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Crystalline symmetry-protected non-trivial topology in prototype compound BaAl$_4$

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The BaAl$_4$ prototype crystal structure is the most populous of all structure types, and is the building block for a diverse set of substructures including the famous ThCr$_2$Si$_2$ family that hosts high-temperature superconductivity and numerous magnetic and strongly correlated electron systems. The MA$_4$ family of materials (M = Sr, Ba, Eu; A = Al, Ga, In) themselves present an intriguing set of ground states including charge and spin orders, but have largely been considered as uninteresting metals. We predict the exemplary compound BaAl$_4$ to harbor a three-dimensional Dirac spectrum with non-trivial topology and possible nodal lines crossing the Brillouin zone, wherein one pair of semi-Dirac points with linear dispersion along the $k_z$ direction and quadratic dispersion along the $k_x/k_y$ direction resides on the rotational axis with $C_{4v}$ point group symmetry. An extremely large, unsaturating positive magnetoresistance in BaAl$_4$ despite an uncompensated band structure is revealed, and quantum oscillations and angle-resolved photoemission spectroscopy measurements confirm the predicted multiband semimetal structure with pockets of Dirac holes and a Van Hove singularity (VHS) remarkably consistent with the theoretical prediction. We thus present BaAl$_4$ as a topological semimetal, casting its prototype status into a role as a building block for a vast array of topological materials.

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INTRODUCTION

The development of a better understanding of the role of topology in electronic states has led to a revolution in exploring both old and new compounds for non-trivial topologies, and has provided a fertile platform to search for new topological fermionic excitations	extsuperscript{1–3}. The discovery of topological insulators (TIs) with robust metallic surface states protected by the topology of the insulating bulk	extsuperscript{4} was followed by the discovery of topological semimetals (TSMs). These are found to have deep connections with particle physics models of relativistic chiral (Weyl) fermions and also provide fermionic excitations without high-energy counterparts	extsuperscript{5–12}. In a Dirac semimetal (DSM), bulk valence and conduction bands cross each other linearly at discrete points protected by time-reversal, inversion, and crystal symmetries. These stable Dirac points with four-fold degeneracy make it possible to simulate massless Dirac fermions	extsuperscript{5–13}. By breaking either inversion or time-reversal symmetry, a Dirac semimetal can be tuned to a Weyl state where the nondegenerate linear touchdowns of the bulk bands come in pairs. Each Weyl point with two-fold-degeneracy has a definite chirality of ±1 and the quasiparticle excitations mimic the relativistic Weyl (chiral) fermions	extsuperscript{5,6,13,14}.

Cd$_3$As$_2$ and Na$_3$Bi were the first theoretically predicted DSM candidates	extsuperscript{15,16}, subsequently confirmed by experiments	extsuperscript{17–20}. Recently, several materials including transition-metal icosenides MA$_4$ (M = V, Nb, and Ta; A = Al, Ga, In)\textsuperscript{21–23}, MgTa$_2$N$_2$\textsuperscript{22,23}, CaAgBi\textsuperscript{24} and PtTe$_2$\textsuperscript{25} were predicted to host Dirac fermions. These form part of an even larger list of TSMs\textsuperscript{26–28} that also exhibit exotic physical properties including high carrier mobilities, chiral anomaly physics and topological superconductivity. Extremely large magnetoresistance (MR) is another symptom of such materials, which is usually very small in non-magnetic, non-compensated metals according to semiclassical transport theory. However, several TSMs—including Dirac semimetals Cd$_3$As$_2$ and ZrSiS\textsuperscript{29–31}, the NbAs$_2$ family\textsuperscript{32–35}, the type-II Weyl semimetal WTe$_2$\textsuperscript{36} and several other TSMs such as NbSb$_2$, PtSn$_4$, LaSb\textsuperscript{37}, exhibit extremely large MR behavior which could have potential application in magnetic sensors, spintronics, and memories. Very recently, multiple topological states have been predicted and observed in the iron-based superconductors LiFeAs and Fe(Se, Te)\textsuperscript{38}, while possible Dirac fermions are predicted in heavy fermion superconductors Ce(Co,Rh)In$_5$\textsuperscript{39}.

