

# Termination Dependent Topological Surface States in Nodal Loop Semimetal HfP<sub>2</sub>

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Symmetry plays a major role in all disciplines of physics. Within the field of topological materials there is a great interest in understanding how the mechanics of crystalline and internal symmetries protect crossings between the conduction and valence bands. Additionally, exploring this direction can lead to a deeper understanding on the topological properties of crystals hosting a variety of symmetries. Here we report the experimental observation of topological surface states in the nodal loop semimetal HfP<sub>2</sub> using angle resolved photoemission spectroscopy (ARPES) which is supported by our first principles calculations. Our study shows termination dependent surface states in this compound. Our experimental data reveal surface states linked to three unique nodal loops confirmed by theoretical calculations to be topologically non-trivial. This work demonstrates that transition metal dipnictides provide a good platform to study non-trivial topological states protected by non-symmorphic symmetry.

## INTRODUCTION

Topological quantum matter is a growing field where the study of symmetry is applied to materials that host exotic surface states. The discovery of topological materials protected by crystalline symmetries and internal symmetries has sparked an interest in symmetry protected topological invariants [1–7]. To date, three types of topological semimetals have been discovered, Weyl semimetals (WSM) [8–11], Dirac semimetals (DSM) [12, 13], and nodal line semimetals (NLSM) [14–19]. A Dirac semimetal possesses relativistic massless Dirac fermions topologically protected by crystalline symmetry and time-reversal symmetry. When either time-reversal or inversion symmetry is broken, a Dirac point may split into two Weyl points with opposite chirality, which are connected by surface Fermi arcs [10, 11]. Interestingly, topological nodal lines formed by continuous nodal points are robust and have been classified according to the crystalline symmetry that protects these states [20, 21]. The non-trivial nodal loops generate enclosed surface states which are analogous to the membrane that stretches over the open end of a drum, known as “drumhead” surface states. Crystalline symmetry protected topological states provide useful insight for investigating topological properties in symmorphic or non-symmorphic materials [22, 23]. This motivates to study complex semimetals containing transition metals and multiple-compound semimetals based on a desired space group for the existence of topological states [9, 23]. One such focus is the study of nodal-line semimetals protected by crystalline symmetries which enforce robust topolog-

ical states. Therefore, it is interesting to identify novel materials exhibiting topological nodal lines, protected by crystalline symmetry, more specifically materials belonging to the non-symmorphic space group which contain glide and/or screw symmetries [24, 25].

It is believed that extremely large magnetoresistance (XMR) is linked to either topological states or electron-hole compensation. To date, there has been no clear indication of the relationship between XMR and nodal line/loop states. Recent studies show that transition metal dipnictides exhibit topologically non-trivial states [26–32]. In addition, NbAs<sub>2</sub> has been observed to be superconducting and topologically robust at high pressures [33]. TaSb<sub>2</sub> has been discovered to host XMR and a non-trivial state [34, 35]. While most of the previous experiments have been based on transport measurements, recent angle resolved photoemission spectroscopy (ARPES) studies in WP<sub>2</sub> and MoP<sub>2</sub> [36–39] revealed some transition metal dipnictides to be type-II Weyl semimetals. In general, it has been determined that transition metal dipnictides are mostly topologically non-trivial and also exhibit XMR. The emergence of topological states in TaSb<sub>2</sub>, NbAs<sub>2</sub> and XP<sub>2</sub> (X = Mo, W) motivated us to study Hafnium dipnictides with ARPES to further understand how the topological states arise and how they are protected. While all of the previously studied transition metal dipnictides have a OsGe<sub>2</sub>-type monoclinic *C121* structure, our material is the first transition metal dipnictide that crystallizes in the PbCl<sub>2</sub>-type orthorhombic *Pnma* structure [40].

