves, showing an ideal stoici-
ometry. (F) Temperature dependence of magnetization curve under zero field-
cooling (ZFC) and field-cooled (FC) conditions; the applied field is 0.1 T. The Curie
point at 130 K is indicated. The inset shows the magnetic field dependence below
and above the Curie temperature. The measurements were taken along the
[100] direction.
along the M-Γ direction in our experimental data, we conclude that the Weyl point must be located slightly above the Fermi level.

Fermi arc surface states are a hallmark of Weyl points in topological semimetals. Therefore, the Weyl points in CoS₂ must be accompanied by Fermi arc surface states that are connecting the projections of the Weyl points in the surface Brillouin zone. We used surface-sensitive VUV-ARPES to investigate the surface electronic structure of the (100) surface in CoS₂, the results of which are displayed in Fig. 4. Figure 4A shows the experimentally obtained Fermi surface, which was measured on a strongly tilted crystal plane. The photon energy dependence of the Fermi surface maps (see the Supplementary Materials) indicates that all Fermi surface pockets measured by VUV-ARPES are surface states and that the signal from bulk states is mostly suppressed in this photon energy range. The positions of the projections of the Weyl point in the (100) surface Brillouin zone are shown in Fig. 1D. From our ab initio calculations, we expect that there should be two Weyl cone projections with total Chern numbers \( C = \pm 2 \) in the vicinity of the \( \Gamma \) point of the surface Brillouin zone, which originate from the Weyl cones in the vicinity of the M point of the bulk Brillouin zone that we have experimentally observed in Fig. 3 (E to G). These two Weyl points have to be connected by two Fermi arcs, which can form a circular Fermi surface (see Fig. 4B). This relationship between Weyl cone projections and topological surface states is precisely what we observe in our experimental data in Fig. 4A, which shows small circular Fermi surface pocket centered at the \( \Sigma \) point. A corresponding line cut of the experimental data along the \( \Sigma - \Gamma - \Sigma \) path is shown in Fig. 4C. It displays a surface state band crossing the Fermi level that connects two hole-like pockets that are located at the \( \Sigma \) points at opposite ends of the Brillouin zone. Our ab initio calculations of the surface electronic structure displayed in Fig. 4D confirm that this surface state is a Fermi arc that connects two Weyl points. Note that the renormalized energy scale of the Fermi arcs in the calculation compared to the experiment is expected owing to the reduced exchange splitting, which we already observed for the bulk band structure. Therefore, the Fermi arcs cross the Fermi level in the experiment, while they are located below the Fermi level in the calculation. Figure 4 (E to G) shows that the same line cut is measured at different photon energies, which shows that the Fermi arc dispersion is independent of the \( k_z \) momentum, which proves its two-dimensional nature. Since the Fermi arcs are derived from majority-spin bulk bands, they have majority-spin character (see the Supplementary Materials for calculations of their spin polarization). This will influence the spin polarization of electrons at the Fermi level at heterostructure interfaces where CoS₂ can act as a spin injector.

**DISCUSSION**

One may wonder whether the appearance of the conical bulk-band pockets connected by surface states could just be a coincidence, and whether the circular surface state pocket observed here may actually be just a trivial surface state. However, such a coincidence would require an unrealistic degree of fine-tuning, because there are no symmetry constraints that should pin a trivial surface state to the projections of the conical bulk bands. The only plausible explanation is, therefore, that the surface states mentioned above are Fermi arcs, and the observed linear bulk bands are part of a Weyl cone. Although we cannot directly observe the Weyl point since it is located

---

**Fig. 2. Bulk band structure of the \( k_z = \pi \) plane measured on the (111) surface.**

(A) Experimental Fermi surface was measured on the (111) cleavage plane with photon energy \( h\nu = 602 \text{ eV} \) and linear-vertical polarization, integrated over 50 meV below the Fermi energy. The red arrow indicates an electron pocket located at the \( \Gamma \) point. The black arrow indicates the position of the line cut shown in (C). (B) Calculated Fermi surface spectral function \( A(k\varepsilon) \) for the same plane as shown in (A) obtained with the LSDA. (C) Line cut along the \( R-X-R \) direction as shown in (A); red arrows indicate the electron pockets at the \( \Gamma \) point. (D) Energy distribution curves for the two \( R \) points shown in (E). The black arrow indicates the magnitude of the exchange splitting of \( \Delta \varepsilon = 0.60(3) \text{ eV} \). (E) Calculated band structure obtained with LSDA; red arrows indicate majority-spin electron pocket.
that the k-path is passing through the Weyl point in the vicinity of M.