The MA$_4$ family of materials (M = Sr, Ba, Eu; A = Al, Ga, In) form the prototype parent crystal structure of a large family of compounds including the ThCr$_2$Si$_2$-based iron superconductors\textsuperscript{40}, classic heavy fermions systems such as CeCu$_2$Si$_2$\textsuperscript{41,42}, and numerous non-centrosymmetric compounds\textsuperscript{30}. In addition, the MA$_4$ family itself presents a rich variety of ground states. For instance, SrAl$_4$ exhibits a charge density wave transition at 200 K, while Eu(Ga, Al)$_4$ orders antiferromagnetically at 15 K and is thought to also exhibit charge density wave order\textsuperscript{43,44}. In this work, we present the comprehensive combined experimental and theoretical study of topology in the classic prototype compound BaAl$_4$, including first-principles electronic structure calculations, transport measurements, and angle-resolved photoemission (ARPES) studies. We predict BaAl$_4$ to be a topological three-dimensional Dirac semimetal, where one pair of type-I Dirac points resides on the rotational axis with the $C_{4v}$ point group symmetry, and confirm this prediction using ARPES and quantum oscillations experiments. The calculated band structure is in excellent agreement with the experimental data.

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agreement with ARPES spectra, and Hall resistivity and quantum oscillations measurements confirm the multiband structure with electron and hole pockets, and is consistent with the predicted presence of Dirac hole pockets. Together with an extremely large MR that does not saturate in fields up to 32 T, our results indicate BaAl₄ is a topological semimetal, and point to the MA₄ family of materials as fertile territory for the exploration of a basis of topological systems.

RESULTS

Non-trivial topology in BaAl₄

Figure 1 a, b presents schematic illustrations of both the crystal structure and the bulk Brillouin zone of BaAl₄. The high quality of single crystals grown by a self-flux method (see Fig. 1c) is confirmed by X-ray diffraction (Fig. S1 in SM) and core-level photoemission spectrum, as shown in Fig. 1d. Rietveld refinement of powder X-ray diffraction spectra confirms our samples to have the body-centered tetragonal structure with space group I4/mmm (No. 139). Clear peaks from Ba-5s, Ba-5p, and Al-2p core-level electrons observed by photoemission spectroscopy confirm the correct chemical composition.

In the BaAl₄ unit cell, the Ba atoms sit at the Wyckoff position 2a, while the Al atoms sit at two non-equivalent Wyckoff positions 4d and 4e, as shown in Table I in the Supplementary Materials. Among them, 2a and 4d sites are the maximal Wyckoff positions, but 4e is not. The 4e Wyckoff position has a stabilizer group which is a subgroup of the stabilizer group of the maximal position 2a or 2b. Figure 1e, f shows the calculated bulk electronic structure along high-symmetry lines without (with) spin-orbit coupling, showing its semimetallic ground state feature. One observes that there are several crossing points along the Γ–X, Γ–Σ, and Z–Σ₁ directions in different mirror reflection planes from two quasi-linear bands close to the Fermi level (E_F) in the band structure without SOC. These Dirac nodal points could give rise to a variety of Dirac nodal lines in each mirror plane and also exotic surface states, which deserve further study.

Once the SOC is included, most of these crossing points open small gaps because the two crossing bands belong to the same irreducible representation of the point group indicated by the eigenvalue analyses. For example, the two bands crossing each other along the Γ–Σ d i r e c t i o n a t ~ 0 . 1 e V b o t h b e l o n g t o ∆₅ representation and then the crossing point is gapped out. However, the crossing point along the Γ–Z direction is different. On Γ–Z path which is along the rotational axis, the point group symmetry is of C₄ᵥ. The two doubly degenerate crossing bands (highlighted by the red square in Fig. 1f) are found to form two distinct irreducible representations Γ₆ and Γ₇ representation of the C₄ᵥ double group. In Fig. 1g, we show these two bands belong to different representations of the symmetry group;
for each band. Referring to the character tables in the Bilbao Crystallographic Server (BCS), we successfully assign all the valence bands to corresponding irreducible representations (irreps). The irrep characters of the valence bands are listed in Table III in the Supplementary Materials. One can check if those valence bands are decomposed into a linear combination of pEBRs. It turns out they cannot, which means those valence bands cannot be topologically trivial.

Therefore, the intersection of the two double-degenerate bands is protected by the crystalline symmetry, \( C_{\alpha\nu} \), forming a massless Dirac fermion. Figure 1h, i shows the zoomed dispersion along the out-of-plane \( k_z \) direction. All spectra shown in (a–d) are obtained by integrating intensities in the energy window of ±20 meV at \( E_F \). The red lines superposed in all panels here are the DFT calculation results for BaAl\(_4\). The locations of Dirac point are marked with green dots in (a, d). For a direct comparison, all Fermi surfaces (a–d) and all energy and momentum cuts (e–h) shown here are centered at \((k_x, k_y, k_z) = (0, 0, 0)\) and symmetrized.