Using ARPES we report the direct observation of termination-dependent topological states in the nodal

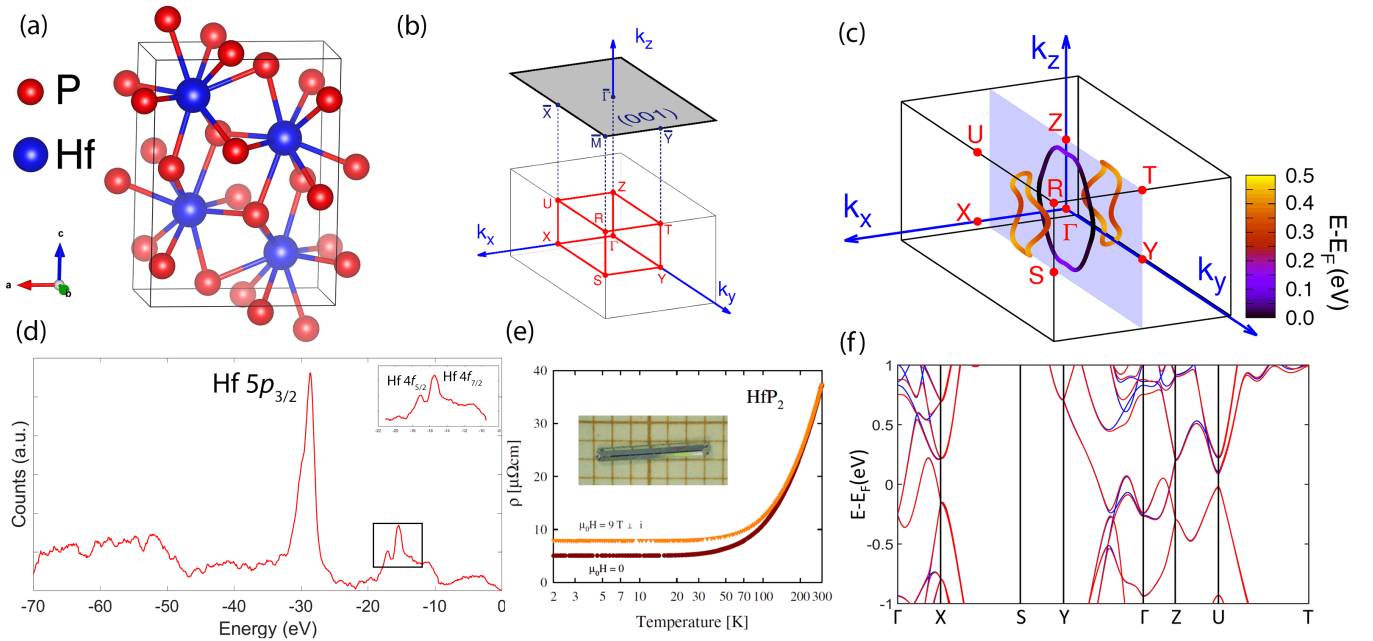


FIG. 1: **Crystal structure and sample characterization.** (a) The crystal structure of HfP<sub>2</sub> with orthorhombic space group *Pnma* (No. 62). (b) 3D bulk Brillouin zone of the crystal and its projection on the rectangular (001) surface. High symmetry points are marked on the plot. (c) Nodal loops in *k*-space where the color corresponds to the energy where the touching points occur. (d) Core level spectroscopic measurement of HfP<sub>2</sub>. Sharp peaks of Hf 5*p*<sub>3/2</sub>, Hf 4*f*<sub>5/2</sub>, and Hf 4*f*<sub>7/2</sub> are observed. (e) Temperature dependence of the electrical resistivity of HfP<sub>2</sub> measured in zero magnetic field (brown) and in an external magnetic field of 9 T (orange), where the magnetic field is applied perpendicular to the current flowing along the *b* axis of the crystallographic unit cell. The inset shows a single crystal of HfP<sub>2</sub>. (f) Calculated bulk bands with (red) and without (blue) spin orbit coupling (SOC).

loop semimetal HfP<sub>2</sub> which are confirmed by first principles calculations. Our study shows that the surface states are induced by two non-trivial nodal loops that exist away from the center of the Brillouin zone (BZ). Our findings provide an insight for the discovery of new topological quantum phases which emerge due to crystalline symmetries.

