Observation of chirality-neutral Fermi surface in Weyl semimetal candidate SrSi$_2$

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Quasiparticle excitations described by the Weyl equation in solids have attracted massive attention in recent years. So far, a wide range of solids have been experimental realized as Weyl semimetals (WSMs). On the other hand, for a compound to display Weyl points it must exhibit either inversion symmetry breaking or time reversal symmetry breaking. Hence, the Weyl fermions are vulnerable to annihilation from structural distortions or lattice imperfections. In the absence of both mirror and inversion symmetry, SrSi$_2$ has been predicted as a robust WSM by recent theoretical works. Here, supported by first-principles calculations, we present systematical angle-resolved photoemission studies of undoped SrSi$_2$ and Ca-doped SrSi$_2$ single crystals. However, our result shows no evidence of the predicted Weyl fermions at the $k_z = 0$ plane, as well as the Fermi arcs on (001) surface. Combined with the first-principles calculations, we suggest that SrSi$_2$ is a topologically trivial semiconductor.
There has been a surge of interest in gapless topological phases that arise in multi-band fermionic systems, where the band crossing points have nonzero Chern numbers [1-18]. This interest led to the discovery of quasiparticle excitations of the Weyl fermions, whom can be described with the same equations as their counterpart in high-energy physics [19]. By breaking either time-reversal or inversion symmetry, Weyl fermions are realized in solids as two linearly dispersing crossing bands. The topology of Weyl nodes is characterized by a Chern number \( C \) that is related to the Berry curvature. Meanwhile, another important hallmark of Weyl semimetals (WSMs) is the topologically protected Fermi arcs. Different from the bulk bands related Weyl nodes, Fermi arcs are surface states which terminate at projections of Weyl nodes with opposite chiral charges. By counting connected Fermi arcs, the chiral charge of a Weyl node can be determined [17-18]. In recent years, WSMs are experimentally identified in a wide range of materials, for example TaAs [2,4], WP2 [10], Co3Sn2S2 [11], Co2MnGa [12], etc. Although quasiparticles within electronic band structures need not necessarily follow the Poincaré symmetry pertaining to high-energy physics, they adhere to the crystal symmetry instead. Therefore, the stability of a WSM crystal structure is crucial for the existence of the Weyl fermions. Moreover, it is important for device manufacturing as well as applications.

Among the realized WSMs, the Weyl fermions are mostly protected by either inversion symmetry or mirror symmetry. Lattice distortion caused by external force or lattice imperfections can break the crystal symmetries which protect the Weyl fermions. In the searching for robust WSM systems, one of the promising ways is to find a WSM that has crystal structure with lower symmetries. The inversion-asymmetric chiral compound strontium disilicide, SrSi2, was predicted to be the first WSM which lacks both mirror and inversion symmetries [20-21]. This reduced symmetry ensures SrSi2 to be a robust WSM candidate. SrSi2 crystallizes in a simple cubic lattice system, with lattice constant \( a = 6.563 \, \text{Å} \) and the space group is \( P4_132 \). As shown in Fig. 1(a), the crystal lacks both inversion and mirror symmetries. First-principles band structure calculations without spin-orbit coupling (SOC) show one electron band and one hole
band along Γ-X direction in the Brillion zone (BZ). These two bands have an overlap of \( \sim 0.25 \) eV with two crossing points, as the calculated band structure shows in Fig. 1(c), which create a pair of Weyl fermions of opposite charges, as indicated by the dots in two colors shown in Fig. 1(b). In the presence of SOC, the linear band dispersion near the Weyl nodes turns into quadratic dispersion. As a result, the Weyl nodes turn into double-chiral states which carry higher chiral charge of \( \pm 2 \). Besides the Weyl nodes, first-principles calculations also predict long Fermi arcs across all over the BZ on (001) surface. In addition, another theoretical work suggests that, with Ca-doping, the lattice of SrSi\(_2\) will shrink, and the overlap between the hole and electron bands will be increased. As a result, the topological strength of SrSi\(_2\) will be expected to increase [21]. However, to our best knowledge, due to difficulty of sample growth [22], no experimental research has been carried out on SrSi\(_2\) system so far. A direct evidence of the existence or absence of the Weyl node is still awaiting.