### Angle-resolved photoemission

To verify band structure calculations, we measured ARPES to obtain the electronic structure of BaAl\(_4\) at various photon energies, using in situ cleaved single crystals of BaAl\(_4\) where the (001) surface cleavage plane is determined by X-ray diffraction (Fig. S1b of Supplementary Information). Figure 2 shows the measured ARPES spectra compared to the calculation (red curves). The intensity variation across the measured ARPES data is attributed to photoemission matrix element effects. Note that we shifted the angle-resolved photoemission matrix element effects. Note that we shifted the ARPES spectra of energy versus momentum cuts along the high-symmetry directions: \( \Sigma \bar{1} \)–\( \bar{1} \Sigma \) (e), \( \Sigma \bar{1} \)–\( \bar{1} \Sigma \bar{1} \) (f), and \( \Sigma \bar{1} \)–\( \bar{1} \Sigma \bar{1} \) (g). h ARPES spectra of energy versus momentum cut crossing the DP along the in-plane direction \( k_x \). All spectra shown in (a–d) are obtained by integrating intensities in the energy window of ±20 meV at \( E_F \). The red lines superposed in all panels here are the DFT calculation results for BaAl\(_4\).

#### Fig. 2 ARPES spectra near the Fermi level compared to DFT calculation of BaAl\(_4\). a–c Constant energy maps at \( E_F \) in the high-symmetry planes: the \( k_z \)-\( k_y \) plane (perpendicular to the surface (001)-plane) (a) using the incident photon energy ranging from 80 to 120 eV, the \( k_z \)-\( k_x \) plane crossing \( \Gamma \) (b) using the incident photon energy of 95 eV, and the \( k_z \)-\( k_y \) plane crossing \( Z \) (c) using the incident photon energy of 112 eV. Black solid line represents the bulk Brillouin zones (BZ), marked with high-symmetry points. d Constant energy map at \( E_F \) crossing the location of Dirac point (DP) using the incident photon energy of 86 eV. e–g ARPES spectra of energy versus momentum cuts along the high-symmetry directions: \( Z \bar{1} \)–\( \bar{1} Z \) (e), \( \Sigma \bar{1} \)–\( \bar{1} \Sigma \) (f), and \( \Sigma \bar{1} \)–\( \bar{1} \Sigma \bar{1} \) (g). h ARPES spectra of energy versus momentum cut crossing the DP along the in-plane direction \( k_x \). Therefore, the intersection of the two double-degenerate bands is protected by the crystalline symmetry, \( C_{\alpha\nu} \), forming a massless Dirac fermion. Figure 1h, i shows the zoomed dispersion along the out-of-plane \( k_z \) direction. All spectra shown in (a–d) are obtained by integrating intensities in the energy window of ±20 meV at \( E_F \). The red lines superposed in all panels here are the DFT calculation results for BaAl\(_4\). The locations of Dirac point are marked with green dots in (a, d). For a direct comparison, all Fermi surfaces (a–d) and all energy and momentum cuts (e–h) shown here are centered at \((k_x, k_y, k_z) = (0, 0, 0)\) and symmetrized.
Fig. 3  Lifshitz point and Van Hove singularity in BaAl₄. a The bulk BZ marked with the location of Dirac point (DP, green dot) and Van Hove singularity of saddle point type (VHS, light blue point). The light green plane represents the location for the constant energy contours shown in (b,e–j). b Constant energy map at E_F. The light blue square shows the location for (e–j). Red lines in (a,b) are the high-symmetry lines for the energy and momentum cut shown in (c). c ARPES spectra of energy versus momentum cuts along the Z−Γ−Σ. The local maximum and minimum are observed at the same momentum Γ point, showing the saddle point singularity VHS. d Energy distribution curve (EDC) obtained by integrating the ARPES intensity in the vicinity of Γ point (window size: ±0.02 Å⁻¹). The peak of the EDC marks the VHS at E_b = −450meV where the topology of Fermi surface changes.

Electronic dispersions are consistent with band structure calculations for all directions. Similar to graphene, multiple Dirac dispersions in BaAl₄ create a saddle-point singularity in between the two DPs in momentum space as a result of a change in electronic topology, reminiscent of a Lifshitz transition in the electronic structure. Figure 3a shows the location of the DP and VHS in the bulk BZ of BaAl₄. To identify the saddle-point singularity experimentally, we show the energy and momentum dispersion along the Z−Γ−Σ direction (along the red line in Fig. 3a, b) in Fig. 3c. While the tail of the Dirac dispersion has the local energy minimum in the orthogonal direction (in-plane direction, Γ−Σ) with various binding energies, emphasizing the change of topology of electronic structure, a Van Hove singularity (VHS) is observed at the same momentum Γ point (see the blue square in Fig. 3b) with various binding energies. These maps and the energy and momentum cut (c) shown here are centered at (k_x, k_y, k_z) = (0, 0, 0).

