Weyl semimetal phase in the non-centrosymmetric compound TaAs

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SI A: Photon energy dependent measurements on the electronic structure of TaAs

In an ARPES measurement, the in-plane electron momentum ($k_\parallel$, parallel to the sample surface) can be naturally determined by the momentum conservation of photoelectrons; while determining the out-of-plane momentum component ($k_z$) requires a series of ARPES measurements performed at different photon energies.

Based on the free-electron final state approximation with a potential parameter $V_0$ (also known as the inner potential) describing the energy difference from the bottom of the valence band to the vacuum level, we can derive the $k_z$ as:

$$k_z = \sqrt{\frac{2m_e(E_k \cos^2 \theta + V_0)}{\hbar}}$$

where $\theta$ is the emission angle and $E_k$ is the kinetic energy of the emitted electron, which satisfies:

$$E_k = h\nu - w - E_B$$

where $h\nu$ is the photon energy, $w$ is the work function of the sample and $E_B$ is the electron binding energy. Therefore, photon energy dependent ARPES measurements probe the electronic structure with different $k_z$ values and can be used to identify surface electronic states (which do not disperse along the $k_z$ direction) from bulk electronic states (which usually show variation along the $k_z$ direction).

The $k_z$ evolution of the electronic structure around the $\bar{Y}$ point is briefly discussed in the main text (Fig. 2g, h). Here we provide with more details: Fig. S1 below shows more dispersions along high symmetry directions around $\bar{Y}$ probed by 64eV, 80eV and 23eV photons. Along the $\bar{Y}$ - $\bar{T}$ direction, the majority part of dispersions show negligible variation between the two photon energies used (64eV and 80eV, Fig. S1b(i), d(i)), indicating the observed bands are mainly surface state bands (SSBs). Their surface nature is further confirmed by the excellent agreement between the bands observed and the ab initio calculation results for the surface states (overlaid red curves), especially those with Fermi-crossings. As these bands form the spoon-like $\alpha$-Fermi surfaces (FSs), we therefore conclude this set of FSs are of surface origin. In
addition, the constant energy contour of the spoon-like α-FS measured with 80eV photons is the same as that measured with 64eV photons (Fig. S2), further proving the surface nature of the α-FSs.

Figure S1. Photon energy dependent measurements on the electronic structure of TaAs near \( \bar{Y} \). a. 3D plot of the electronic structure measured with 64eV photons. b. ARPES intensity spectra along high symmetry \( \bar{\Gamma} - \bar{Y} - \bar{\Gamma} \) (i) and \( \bar{M} - \bar{Y} - \bar{M} \) (ii) directions measured with 64eV photons. \textit{Ab initio} calculation results for the surface states are overlaid on the spectra. For better comparison with calculations, the experiment plot has been symmetrized with respect to \( k_y = \frac{\pi}{a} \) according to the crystal symmetry (same in d below). c. 3D plot of the electronic structure measured with 80eV photons. d. ARPES intensity spectra along high symmetry \( \bar{\Gamma} - \bar{Y} - \bar{\Gamma} \) (i) and \( \bar{M} - \bar{Y} - \bar{M} \) (ii) directions measured with 80eV photons. \textit{Ab initio} calculation results for the surface states are overlaid on the spectra. e. ARPES intensity spectrum along \( \bar{Y} - \bar{M} \) direction measured with 23eV photons. \textit{Ab initio} calculation results for the surface states are overlaid on the spectra. Note that the calculated results are directly overlaid on the measured ARPES spectra without scaling or shift.

The situation for the bowtie-like β-FSs is more complicated. On the high symmetry \( \bar{Y} - \bar{M} \) cut at three different photon energies (Fig. S1b(ii), d(ii) and e) we could locate two sets of bands (one crosses the \( E_F \) and the other below the \( E_F \)) which do not change with photon energies used and show good agreement with the calculation of the SSB. In addition to these bands, another broad feature is detected near the \( E_F \) and seems to change at different photon energies, suggesting the bowtie-like β-FS has mixed contribution from both surface and bulk states.
to this bulk contribution, the β-FS always looks broad in the constant energy contour and looks different measured with 80eV and 64eV photons (Fig. S2, Fig. 2e).