Here, supported by first-principles band structure calculations, we present a comprehensive angle-resolved photoemission spectroscopy (ARPES) investigation on the high-quality single crystal SrSi\(_2\) and Ca-doped SrSi\(_2\). The ARPES experiments were carried out by vacuum-ultraviolet ARPES (VUV-ARPES) at Bloch beam line at MAX IV with a DA30L analyzer, and soft x-ray ARPES (SX-ARPES) at ADRESS beam line at Swiss Light Source [23] with a PHOIBOS-150 analyzer [24]. The data were collected using photon energies in the ultraviolet and soft x-ray regions, with an overall energy resolution on the order of 15 meV and 50-80 meV, respectively [25]. For the \textit{ab-initio} calculations we employ density-functional theory (DFT) as implemented in the Vienna \textit{ab-initio} simulation package (VASP) [26] using pseudopotentials and augmented plane waves as basis set. The exchange-correlation potential is included utilizing the hybrid HSE approximation [27]. To allow for a more detailed investigation through the BZ, maximally localized Wannier functions are created from the DFT wavefunctions using the program Wannier90 [28]. With the resulting tight-binding Hamiltonian a dense search for possible Weyl crossings is performed. With a systematic study, we found no evidence of predicted Weyl nodes from ARPES at \( k_z = 0 \) plane in BZ for both undoped
and Ca-doped SrSi$_2$ samples. Therefore, our calculation using hybrid functional HSE suggests that SrSi$_2$ is a topological-trivial semiconductor.

The samples with a typical size of $\sim 8\times 2\times 2$ mm$^3$ were cleaved in-situ at 15 K in a high-vacuum chamber, with a base vacuum better than $5\times 10^{-11}$ torr. The core-level photoemission measurements of SrSi$_2$ were acquired with $h\nu = 200$ eV, as shown in Fig. 2(a). The ARPES spectrum shows the characteristic core levels of Sr and Si elements, confirming the chemical composition of our samples. By VUV-ARPES, we first perform Fermi surface (FS) mapping on (001) surface with $h\nu = 118$ eV. The FS mapping is shown in Fig. 2(c). Four FS pockets are located along $\Gamma$-X direction as a result of the $C_4$ rotation symmetry. The out-of-plane FS is taken with $h\nu$ in range of 50-140 eV, as shown in Fig. 2(b). Due to the Heisenberg uncertainty principle, the finite photoelectron escape depth results in finite intrinsic resolution in the out-of-plane momentum $k_z$ with the $k_z$ broadening inversely proportional to the escape depth [24]. Photoelectrons emitted by ultraviolet photon have relatively low escape depth. Therefore, ARPES intensity is integrated over a relatively large $\Delta k_z$, and the out-of-plane FS contours are broadened along the $k_z$ direction. As a result, the FS pockets shown in the out-of-plane FS have an ellipsoidal rather than the round shape seen in the in-plane FS. However, both in-plane and out-of-plane FS contours show no signature of the predicted Fermi arcs of the surface states, albeit strongly depending on the terminations and surface chemical environment, in difference from the bulk states. As the Fermi arcs are produced by the Weyl nodes, the topological nature of SrSi$_2$ appears questionable.

Since the Weyl nodes are band crossings of the bulk states, we will now turn to the bulk states of SrSi$_2$ measured with SX-ARPES to achieve higher bulk sensitivity and much better $k_z$ resolution. The out-of-plane FS of SrSi$_2$, as shown in Fig. 3(a), is acquired within $k_x$-$k_z$ plane, with photon energies in the range of 350-800 eV. Similarly, to the out-of-plane FS taken by VUV-ARPES, each BZ in Fig. 3(a) encloses four FS pockets along the high-symmetry $\Gamma$-X direction. In Fig. 2(c), we present the in-plane FS map at $k_z = 0$, acquired with $h\nu = 704$ eV photon. Due to the cubic crystal structure,
the in-plane FS map is consistent with the out-of-plane FS map in Fig. 3(b), which also shows four FS pockets along Γ-X direction. In order to find out the predicted Weyl nodes shown in Fig. 1(c), a high-resolution spectrum along the Γ-X direction is acquired at $k_z = 0$ plane with $h\nu = 704$ eV, as shown in Fig. 3(c). Only one hole band is observed along this direction. The top of the hole band is located just above the Fermi energy ($E_F$) and forms the FS pockets which we have just seen in the in-plane and out-of-plane FSs. However, no electron band is observed to have crossings with the hole band. In order to study the unoccupied states, we apply first-principles calculation using hybrid functional HSE. As shown in Fig. 3(d), the calculated band structure along Γ-X direction has excellent agreement with the ARPES spectrum. In the unoccupied states, the energy maximum of the hole bands is located at ~ 0.05 eV above $E_F$. With an energy gap of ~ 0.1 eV, the bottom of the electron bands is located above the hole bands, without any crossings.