Because the Dirac point protected by C₄ᵥ symmetry is above E_F and hence not accessible to ARPES, we cannot directly observe the vicinity of DP. However, the excellent agreement between our ARPES results and the first-principles calculation validates the theoretical prediction of Dirac fermions above E_F, confirming BaAl₄ as a topological semimetal with Dirac points. Additionally, a VHS has been considered the key to inducing various correlated states, especially when close to the Fermi level, as shown in high-Tc superconductors and bilayer graphenes. While further studies are needed to shift the Fermi level close to VHS with several techniques, such as chemical doping and gating techniques, our observation suggests that BaAl₄ is an ideal 3D analog of graphene, similar to Na₃Bi and provides a platform to study correlated effects induced by a VHS. Moreover, in BaAl₄, while the Dirac dispersion along the out-of-plane axis (k_z) has a linearly type-I dispersion, the dispersion is quadratic along the in-plane axis (k_x/k_y) as shown in Figs. 1h, i and 2e, h. Hence these DPs can be classified as semi-Dirac points where massless and massive fermions can coexist at the same point in momentum space. Similar semi-Dirac points are theoretically predicted and/or experimentally observed in two-dimensional systems such as a silicene oxide Si₂O and black phosphorus, and could result in interesting properties including highly anisotropic transport, distinct Landau level spectrum in a magnetic field, non-Fermi liquid, and Bloch-Zener oscillations. Additionally, two-photon photoelectron spectroscopy experimental technique may enable the investigation of the detailed electronic structure above E_F, including the DP. As well as a thorough investigation and characterization, it is worth studying light-induced response by 2PPE because of the structure of DP in BaAl₄. Such massive and anisotropic DP may induce a prolonged lifetime and electron-hole pairs.
Magnetoresistance and quantum oscillations

Figure 4 presents the electrical transport properties of single-crystalline BaAl₄ samples. Extremely high mobilities approaching 200,000 cm²/Vs (see Hall analysis below) are reflective of the high quality of the samples, also indicated by very large residual resistivity ratios (RRR = ρ(300K)/ρ(2K) = 1500 in Sample A) and tiny residual resistivities (~ 90 nΩ cm). As observed in other TSMs such as WTe₂, NaBi₃, Cd₃As₂, TaAs, LaBi, and other related compounds⁴, a dramatic onset of strong MR develops at low temperatures and presents astonishingly high and unsaturated MR values attributed to the opening of an energy gap by magnetic fields. In BaAl₄, the MR approaches 2 × 10⁵% at 14 T (shown in Fig. 4a and also in Fig. S2 of supplementary materials). For Sample A with the highest quality of the samples, also indicated by very large RRR = 1500, the MR approaches 2 × 10⁵% at 14 T (shown in Fig. 4a).

As shown in Fig. 4c, the Hall resistivity ρₜₓᵧ is positive above 50 K and nearly linear with field, indicating holes as the majority carriers at high temperatures. However, ρₜₓᵧ deviates from linear at temperatures below 50 K, and even changes sign at low temperature and high field, indicating coexistence of electrons and holes. It has been proposed that the extremely large MR in several semimetals arises due to a perfect compensation between electron and hole carrier concentrations. The calculated band structure of BaAl₄ does indeed show complex coexistence of electron and hole pockets. The hole pockets (see Fig. 5a) corresponding to the Dirac point along the Γ−Z direction mostly consist of two separated hollow cylinders surrounding the Z points, while theelectron pocket is a one-piece structure centered at the Γ point shown in Fig. 5b. However, the volume surrounded by the hole and electron pockets is different. To estimate the carrier densities and mobility, a semiclassical two-band model is used to analyze the longitudinal conductivity σₓₓ(B) and Hall conductivity σᵧᵧ(B) in the magnetic fields B:

\[
\sigma_{xx}(B) = \frac{n_e q \mu_e}{1 + (\mu_e B)^2} + \frac{n_e q \mu_e}{1 + (\mu_h B)^2},
\]

\[
\sigma_{yy}(B) = \left[ \frac{n_e q \mu_e^2}{1 + (\mu_e B)^2} - \frac{n_h k_B^2}{1 + (\mu_h B)^2} \right] eB.
\]

Here nₜ (μₜ) and nₜ (μₜ) are the carrier densities (mobilities) of electrons and holes, respectively. σₓₓ(0) is the longitudinal conductivity at 0 T. The typical fitting results at several different temperatures are shown in Fig. S3a, b in the Supplementary Materials, and the fitting parameters are shown in Fig. 4d, e in the temperature range 2 K−50 K. At low temperatures, holes are the minority carriers, but their mobility is nearly one order higher than the mobility of electrons. At 2 K, μₑ approaches ~20 m²/Vs. With increasing temperature, μₑ decreases significantly and becomes comparable to μₑ. Hence, the minority hole carriers dominate the
transport in the entire temperature range because of their high mobility. This is consistent with the calculated electronic structure, where the Dirac pockets have hole characteristics.