**Figure S2.** *Constant energy contours around the Y point measured with 80eV photons.* **a.** Constant energy contours of TaAs around the Y point from EF to 250 meV binding energy. For better comparison with calculations, the experiment plot has been symmetrized with respect to kx = 0 plane according to the crystal symmetry. **b.** Ab initio calculations show great correspondence from ARPES measurements. Note that the overall structure of the constant energy contours shows weak variation with photon energies (see Fig. 2 in the main text).

ARPES measurements with more photon energies along both the high symmetry \( \Gamma - K \) - \( \Gamma \) and \( \Gamma - Y - \Gamma \) directions are plotted in Fig. S3. Over the energy range between 56eV and 68eV, the main features near the EF marked by SS1-SS3 (SS1'-SS3') along \( \Gamma - K - \Gamma \) (\( \Gamma - Y - \Gamma \)) show the same dispersion across a large kz range (the intensity may vary due to matrix element effect) and again prove their surface nature. Some other bands, such as the ones near the \( K \) point and at high binding energies, show variations with photon energies, indicating the mixture of the contribution from the bulk states.
Figure S3. Photon energy dependent measurements on the dispersions along the high symmetry Γ - X - Γ (a) and Γ - Y - Γ (b) directions. The SSBs (labelled as SS1 to SS3 along Γ - X - Γ and SS1' to SS3' along Γ - Y - Γ) show negligible variation at different photon energies. For better comparison with calculations, the experiment plot has been symmetrized with respect to k_x = π/a (a) or k_y = π/a (b) according to the crystal symmetry.

SI B: Further proof of the Fermi arcs and their topology on the (001) surface of TaAs

In topology, a sufficient criteria to determine whether a group of curves (e.g. FSs in our case) have unclosed ones (e.g. Fermi-arcs) is to use reference loops, as can be seen in Fig. S4. If there are only closed curves (or closed FSs, see Fig. S4a, b), the reference loop will always cross these closed curves/FSs an even number of times (zero is also an even number); however, if one can find a reference loop that has an odd number of crossings (e.g. Fig. S4c, d), this reference loop must cross an odd number of unclosed curves/Fermi-arcs.
Figure S4. Use reference loop to determine the existence of unclosed FSs (i.e. Fermi-arcs).

a, b. For a group of closed FSs, any reference loop can only have even (or zero) number of Fermi-crossings.

c, d. Example of reference loops that cross the FSs an odd number of times. In this case, the reference loops must cross an odd number (minimum 1) of Fermi-arcs.

Thus if we can find a reference loop in the BZ of TaAs that has an odd number of Fermi-crossings, we can prove that there must exist Fermi-arcs. In Fig. 3 of the main text, we found such a reference loop (\( \Gamma - \mathbf{Y} - \mathbf{M} - \Gamma \)) with odd number (seven) of Fermi-crossings, thus proved the existence of Fermi-arcs in the BZ.

Below in Fig. S5, we show that the Fermi-crossing counting along the \( \mathbf{\Gamma} - \mathbf{X} - \mathbf{M} - \mathbf{\Gamma} \) reference loop can also yield an odd number of Fermi-crossings. The dispersions along the high symmetry \( \mathbf{\Gamma} - \mathbf{X} - \mathbf{\Gamma} \), \( \mathbf{M} - \mathbf{X} - \mathbf{M} \), and \( \mathbf{M} - \mathbf{\Gamma} - \mathbf{\mathbf{M}} \) directions are illustrated in Fig. S5b-d. There are five Fermi-crossings along \( \mathbf{X} - \mathbf{\Gamma} \), four along \( \mathbf{X} - \mathbf{M} \) and zero along \( \mathbf{\Gamma} - \mathbf{M} \), respectively, which gives a total of nine Fermi-crossings along \( \mathbf{\Gamma} - \mathbf{X} - \mathbf{M} - \mathbf{\Gamma} \). Thus we also establish the existence of Fermi-arcs around the \( \mathbf{X} \) point of the BZ.
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a, b. For a group of closed FSs, any reference loop can only have even (or zero) number of Fermi-crossings.