## METHODS

Single crystals of HfP<sub>2</sub> were grown by chemical vapor transport method using iodine as transport agent. The crystals had a form of massive rods with dimensions up to 1×1×8 mm<sup>3</sup>. The chemical composition was proven by energy-dispersive X-ray analysis using a FEI scanning electron microscope equipped with an EDAX Genesis XM4 spectrometer. The crystal structure was examined at room temperature on a Kuma-Diffraction KM4 four-circle X-ray diffractometer equipped with a CCD camera using Mo K $\alpha$  radiation. The experiment confirmed the orthorhombic PbCl<sub>2</sub>-type structure (space group No. 64, *Pnma*) [40] and yielded the lattice parameters:  $a = 6.48$  Å,  $b = 3.51$  Å, and  $c = 8.69$  Å.

The electrical resistivity of single-crystalline HfP<sub>2</sub> was

measured in the temperature range of 2-300 K employing a Quantum Design PPMS platform. The measurements were carried out using a standard ac four-point technique with electric current flowing along the crystallographic *b* axis in zero magnetic field and in a field of 9 T applied perpendicular to the current. Synchrotron-based ARPES measurements were performed at the Advanced Light Source (ALS) Berkeley at Beamline 10.0.1.1 equipped with a high efficiency R4000 electron analyzer. The energy resolution was better than 20 meV and the angular resolution was better than 0.2°. Samples were cleaved in-situ and measured between 10 and 80 K in a vacuum better than 10<sup>-10</sup> torr.

The electronic structure calculations were carried out within the Density Functional Theory (DFT) framework using the VASP package [41]. We employed the Perdew–Burke–Ernzerhof [42] implementation of the generalized gradient approximation (GGA) for the exchange–correlation functional. Projector augmented-wave pseudopotentials were used with an energy cutoff of 350 eV for the plane-wave basis, which was found to be sufficient to converge the total energy. The Brillouin zone (BZ) was sampled with a 8×15×6 *k*-point grid. By fully relaxing the crystal structure, the calculated lattice parameters show excellent agreement with the experimental