Quantum oscillations measurements further clarify the nature of carriers in BaAl4. As shown in Fig. 4b, the measured MR of several BaAl4 crystals exhibits clear Shubnikov–de Haas oscillations. Subtracting a background MR yields an oscillatory signal composed of several components observable down to a few Teslas, as shown in Fig. 5c. The oscillation frequencies of different pockets in the calculated Fermi surface are extracted by finding the supercell k-space extremal area implemented in the SKEAF code60 and are compared to the frequencies by Fourier transform analysis of the experimental curves, correspondingly the oscillation frequencies obtained by Fourier transform of our experiment (in Fig. 5d) are assigned to different pockets of the calculated Fermi surface. Our experimental results are consistent with the calculated Fermi surface shown in Fig. 5a, b, and also most of them are close to the previous report reports47, as shown in Table IV of SM. In the high frequency region as shown in the inset of Fig. 5d, the frequency $F_1 \sim 2.5$ kT corresponds to the electron pocket shown in Fig. 5b, and the other frequency $F_2 \sim 1.6$ kT corresponds to the outer branch of the hole pocket surrounding $\Gamma$ point in Fig. 5a. A small frequency $F_0 \sim 300$ T corresponds to the inner branch of the hole pocket. In addition to the detailed angular dependence of these frequencies previously reported47, two very close oscillation frequencies $F_{a1} \sim 100$ T and $F_{a0} \sim 106$ T which are missing in previous report47, are observed. These two close frequencies give a clear beating behavior shown in Fig. 5, and correspond to the small hole pockets along $\Gamma - X$ lines. Lifshitz–Kosevich analysis of the temperature-dependent oscillation amplitude (Fig. S4 of SM) for these two frequencies $F_{a1}$ and $F_{a0}$ reveals a similar effective mass of $-0.2(1)m_e$. This small effective mass of the hole pockets is consistent with the calculated hole-like Dirac spectrum (with a mass of about $0.15m_e$ shown in Table IV of SM) and the ARPES measurement.

**DISCUSSION**

Quantum oscillations, Hall resistivity and ARPES results reveal that although the electron and hole pockets coexist in BaAl4, they harbor different densities. This implies that some other mechanism beyond the perfect compensation between electron and hole pockets should govern the extremely large MR found in BaAl4, which may be related to the Dirac spectra as discussed for other TSMs. The extremely small residual resistivity $\sim 90$ nΩ cm is quite anomalous given the low carrier density $\sim 10^{20}$ cm$^{-3}$, and is similar to the case for other topological semimetals such as WTe$_2$ ($\sim 30$ nΩ cm) and La(Bl,5b) ($\sim 0.1$ μΩ cm), suggesting a topology-driven mechanism for reduction in scattering and large MR\(^{26,51}\).

Although the Fermi surface is about 0.4 eV away from the Dirac points, the winding feature of the Wilson loop spectrum can still be stabilized by the $C_{4z}$ symmetry. Figure 5 shows the Wilson loop spectrum on a spherical surface enclosing the Dirac point $(0, 0, k_z^\pm)$ (e) and the phase $\phi_j$ of the individual loop eigenvalues ($e^{i\theta}$) as a function of the azimuthal angle $\theta$.

**Fig. 5** Fermi surface and quantum oscillation of Dirac semimetal BaAl4. a, b Calculated hole pockets (a) and electron pockets (b) in the Fermi surface for BaAl4 by density function theory with spin-orbit coupling. c The quantum oscillation in the magnetoresistance of BaAl4 single crystal at 2 K. The inset shows the FFT spectrum of the quantum oscillation. d Enlarged part of the low frequency region of the FFT spectrum of the quantum oscillation for Sample B of BaAl4 at different temperatures. The inset shows the detail of the FFT spectrum in high frequency region at 2K.

K. Wang et al. npj Quantum Materials (2021) 28
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hybridize with each other, giving rise to a stable crossing in the Wilson loop spectrum. As long as the surface states are C_{4z} symmetric, the winding feature of the Wilson loop spectrum is stable. This could, for instance affect the bulk transport properties, but requires further investigation.