c, d. Example of reference loops that cross the FSs an odd number of times. In this case, the reference loops must cross an odd number (minimum 1) of Fermi-arcs. Thus if we can find a reference loop in the BZ of TaAs that has an odd number (seven) of Fermi-crossings, we can prove that there must exist Fermi-arcs. In Fig. 3 of the main text, we found such a reference loop (\(\Gamma \rightarrow Y \rightarrow M \rightarrow \Gamma\)) with odd number (seven) of Fermi-crossings, thus proved the existence of Fermi-arcs in the BZ.

Below in Fig. S5, we show that the Fermi-crossing counting along the \(\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma\) reference loop can also yield an odd number of Fermi-crossings. The dispersions along the high symmetry \(\Gamma \rightarrow X\), \(X \rightarrow M\), and \(M \rightarrow \Gamma\) directions are illustrated in Fig. S5 b-d. There are five Fermi-crossings along \(X \rightarrow \Gamma\), four along \(X \rightarrow M\) and zero along \(M \rightarrow \Gamma\), respectively, which gives a total of nine Fermi-crossings along \(\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma\). Thus we also establish the existence of Fermi-arcs around the \(X\) point of the BZ.

Figure S5. Additional proof for the existence of the Fermi arc in TaAs. a. The BZ of TaAs with Weyl points marked by red and blue dots and Fermi crossings marked by green arrows as in b, c. The \(\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma\) loop is highlighted by bold yellow lines. b-d. The band dispersions along high symmetry directions \(\Gamma \rightarrow X\) (b), \(X \rightarrow M\) (c) and \(M \rightarrow \Gamma\) (d). The measurement again agrees with the \textit{ab initio} calculations (red overlaid curves) excellently, we can thus determine that there are five Fermi-crossings along \(\Gamma \rightarrow X\), four along \(X \rightarrow M\) and zero along \(M \rightarrow \Gamma\), which gives a total of 9 (odd number) Fermi-crossings along the \(\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma\) loop and proves the existence of the Fermi-arc around the \(X\) point of the BZ. For better comparison with calculations, the experiment plot has been symmetrized with respect to \(k_x=\pi/a\) (b), \(k_y=0\) (c) or \(k_\parallel=0\) (d) according to the crystal symmetry.

SI C: Calculated spin texture of the Fermi surface of TaAs

In order to reveal the spin texture of the surface Fermi surfaces and help identify the evolution of different Fermi surface pieces, we performed \textit{ab initio} calculation on the spin polarization of the Fermi surface.

The calculated spin texture of the Fermi surface (Fig. S6) suggests those electronic states with mostly surface contributions (including the spoon-like and bowtie-like Fermi surfaces) show large in-plane spin polarization while the spin moment for the bulk states is almost zero. As an example, the electrons from the spoon-like bands 1 and 2 close to the \(\bar{Y}\)
point (Fig. S6b) show complex spin texture while the inner band 3 has almost no net in-plane spin moment.

It is worth noting that across the Weyl points, the spin polarization in band 1 shows discontinuity and quickly reduces to zero as it diminishes, while band 2 illustrates continuous sizable spin texture across the crossing points (Fig. S6c). Such observation supports our conclusion that band 1 is a Fermi arc surface state terminating at the Weyl points.