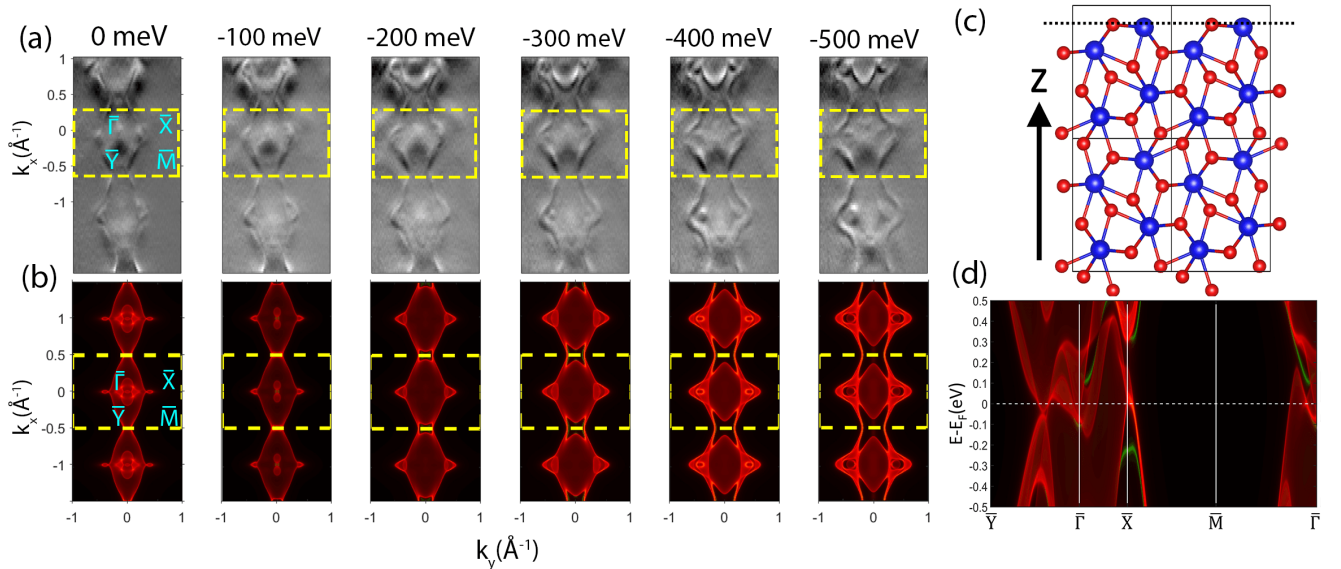


FIG. 2: **Fermi surfaces and constant energy contours of P6-terminated (001) HfP<sub>2</sub> surface.** (a) Second derivative of experimentally measured constant energy contours and Fermi surface (Photon energy  $h\nu = 57$  eV) from  $E - E_F = 0$  to -500 meV. (b) Calculated Fermi surface. The yellow dashed rectangles in (a) and (b) indicate the surface first Brillouin zone (SFBZ). The size of the SFBZ along the  $k_y$  direction is 3 times larger than that along  $k_x$ . (c) Side view of the crystal structure of the P6-terminated (001) surface denoted with a dashed line. (d) Calculated surface band structure of the (001) P6-terminated surface. Red (green) color indicates projected bulk (surface) states.

data, the mismatch being below 0.3% for each unit cell direction. A Wannier function-based model of the system was obtained by employing the Wannier90 code [43], from which the electronic structure of the semi-infinite HfP<sub>2</sub> was calculated through an iterative surface Green function matching technique (SGFM) [44] within the Wannier tools package [45]. The spin orbit coupling (SOC) was included self-consistently in the bulk band structure calculations at the DFT level. Since the effect in the electronic structure was found to be rather small -see Fig. 1(f)-, the SOC was not included thereafter in the computation of the Wannier function-based model. The inclusion of SOC gaps out the nodal loops in this system with direct and indirect band gaps of around  $\sim 20$  meV. Furthermore, we do not consider possible surface reconstructions on the calculations of the surface states. The theoretical Fermi level has been shifted by -200 meV hereafter, corresponding to doping effect observed in ARPES measurements. An energy disagreement between calculation and experiment is typical up to a level of around 200 meV.

## RESULTS AND DISCUSSION

Figure 1(a) shows the crystal structure of HfP<sub>2</sub> where each Hf atom is coordinated by nine P atoms forming an equatorial tricapped trigonal prism. The Brillouin zone is shown in Fig. 1(b). The (001) surface of the first

Brillouin zone (SFBZ) is also displayed in Fig. 1(b). Fig. 1(c) shows the emergence of two sets of nodal loops: the first, centered at  $\Gamma$  lies on the  $yz$ -plane and is protected by glide mirror symmetry in the absence of SOC; the second set consists of two nodal loops away from the mirror plane which are protected by  $PT$ -symmetry without the presence of SOC, namely a combination of time-reversal ( $T$ ) and inversion ( $P$ ) symmetries. A Berry phase calculation along a path enclosing any of the three nodal loops yields a non-trivial value. The core level spectra of HfP<sub>2</sub>, shown in Fig. 1(d), are dominated by sharp peaks of Hf  $5p_{3/2}$  ( $\sim 30$  eV), Hf  $4f_{5/2}$  ( $\sim 16$  eV), and Hf  $4f_{7/2}$  ( $\sim 14$  eV), which are in line with the chemical composition of the compound. The inset shows a high resolution of the two adjacent peaks in the -20 to -10 eV energy range. The peaks appear more prominent due to a change in scale. The temperature variation of the resistivity shown in Fig. 1(e) under zero magnetic field and 9 T is typical of a metallic behavior. Fig. 1(f) shows the calculated bulk band structure with (red) and without (blue) spin orbit coupling.

In this work, we report our ARPES measurements from two kinds of samples: a fresh sample in which measurements were taken right after cleaving and an aged sample which was measured after a long period of time. In order to determine the possible surface termination for each sample, we carry out systematic calculations of the projected bulk and surface states for the (001) cleavage plane