Our results verify BaAl4 as a topological semimetal, as confirmed by calculations, symmetry analysis, photoemission, and transport experiments. Since a large diversity of physical phenomena appears in compounds derived from this prototype structure, one can consider the MA4 family as a playground for exploring the interaction between the non-trivial topology and symmetry-breaking or correlated phases, including superconductivity, heavy fermion and quantum critical systems, charge/spin density wave, etc. It could also be expected that some distortion/modification of the original crystal structure in the derived structures will slightly modify the topological electronic structure and induce phenomena. One interesting direction is to consider the consequences of breaking the inversion symmetry to achieve a non-centrosymmetric structure (e.g. LaPSi3 and other materials), where band splitting could be expected to achieve Weyl or multiple-fermion states. Noncollinear magnetic order (such as in EuAl6) may also induce band splitting, yielding other exotic topological states. 3D Dirac semimetals are on the verge of being topologically non-trivial. However, as long as the momentum is away from a high-symmetry point, the Dirac semimetals, when gapped, always go into a topological state, not a trivial one. One cannot gap a Dirac semimetal, infinitesimally, into a trivial state. The fact that the Dirac node cannot be immediately gapped (with small gapping terms) into a trivial state but only into a topological one brings about the second topological characterization. Finally, we note that a recent theoretical study has proven that Dirac nodes show hinge Fermi arcs as the spectroscopic signatures, similar to Weyl nodes. While it remains a challenge for future research to detect such states in the MA4 family, it offers a rich platform to investigate transport properties reflecting the hinge modes, such as nonlocal quantum oscillations and SQUIDS. Extending the symmetry analysis to the rest of the MA4 family of materials (M = Sr, Ba, Eu; A = Al, Ga, In), as well as the enormous set of derivative structures, will expose more topological materials.

METHODS

Crystal growth

Single crystals of BaAl4 were synthesized by a high-temperature self-flux method. Chunks of Ba (99.98%, Alfa Aesar) and pieces of Al (99.999% metal basis, Alfa Aesar) in the ratio of 2:98 were placed in the Canfield alumina crucible set with a decanting frit (LSP ceramics), sealed in the quartz ampule under partial Ar pressure, heated to 1150 °C, held at that temperature for 6 h, cooled down at 3 degree/h to 950 °C with subsequent decanting of the excess Al with the help of a centrifuge. The crystals tend to grow with large faceted surfaces normal to the (001) crystallographic plane. X-ray diffraction data were taken at room temperature with Cu Kα (λ = 0.15418 nm) radiation in a powder diffractometer.

Transport measurement

Electrical transport measurements up to 14 T were conducted on polished samples in a Quantum Design Physical Properties Measurement System (Dynacool) applying the conventional four-wire contact method. High field MR and dHvA oscillation were measured at the National High Magnetic Field Laboratory (NHMFL) Tallahassee DC Field Facility up to 35 T, using a one-axis rotator in a He-3 cryostat with temperature range 0.35–70 K. In all transport measurements, the electrical current flowing in the ab plane. The magnetization and dHvA oscillations were measured using a piezoresistive cantilever. The magnetic field rotated from a direction parallel to the c-axis to a direction parallel to the ab plane.

Photoemission measurement

ARPES measurements on single-crystalline samples of BaAl4 were performed at the Beamline 4.0.3 (MERLIN) of the Advanced Light Source in Berkley, California. Samples were cleaved in situ to yield clean (001) surfaces and measured at 14–20 K in ultra-high vacuum better than 3 × 10−11 Torr using photon energy of 80–120 eV with Scienta R8000 analyzer. The energy resolution was 20–30 meV and the angular resolution was better than 0.2° for all measurements. The inner potential V0 = 10.5 eV was used to calculate the momentum perpendicular to the surface.

DFT calculation

Theoretical calculations compared to ARPES were performed within generalized gradient approximation (GGA) for bulk BaAl4 as implemented in the VASP package using a relativistic version of PAW potentials. The experimental crystal data (a = b = 4.556 Å and c = 11.278 Å) were used for the bulk calculation. PAW pseudopotentials with a plane wave energy cut-off of 40 Ry were used, and Monkhorst k-mesh was chosen as 24 × 24 × 24. All calculations prepared by VASP were double checked by the QUANTUM ESPRESSO Package.

DATA AVAILABILITY

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary information.