Figure S6. Calculated spin texture of the Fermi surface of TaAs. a. Broad overview, b. detailed plot of the spoon piece and c. zoomed-in plot around the Weyl points of the in-plane spin polarization. The direction/length of the arrows indicates the direction/amplitude of the spin polarization. Different colors represent different FS pieces.

SI D: Line shape analysis of the Fermi surface of TaAs

We carefully conducted the line shape analysis of the momentum distribution curves (MDCs) for the Fermi surface of TaAs and examined the termination behavior of the Fermi arc near the Weyl points. The MDC fitting results are shown in Fig. S7, in which Lorentzian peaks are used for the fitting process.

From the fitting results of the FSs around the \( \bar{Y} \) point, we can see while the peak positions and intensities of FS-2 and 3 evolve smoothly across the Weyl points (also agreeing with the calculations), the peak intensity of FS-1 diminishes quickly after passing the intercepting points (Fig. S7), suggesting its termination at the Weyl points.
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**Figure S7.** Line shape analysis of the MDCs of the FS. a. Photoemission intensity of the Fermi surface around the \( \bar{Y} \) point. Dashed line indicates the position where the band numbers are reduced. Three bands are identified and labeled. For the convenience of fitting, the plot has been symmetrized with respect to the \( k_x=0 \) plane according to the crystal symmetry. b. Stacking plot of the MDCs of the intensity map in (a). Fitted MDC peaks of all the three bands are labelled. c. Photoemission intensity plot of the Fermi surface in the vicinity of the Weyl points. d. Three typical MDCs above, at and below the Weyl points and their corresponding fitting curves as the sum of Lorentzian peaks from all three bands. e. Summary plot of the fitted peak positions for MDCs with different \( k_y \) values. f. Summary plot of the fitted peak intensities for MDCs with different \( k_y \) values.
SI E: ARPES measurement on the bulk electronic states of TaAs

In the measurement of TaAs, we found that with relatively low photon energies (48–68 eV, the available photon energy range in one of our ARPES setups), the dominance of the surface state in this photon energy region prevents us from clearly observing the bulk dispersions (Fig. S8). The dominance of the surface state is possibly due to: i) the surface states are more sensitive (i.e. have large photoemission cross sections) in this photon energy range (48-68eV); ii) the low energy photoelectrons have less elastic mean free path thus the bulk signal was severely suppressed (e.g. in the “universal curve”, the photon energy range 48-68eV shows correspondence to the low mean free path region indicated in Fig. S8a). For these reasons, the bulk band dispersion and Fermi-surface could not be clearly observed in Fig. 1-3.

In order to enhance the signals from the bulk states, we conducted ARPES measurements in higher photon energies region (up to 240eV), which not only allows us to enhance the bulk sensitivity, but also gives us larger momentum coverage so that we can systematically study the bulk band structure across multiple BZs.

The results from high energy ARPES measurements indeed showed convincing bulk band structure with suppressed surface band contribution, which is presented as Fig. 4 in the manuscript.

For the comparison between the bulk and surface states, in Fig. S9, we show the bulk and surface FSs obtained with high (189eV) and low (60eV) energy photons, which show clearly different FS geometry as expected, and the Weyl nodes positions extracted from both FS maps (as labelled by the arrows) show nice agreement, which demonstrates that the Fermi arc indeed starts and ends at the bulk Weyl points.
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Figure S8. Probing bulk and surface electronic states with ARPES. a. The “universal curve” for surface sensitivity in photoemission (“Surface and Interface Analysis”, 1979, John Wiley & Sons, Inc), the shaded region shows the electrons’ kinetic energy range from 40 to 60eV. b. Photoemission measurement along the Γ-X̅ direction using low energies photons (64eV) with the ab initio calculation overlapped, the color scale represents the surface contribution. c. Photoemission measurement along the Γ-X-Z direction using high energy photons (204eV) with the ab initio calculated bulk bands overlapped.