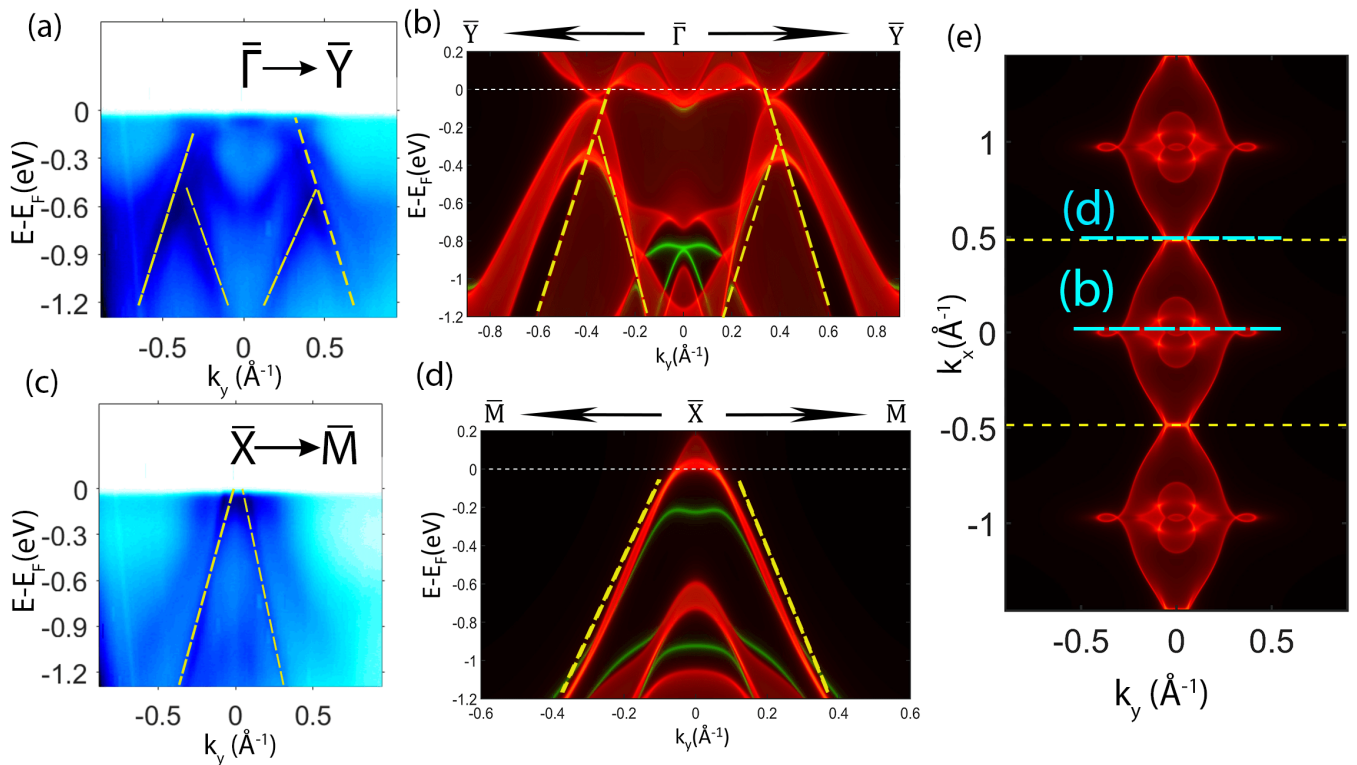


FIG. 3: **High symmetry dispersion maps of P6-terminated (001) HfP<sub>2</sub>.** (a) Experimental dispersion map along the  $\bar{Y}-\bar{\Gamma}-\bar{Y}$  direction with photon energy  $h\nu = 59$  eV. (b) Theoretical band structure of the P6-terminated (001) surface along the  $\bar{Y}-\bar{\Gamma}-\bar{Y}$  direction, where the green (red) color denotes surface states (projections of bulk bands). (c) Experimental dispersion map along the  $\bar{M}-\bar{X}-\bar{M}$  line with photon energy  $h\nu = 59$  eV. (d) Theoretical band structure of the P6-terminated (001) surface along the  $\bar{M}-\bar{X}-\bar{M}$  direction. (e) Calculated Fermi surface of the P6-terminated surface at the Fermi level.

for various (six non-equivalent) surface terminations. Interestingly, the calculations reveal that the surface states are extremely sensitive to the surface termination. We find that the P6-terminated (001) surface (see Supplementary Material [46]), shown in Fig. 2(c), yields surface states in good agreement with the experimental results of the aged sample. The P6 corrugated surface consists of alternating Hf-P dimers along the (001) direction (see Supplementary Material [46]). Fig. 2(a,b) show a comparison of the experimental and theoretical constant energy contours for different energy cuts. As the binding energy decreases from the Fermi level, the bulk states gradually expand and the small handle-like pockets near the  $\bar{X}$  point become bigger and triangular. Fig. 2(d) shows the calculated surface band structure for the P6-terminated (001) surface. The non-trivial surface states in this energy region are difficult to resolve because most of these surface states are buried in bulk states (see Supplementary Material [46]).