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REFERENCES

1. Hasan, M. Z. & Kane, C. L. Colloquium: topological insulators. Rev. Mod. Phys. 82, 3045–3067 (2010).
2. Qi, X.-L. & Zhang, S.-C. Topological insulators and superconductors. Rev. Mod. Phys. 83, 1057–1110 (2011).
3. Hisamitsu, N. P., Mele, E. J. & Vishwanath, A. Weyl and Dirac semimetals in three-dimensional solids. Rev. Mod. Phys. 90, 015001 (2018).
4. Young, S. M. et al. Dirac semimetal in three dimensions. Phys. Rev. Lett. 108, 140405 (2012).
5. Wang, X., Turner, A. M., Vishwanath, A. & Savrasov, S. Y. Topological semimetal and fermi-arc surface states in the electronic structure of pyrochlore iridates. Phys. Rev. B 83, 205101 (2011).
6. Fang, C., Jiang, M. J., Dai, X. & Bernevig, B. A. Multi-Weyl topological semimetals stabilized by point group symmetry. Phys. Rev. Lett. 108, 266802 (2012).
7. Budich, T., Wu, Q., Ruegg, A., Sigrist, M. & Solovyov, A. A. Nodal-chain metals. Nature 538, 75–78 (2016).
8. Burkov, A. A., Hook, M. D. & Balents, L. Topological nodal semimetals. Phys. Rev. B 84, 235126 (2011).
9. Weng, H., Fang, C., Fang, Z. & Dai, X. Topological semimetals with triply degenerate nodal points in δ-phase tantalum nitride. Phys. Rev. B 93, 241202 (2016).
10. Zhu, Z., Winkler, G. W., Wu, Q., Li, J. & Solovyov, A. A. Triple point topological metals. Phys. Rev. X 6, 031003 (2016).
11. Lv, B. Q. et al. Observation of three-component fermions in the topological semimetal molybdenum phosphide. Nature 546, 627–631 (2017).
12. Bradley, B. et al. Beyond Dirac and Weyl fermions: unconventional quasiparticles in conventional crystals. Science 353, aaf537 (2016).
13. Lv, B. Q. et al. Experimental discovery of Weyl semimetal TaAs. Phys. Rev. X 5, 031013 (2015).
14. Xu, S.-Y. et al. Discovery of a Weyl fermion semimetal and topological fermi arcs. Science 349, 613–617 (2015).
15. Wang, Z. et al. Dirac semimetal and topological phase transitions in A3Bi (A = Na, K, Rb). Phys. Rev. B 85, 195320 (2012).
16. Wang, Z., Weng, H., Wu, Q., Dai, X. & Fang, Z. Three-dimensional Dirac semimetal and quantum transport in Cd3As2. Phys. Rev. B 88, 125427 (2013).
17. Borisenko, S. et al. Experimental realization of a three-dimensional Dirac semimetal. Phys. Rev. Lett. 113, 027603 (2014).
18. Neupane, M. et al. Observation of a three-dimensional topological Dirac semimetal phase in high-mobility Cd3As2. Nat. Commun. 5, 3786 (2014).
19. Liu, Z. K. et al. A stable three-dimensional topological Dirac semimetal Cd3As2: Nat. Mater. 13, 677–681 (2014).
20. Jeon, S. et al. Landau quantization and quasiparticle interference in the three-dimensional Dirac semimetal Cd3As2. Nat. Mater. 13, 851–856 (2014).
21. Chang, T.-R. et al. Type-II symmetry-protected topological Dirac semimetals. Phys. Rev. X 6, 011010 (2016).
22. Wu, Q., Piveteau, C., Song, Z. & Yazyev, O. V. MgTa2N3: a reference Dirac semimetal. Phys. Rev. B 98, 081115 (2018).
23. Huang, H., Jin, K.-H. & Liu, F. Alloy engineering of topological semimetal phase transition in MgTeS2–NbN2Se. Phys. Rev. Lett. 120, 136403 (2018).

24. Chen, C. et al. Ternary wurtzite CaAgBi materials: a playground for essential and accidental, type-I and type-II Dirac fermions. Phys. Rev. Mater. 1, 044201 (2017).

25. Yan, M. et al. Lorentz-violating type-II Dirac fermions in transition metal dichalcogenide PtTe2. Nat. Commun. 8, 257 (2017).

26. Zhang, T. et al. Catalogue of topological electronic materials. Nature 566, 475–479 (2018).

27. Vergniory, M. G. et al. A complete catalogue of high-quality topological materials. Nature 566, 480–485 (2019).

28. Topological material database. https://topologicalquantumchemistry.org/.

29. Wang, W. et al. Non-saturating magnetoresistance in NbSe2. Phys. Rev. B 95, 140501 (2017).

30. Ali, M. N. et al. Large, non-saturating magnetoresistance in WTe2. Phys. Rev. Lett. 114, 117201 (2015).

31. Ali, M. N. et al. Butterfly magnetoresistance, quasi-2D Dirac Fermi surface and topological phase transition in ZrSiS. Sci. Adv. 2, e1601742 (2016).