Figure S9. Bulk and surface FS of TaAs. Comparison of the FS maps of TaAs measured with 189eV (a) and 60eV (b) photons. In both (a) and (b), panel (i) shows experimental FS only and panel (ii) shows the calculated FS from the bulk (a) and surface (b) bands overlapped on experimental FS. WP+ and WP- denote the positions of the Weyl points. Note that the bulk FS in (a) is a bit blurry due to the kz broadening and finite experiment resolution.

SI F: Remarks on the constant energy contours in the ky-kz plane

According to our calculations and the previous theoretical work (Ref 1 of the main text), there are clear band inversion and multiple band crossing features near the Fermi level along the Z-N, Z-S and Γ-S lines. Without turning on the spin orbit coupling (SOC), the band crossings are protected by the mirror symmetry, forming “nodal rings” in the Z-N-Γ plane (Fig. S10a).

As the bands near the Fermi energy are mainly formed by Ta 5d orbitals which have large SOC,
we also carried out the calculation with SOC included, resulting that the band crossings in the $Z-N-\Gamma$ plane (“nodal rings” structure) are now gaped with the isolated gapless Weyl nodes appearing slightly off the mirror planes.

Due to the small gap opening around the “nodal rings” region in the $Z-N-\Gamma$ plane, the constant energy contour in the $k_y-k_z$ plane would show up as broken pieces at $E_F$, while recovering to closed, circle-like features at high binding energies (Fig. S10c). In our ARPES experiments, since we need to accumulate enough statistics to show clear evolution of band structure along the $k_z$ direction, we plot the constant energy contour as the integration of photoemission intensities between $E_F-100$meV and $E_F$ (Fig. S10b). Therefore, the observed feature shows nice agreement with the calculated constant energy contours at ~50 meV below $E_F$ (Fig. S10c).

**Figure S10. Constant energy contour in the $k_y-k_z$ plane of TaAs.**

*a.* Schematic of the 3D Brillouin zone of TaAs. Green and yellow planes indicate the mirror planes. Orange curves indicate the positions and shape of the nodal rings while red/blue points notify the predicted location of Weyl points with different chirality. Large grey plane defines the $k_y-k_z$ plane with $k_x=0$, where the ARPES measurement and *ab initio* calculation results are plotted in *b* and *c*. *b.* ARPES measurement on the constant energy contour in the $k_y-k_z$ plane with $k_x=0$. The energy integration window is from 100meV below $E_F$ to $E_F$. *c.* Evolution of the calculated constant energy contours in the $k_y-k_z$ plane with $k_z=0$ at different energies.

**SI G: Study of the Fermi surface evolution of TaAs by in-situ potassium dosing**
In order to study the evolution of different Fermi surface pieces with $E_F$ position and the Fermi-arc nature, we have carried out surface doping measurements (by in-situ potassium deposition on sample surface to n-dope the sample surface thus upshift the $E_F$ position).

In Fig. S11, we show both the comparison of calculated and experimental FS evolution with increasing $E_F$ positions. In both Fig. S11a and b, we not only observe the shrinking of all three pockets (more dramatically for the inner two pockets), but also see the apparent breaking of the outermost pocket (FS1) from the inner ones with the increase of the $E_F$ positions [Panel (ii-iv) of Fig. S11a and Fig. S11b]). This observation again confirms the Fermi-arc nature of FS-1.

As the measurement in the original manuscript actually shows mostly the surface state, the $E_F$ position with respect to the bulk band cannot be accurately determined. In addition to the comparison with the ARPES measurement on the bulk bands with another experimental setup (See Fig. 4 and also Supplementary Materials, part E), the FS evolution with the surface charge doping also helps us increase the accuracy of the identification of the Weyl points.

**Figure S11.** FS evolution with in-situ potassium dosing. a. *Ab initio* calculation on the constant energy contours around the $\bar{X}$ point at various different kinetic energies. b. Photoemission intensity of the Fermi surface around the $\bar{X}$ point after different potassium dosage. WP+ and WP- label the position of the Weyl points.