In addition, to study the band structure evolution under doping, we perform SX-ARPES measurements on two Ca-doped Sr$_{1-x}$Ca$_x$Si$_2$ samples, with $x = 2\%$ and 5\%. The doping-induced changes in the band structure depend on many factors, such as lattice structure, chemical pressure, etc. Hence, we only present a qualitative analysis here. As shown in Fig. 4(a,b), the ARPES spectra of the two doped samples show identical band structures, which are also similar to the undoped sample (Fig. 3(c)). We show the momentum distribution curves (MDCs) taken at $E_F$ in Fig. 4(c-d). By measuring the distance between the MDC peaks, we find an average diameter of the hole FS pocket along Γ-X direction of 0.09 Å$^{-1}$ for the 2% Ca-doped SrSi$_2$. This is slightly higher than 0.073 Å$^{-1}$ measured for the 5% Ca-doped SrSi$_2$, which leads to a larger FS pocket area and thus higher metallicity of the less-doped sample. Although theoretical work predicted increased topological band overlapping in Ca-doped SrSi$_2$, no evidence of Weyl nodes is observed in any of the measured samples.

Our first-principles calculations suggest a gap of ~ 0.1 eV between the electron band and hole band, indicating SrSi$_2$ is a topologically trivial semiconductor. Although, no Weyl nodes is observed in the ARPES experiments below $E_F$, we cannot rule out the
existence of the predicted band crossings above $E_F$. In both scenarios, the FS pockets along $\Gamma$-$X$ direction will enclose either no Weyl nodes or two Weyl nodes with opposite chiral charges, leading to a net Chern number of $C = 0$. Furthermore, there is no evidence of the topological nature of SrSi$_2$ with by Ca-doping. Our first-principles calculation result suggests that the HSE is a more suitable method to describe the exchange-correlation for SrSi$_2$. In summary, the results of systematic VUV-ARPES and SX-ARPES measurements presented here show no signatures of the Fermi arcs formed by surface states on the (001) surface, and no evidence of the bulk Weyl nodes at $k_z = 0$ plane of SrSi$_2$. On Ca-doped SrSi$_2$, we observe a slight evolution of the FS pockets, which will influence the corresponding transport properties.

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**Author contributions**

The ARPES measurements were conducted by M.-Y.Y. and supported by V.N.S. The first-principles calculations were provided by J.N. and Y.S. The single crystals were grown by K.M., with the help of N.K., C.S. All the authors discussed the results. The manuscript was written by M.-Y.Y., with feedback from all the authors. The project was
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Competing financial interests
The authors declare no competing financial interests.

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Fig. 1 (a) Crystal structure of SrSi$_2$. (b) Bulk BZ of SrSi$_2$ with high-symmetry points labeled. The blue and red dots represent the predicted Weyl nodes along Γ-X direction. (c) GGA Calculated band structure along Γ-X direction. Due to lack of mirror-symmetry, the Weyl nodes with opposite charges (blue and red dots) are located at different energy.

Fig. 2 (a) SrSi$_2$ core level spectrum, obtained with $h\nu = 200$ eV. (b) The out-of-plane FS, taken with the photon energy in range of 50-140 eV, with the BZ boundary marked (red lines). (c) The in-plane FS at $k_z = 0$ plane, acquired with $h\nu = 118$ eV.
Fig. 3 (a) The out-of-plane and in-plane FS, acquired with the photon energy in range of 350-800 eV, with BZ boundary marked (red lines). (b) The in-plane FS at $k_z = 0$. (c-d) Photoemission intensity plot along $\Gamma$-$X$ direction and corresponding calculated band structure, respectively.
Fig. 4 (a) High resolution photoemission intensity plot of Ca$_{x}$Sr$_{1-x}$Si$_2$ ($x = 2\%$) along Γ-X direction at $k_z = 0$ plane. (c) MDC of (a) taken at $E_F$. (b,d) Same as (a,c) but for Ca$_{x}$Sr$_{1-x}$Si$_2$ ($x = 5\%$), respectively.