32. Shekhar, C. et al. Extremely large magnetoresistance and ultra-high mobility in the topological Weyl semimetal candidate NbP. Nat. Phys. 11, 645–649 (2015).

33. Zhang, C.-L. et al. Electron scattering in tantalum mononitride. Sci. Rep. 8, 15032 (2018).

34. Yuan, N. F. Q., Isobe, H. & Fu, L. Magic of high-order van hove singularity. Science 359, 654 (2018).

35. Luo, Y. et al. Electron-hole compensation effect between topologically trivial and accidental, type-I and type-II Dirac fermions. Nat. Mater. 14, 280–284 (2015).

36. Stewart, G. R. Heavy-fermion systems. Rev. Mod. Phys. 87, 427–520 (2015).

37. Cano, J. et al. Building blocks of topological quantum chemistry: elementary band representations. Phys. Rev. B 97, 035139 (2018).

38. Markiewicz, E. A survey of the van hove scenario for high-Tc superconductors with high van hove singularity. Adv. Mater. 26, 2984–2989 (2014).

39. Nakamura, A. et al. Characteristic fermi surfaces and charge density wave in SrAl3 and related compounds with the BaAl2-type tetragonal structure. J. Alloys Compounds 654, 290–299 (2016).

40. Nakamura, A. et al. Magnetic and Fermi surface properties of EuGa2. J. Phys. Soc. Japan 82, 104703 (2013).

41. Bradley, B. et al. Topological quantum chemistry. Nature 547, 298–305 (2017).

42. Wang, Z. The open-source code vasprun and end-user button Check Topological Mat are available online at www.cryst.ehues/cryst/checktopologicalmat. (2018).

43. Cano, J. et al. Building blocks of topological quantum chemistry: elementary band representations. Phys. Rev. B 97, 035139 (2018).

44. Nishiyama, Y. et al. Magnetic and Fermi surface properties of EuGa2. J. Phys. Soc. Japan 82, 104703 (2013).

45. Yuan, N. F. Q., Isobe, H. & Fu, L. Magic of high-order van hove singularity. Nat. Commun. 10, 5769 (2019).

46. Kim, J. et al. Observation of tunable band gap and anisotropic Dirac semimetal state in black phosphorus. Science 349, 723–726 (2015).

47. Zhong, C., Chen, Y., Xie, Y., Sun, Y.-Y. & Zhang, S. Semi-Dirac semimetal in silicene oxide. Phys. Chem. Chem. Phys. 19, 3820–3825 (2017).

48. Dietl, P., Pichon, F. & Montambiaux, G. New magnetic field dependence of Landau levels in a graphene-like structure. Phys. Rev. Lett. 100, 236405 (2008).

49. Lim, L.-K., Fuchs, J.-N. & Montambiaux, G. Bloch–zener oscillations across a merging transition of Dirac points. Phys. Rev. Lett. 108, 175303 (2012).

50. Soluyanov, A. A. et al. Type-II Weyl semimetals. Nature 527, 495–498 (2015).

51. Rourke, P. & Julian, S. Numerical extraction of de Haas–van Alphen frequencies from calculated band energies. Comput. Phys. Commun. 183, 324–332 (2012).

52. Jiang, J. et al. Signature of strong spin-orbital coupling in the large nonsaturating magnetoresistance material WTe2. Phys. Rev. Lett. 115, 166601 (2015).

53. Wieder, B. J. et al. Strong and fragile topological Dirac semimetals with higher-order fermi arcs. Nat. Commun. 11, 627 (2020).

54. Schindler, F. et al. Higher-order topology in bismuth. Nat. Phys. 14, 918–924 (2018).

55. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).

56. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558–561 (1993).

57. Kresse, G. & Furthmuller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–50 (1996).

58. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).

59. Bloch, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).

60. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).

61. Giannozzi, P. et al. Quantum espresso: a modular and open-source software project for quantum simulations of materials. J. Phys.: Condens. Matter 21, 395502 (2009).

62. Giannozzi, P. et al. Advanced capabilities for materials modelling with quantum espresso. J. Phys.: Condens. Matter 29, 465901 (2017).

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AUTHOR CONTRIBUTIONS

J.P., K.W., and A.L. initiated and directed this research project. The samples were grown and characterized by K.W. Transport measurements were carried out by K.W. with the assistance of D.E.G. R.M., J.H.M., and D.W.L. carried out ARPS measurements with the assistance of J.D., and R.M. analyzed the data. L.W. and R.M. did a portion of the calculation. Z.W. and B.A.B. did the calculation and symmetry analysis. K.W. and R.M. wrote the text, with feedback from all authors. All authors contributed to the scientific planning and discussions.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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