hand, hole doping with iron has been suggested to transform CoS$_2$ into a minority-spin Fermi cone, and it has recently been speculated that Fermi arcs in Pt- and Pd-based chiral magnetic semimetals have already been successfully implemented for applications in spin-to-charge conversion and magnetic switching (29, 30), and theoretically, proposals have highlighted the importance of interfacial spin accumulation (31). We therefore expect that our results will inform the design of future spintronic prototypes that use magnetic Weyl semimetals, for instance, for spin-to-charge conversion (11). There may be magnetic domains on the sample surface that are smaller than the size of our beamspot (diameter of 50 to 70 μm), but on the basis of our ab initio calculations, we believe that the direction of the magnetization vector will have a negligible effect on the interpretation of the Fermi arc structure. This is because spin–orbit coupling is relatively small in CoS$_2$, and its inclusion has only a negligible effect on the band dispersion in our ab initio calculations (see the Supplementary Materials for further discussion). CoS$_2$ is also known as a good catalyst, e.g., for the hydrogen evolution reaction (32), and it has recently been speculated that Fermi arcs in Pt- and Pd-based chiral magnetic semimetals (33, 34) may play a role in catalysis due to their d-electron character and their robustness against hydrogen passivation (35, 36). Since the Fermi arcs in CoS$_2$ are also derived from bulk bands of d orbital character (see the Supplementary Materials), they may contribute to the catalytic performance of CoS$_2$.

in the unoccupied part of the DOS, the overall agreement between the experimental data and LSDA calculations in conjunction with experimentally observed momentum space alignment between surface states and bulk bands provides sufficient evidence to conclude that CoS$_2$ is a magnetic Weyl semimetal.

Because of the relatively low effective mass of the minority-spin electron pocket at the R point, the minority-spin DOS at the Fermi level is large, and some calculations suggested that CoS$_2$ is a minority-spin conductor (18). Our discovery of the majority-spin Fermi arc surface states implies that the total interface spin polarization of a heterostructure involving CoS$_2$ will be reduced compared to the bulk value. Compared to trivial dangling bond surface states, Fermi arc surface states are more robust against attempts of passivation, because they are protected by the topological invariants (the Chern numbers) of the bulk Weyl points; hence, engineering of the interface potential cannot easily remove the Fermi arcs. On the other hand, hole doping with iron has been suggested to transform CoS$_2$ from a minority-spin to a majority-spin conductor and ultimately to a full half-metal by depopulation of the minority-spin bulk electron pocket (18). Such a transition will be facilitated by the majority-spin Fermi arcs at interfaces in heterostructures since they compensate the DOS of the minority-spin electron pocket. Therefore, CoS$_2$ provides a prime example of a spintronic material whose performance is affected by its topologically nontrivial band structure. Note that nonmagnetic Weyl semimetals have already been successfully implemented for applications in spin-to-charge conversion and magnetic switching (29, 30), and theoretically, proposals have highlighted the importance of topological Fermi arcs for interfacial spin accumulation (31). We therefore expect that our results will inform the design of future spintronic prototypes that use magnetic Weyl semimetals, for instance, for spin-to-charge conversion (11). There may be magnetic domains on the sample surface that are smaller than the size of our beamspot (diameter of 50 to 70 μm), but on the basis of our ab initio calculations, we believe that the direction of the magnetization vector will have a negligible effect on the interpretation of the Fermi arc structure. This is because spin–orbit coupling is relatively small in CoS$_2$, and its inclusion has only a negligible effect on the band dispersion in our ab initio calculations (see the Supplementary Materials for further discussion). CoS$_2$ is also known as a good catalyst, e.g., for the hydrogen evolution reaction (32), and it has recently been speculated that Fermi arcs in Pt- and Pd-based chiral magnetic semimetals (33, 34) may play a role in catalysis due to their d-electron character and their robustness against hydrogen passivation (35, 36). Since the Fermi arcs in CoS$_2$ are also derived from bulk bands of d orbital character (see the Supplementary Materials), they may contribute to the catalytic performance of CoS$_2$.