Figure 3 shows further comparison of the experimental and theoretical energy dispersion along the  $\bar{Y}-\bar{\Gamma}-\bar{Y}$  and the  $\bar{M}-\bar{X}-\bar{M}$  high symmetry lines. The calculated energy dispersion along  $\bar{Y}-\bar{\Gamma}-\bar{Y}$  in Fig. 3(b) is in good agreement

with experiment [Fig. 3(a)]. The bulk states dominate the cut while the surface states predicted in Fig. 3(b) are difficult to resolve in Fig. 3(a). The dashed lines are shown to guide the eyes on the dominant bulk states in this high symmetry direction. The slope of the states along the  $\bar{M}-\bar{X}-\bar{M}$  direction, marked by the dashed lines in Fig. 3(c), are in good agreement with the calculations in Fig. 3(d). However, it is difficult to distinguish the non-trivial P6-terminated surface states since they are embedded in the bulk states. When we conduct photon energy dependent measurements, we see that the location of the parabolic bulk band dispersion changes with photon energy. Therefore, at this photon energy ( $h\nu = 59$  eV) we see both the topological surface state and the bulk state at a photon energy that sets  $k_z$  away from the plane that we have selected for the calculations. As we tune the photon energy, we see this bulk state begins to merge with the surface state that matches the band dispersion seen in calculations in Fig. 3(d) (see Supplementary Material [46]).

In order to further understand the non-trivial surface states, we have systematically investigated various samples which are measured with different times of exposure