Fig. 3. Bulk band structure of the $k_z = 0$ plane. (A) Experimental Fermi surface measured on the (111) cleavage plane with photon energy $h\nu = 512$ eV and linear-vertical polarization, integrated over 50 meV below the Fermi energy. The black arrow indicates the position of the line cut shown in (E). (B) Calculated Fermi surface spectral function for the same plane as shown in (A) obtained with LSDA. (C) Experimental Fermi surface spectral function $A(k,F)$ measured on the (100) cleavage plane with photon energy $h\nu = 475$ eV and linear-vertical polarization, integrated over 50 meV below the Fermi energy. The black arrow indicates the position of the line cut shown in (E). (D) Calculated Fermi surface for the same plane as shown in (C) obtained with LSDA. (E) Line cuts along the M–Γ direction from the (111) surface, as shown in (A), and the Γ–M direction from the (100) surface, as shown in (C). (F) Second-derivative spectrum of (E). (G) Result of the momentum distribution curve (MDC) fitting of the bands along the M–Γ direction, where blue circles originate from data of the (111) plane, and red circles originate from data of the (100) plane. (H) Calculated band dispersion along the M–Γ direction. (I) Band dispersion along the M*–Γ direction where M* (0,0.5,0.4581) is a point slightly displaced from the M point (see Fig. 1D), such that the k-path is passing through the Weyl point in the vicinity of M.
Ab initio calculations

We used density functional theory as implemented in the Vienna Ab Initio Simulation Package. For the GGA calculations, the exchange correlation term is described according to the Perdew-Burke-Ernzerhof prescription together with projected augmented wave (PAW) pseudopotentials, while for the LSDA, the exchange correlation term is described according to the Dudarev simplified, rotationally invariant approach, together with PAW pseudopotentials. The kinetic energy cutoff was set to 400 eV. For the self-consistent calculation, a grid of \( 7 \times 7 \times 7 \) k points was used, with 1000 energy points. The spectral function of the Fermi surfaces shown in Figs. 2 and 3 was computed with the programs Wannier90 (41) and WannierTools (42). Using ab initio calculation of bands, we constructed maximally localized Wannier functions considering d orbitals for cobalt sites and p orbitals for sulfur sites using the Wannier90 software (41). We computed an effective tight-binding model that accurately reproduces the band structure of the bulk system. We then computed the spectral function of the Fermi surfaces shown in Figs. 2 and 3 by the method of iterative Green’s function as implemented in WannierTools (42) software for a slab of 50 unit cells.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/51/eabd5000/DC1

**REFERENCES AND NOTES**

1. Y. Fan, P. Upadhyaya, X. Kou, M. Lang, S. Takei, Z. Wang, J. Tang, L. He, L. T. Chang, M. Montazeri, G. Yu, W. Jiang, T. Nie, R. N. Schwartz, Y. Tserkovnyak, K. L. Wang, Magnetization switching through giant spin–orbit torque in a magnetically doped topological insulator heterostructure. Nat. Mater. 13, 699–704 (2014).
16. C. Leighton, M. Manno, A. Cady, J. W. Freeland, L. Wang, K. Umemoto, R. M. Wentzcovitch, L. Wang, T. Y. Chen, C. L. Chien, C. Leighton, Sulfur stoichiometry effects in highly spin
15. T. Shishidou, A. J. Freeman, R. Asahi, Effect of GGA on the half-metallicity of the itinerant
22. V. N. Strocov, Intrinsic accuracy in 3-dimensional photoemission band mapping.


citation.
was supported by the Swiss National Science Foundation under grant no. 159690. D.P. acknowledges the support from the Chinese Scholarship Council. J.A.K. acknowledges support by the Swiss National Science Foundation (SNF-Grant no. 200021_165910). **Author contributions:** This project was led jointly by N.B.M.S., M.G.V., and L.M.S. N.B.M.S. performed the ARPES experiments with support from J.A.K., D.P., T.Y., S.S., and V.N.S. I.R., F.d.J., and M.G.V. performed the ab initio calculations and theoretical analysis with support from A.S. and A.B. S.K. and R.J.K. performed the sample growth and structural and magnetic characterization. T.S., P.D., T.K.K., C.C., and V.N.S. maintained the ARPES endstations and provided experimental support. The project was supervised by M.G.V. and L.M.S. All authors discussed the results and contributed to the writing of the manuscript. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 24 June 2020
Accepted 5 November 2020
Published 18 December 2020
10.1126/sciadv.abd5000

**Citation:** N. B. M. Schröter, I. Robredo, S. Klemenz, R. J. Kirby, J. A. Krieger, D. Pei, T. Yu, S. Stolz, T. Schmitt, P. Dudin, T. K. Kim, C. Cacho, A. Schnyder, A. Bergara, V. N. Strocov, F. de Juan, M. G. Vergniory, L. M. Schoop, Weyl fermions, Fermi arcs, and minority-spin carriers in ferromagnetic CoS$_2$. *Sci. Adv.* 6, eabd5000 (2020).