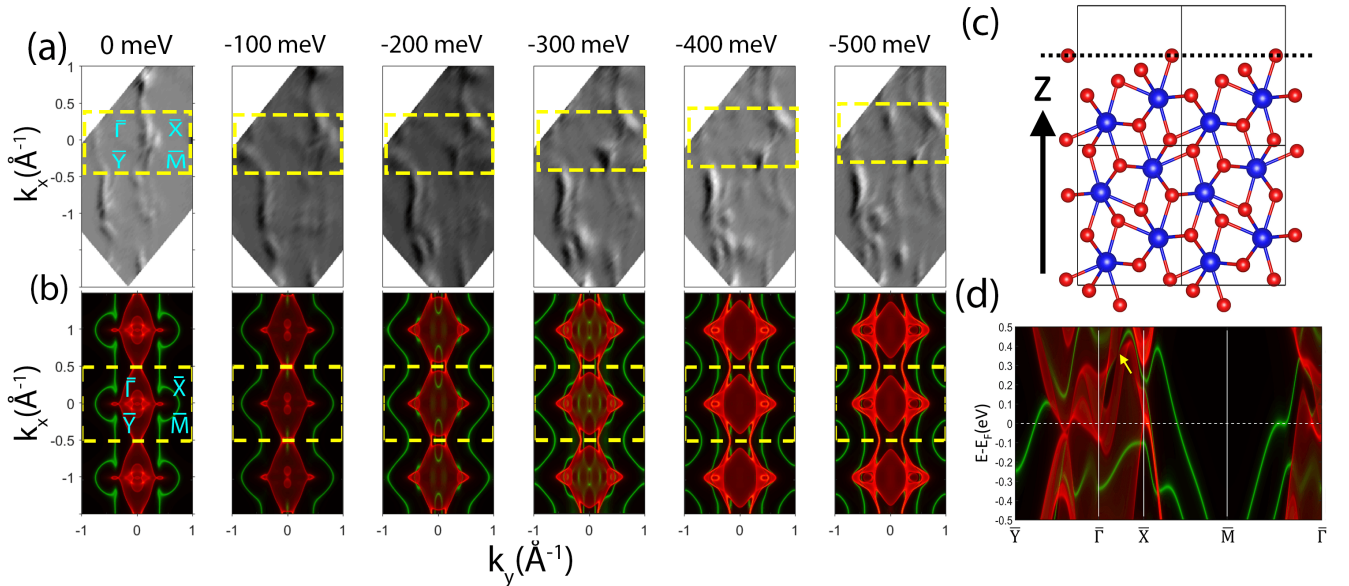


FIG. 4: **Fermi surface and constant energy contours of the P7-terminated (001) surface of HfP<sub>2</sub>.** (a) Second derivative of experimentally measured constant energy contours and Fermi surface (photon energy  $h\nu = 57$  eV) from  $E - E_F = 0$  to  $-500$  meV. (b) Calculated Fermi surface of the P7-terminated (001) surface. The yellow dashed rectangles indicate the SFBZ. (c) Crystal structure of the (001) P7-terminated surface indicated by the dashed line. (d) Calculated surface band structure for the P7-terminated surface. The bulk (surface) states are denoted by red (green) and the yellow arrow indicates a nontrivial crossing point from which the non-trivial surface states emerge.

after cleavage. The results of the ARPES measurements in a freshly cleaved sample are shown in Fig. 4 where we see the emergence of two stripe-like Fermi surfaces along the  $k_x$  direction which move apart from the zone center as the binding energy decreases from the Fermi level to  $-500$  meV. This feature is absent in the theoretical band structure of the P6-terminated (001) surface [Fig. 2(b)], which implies a different surface termination. We believe that the P7-terminated surface requires lower cleavage energy and can be easily formed upon cleaving. However, the dangling bonds of the phosphorous surface atoms are unstable. Therefore, these P surface atoms can be evaporated or removed by the high energy photons in beam-lines and hence reform the surface to the next-termination plane which is more stable. In the end, the surface becomes P6-terminated over a relatively short period of time ( $< 2$  hours).

In order to resolve the different experimental results, we have theoretically investigated several other (001) surface terminations and find that the calculated Fermi surface of the P7-terminated (001) surface, shown in Fig. 4(c), is in good agreement with experiment. Fig. 4(b) shows the calculated stripe-like Fermi surface consisting of non-trivial surface states surrounding the bulk pocket, which move away from the center as the energy is lowered from the Fermi level to 500 meV below it. Note that the zigzag-shaped P7-terminated surface which is composed solely of phosphorous atoms in Fig.

4(c) exhibits a larger degree of roughness compared to the P6-terminated surface [Fig. 2(c)] (see Supplementary Material for unrotated data [46]). Due to this surface environment, the energy dispersion of surface states varies across Fermi level and can be easily observed in regions where bulk states are gapped out [see Fig. 4(d)]. These non-trivial surface states emerge from the crossing point between the  $\bar{\Gamma}$  and  $\bar{X}$  points [indicated by a yellow arrow in Fig. 4(d)] which is projected from the  $PT$  symmetry-protected nodal loop away from the  $yz$ -plane in Fig. 1(c). These surface states are difficult to resolve on the P6-terminated surface [Fig. 2(d)]. The calculations reveal how the surface conditions and terminations affect the sensitivity of the energy dispersion of topologically non-trivial surface states.

## CONCLUSION

In conclusion, we perform a systematic study of HfP<sub>2</sub> using ARPES and first-principles calculations. Our theoretical study leads to the discovery of non-trivial surface states that exist as a result of topological nodal lines in our system. Our experimental data shows surface states predicted by calculations and support the discovery of non-trivial topology in the nodal-line semimetal HfP<sub>2</sub>. While the bulk states remain largely unaffected, the surface termination of cleaved HfP<sub>2</sub> plays a crucial role in the resulting non-trivial band structure of the (001) sur-

face. The ARPES results show that the Fermi surface in an aged (fresh) sample matches with the calculation of the P6 (P7) terminated (001) surface. Since the surface with P6 termination [Fig. 2(d)] likely has higher formation energy than the P7 termination [Fig. 4(d)], it is plausible that a cleaved surface could gradually degrade from P7 to P6 termination. Our results provide evidence that surface termination or local environment plays important role into the surface electronic structure of HfP<sub>2</sub>.

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