Roton pair density wave in a strong-coupling kagome superconductor

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The transition metal kagome lattice materials host frustrated, correlated and topological quantum states of matter1–7. Recently, a new family of vanadium-based kagome metals, AV3Sb5 (A = K, Rb or Cs), with topological band structures has been discovered10,11. These layered compounds are nonmagnetic and undergo charge density wave transitions before developing superconductivity at low temperatures11–19. Here we report the observation of unconventional superconductivity and a pair density wave (PDW) in CsV3Sb5 using scanning tunnelling microscope/spectroscopy and Josephson scanning tunnelling spectroscopy. We find that CsV3Sb5 exhibits a V-shaped pairing gap $\Delta_0 = 0.5$ meV and is a strong-coupling superconductor ($2\Delta_0/k_B T_c - 5$) that coexists with $4a_0$ unidirectional and $2a_0 \times 2a_0$ charge order. Remarkably, we discover a 3Q PDW accompanied by bidirectional $4a_0/3$ spatial modulations of the superconducting gap, coherence peak and gap depth in the tunnelling conductance. We term this novel quantum state a roton PDW associated with an underlying vortex–antivortex lattice that can account for the observed conductance modulations. Probing the electronic states in the vortex halo in an applied magnetic field, in strong field that suppresses superconductivity and in zero field above $T_c$, reveals that the PDW is a primary state responsible for an emergent pseudogap and intertwined electronic order. Our findings show striking analogies and distinctions to the phenomenology of high-$T_c$ cuprate superconductors, and provide groundwork for understanding the microscopic origin of correlated electronic states and superconductivity in vanadium-based kagome metals.
The spatially averaged $dI/dV$ spectra (Fig. 2a) show the V-shaped gap on both Cs and Sb surfaces with two gap-edge peaks at energies symmetric with respect to $E_c$. The V-shaped gap is consistent with the gap nodes seen in conductivity measurements, but the nonzero local density of states (LDOS) at zero bias, lower on the Cs than on the Sb surface (Supplementary Fig. 4), indicates additional in-gap quasiparticle states possibly due to line nodes or ungapped Fermi surface sections. From the $dI/dV$ spectra collected over nearly fifty 30 nm × 30 nm regions, we obtain the average SC gap size ($\Delta$) = 0.52 ± 0.1 meV (Supplementary Fig. 5). The temperature evolution of the $dI/dV$ spectra on the Sb surface (Fig. 2b) shows that the V-shaped gap reduces with increasing electron temperature and vanishes around ~2.3 K.

As the suppression of the LDOS near $E_c$ can arise from physics other than superconductivity, it is crucial to directly probe the superfluid for SC phase coherence. We thus construct a Josephson STM (Fig. 2c) by fabricating a SC Nb STM tip (Methods and Supplementary Fig. 6). The sharp zero-bias peak with two negative differential conductance dips is observed due to Josephson tunnelling of Cooper pairs (Fig. 2d), which provides strong evidence that the CsV$_3$Sb$_5$ surface is in the SC phase (Supplementary Fig. 7). The temperature-dependent $dI/dV$ spectra are then obtained (Fig. 2e, f). When the electron temperature increases to about 900 mK, two sets of peaks can be clearly resolved with particle-hole symmetry. The outer peaks correspond to the sum $\Delta_{tp} + \Delta_{sample}$ of the paring gaps in the tip and the sample, while the inner peaks relate to the difference $\Delta_{tp} - \Delta_{sample}$. On further increasing the temperature, the outer peaks disappear at a transition temperature of ~2.3 K, leaving the two remaining peaks from $\Delta_{tp}$. As the $T_c$ of the Nb tip is higher than 4 K (Supplementary Fig. 6), the transition indicates that superconductivity in the sample is completely suppressed at this temperature. The SC gap of the sample is in excellent agreement with the value measured by the normal W tip. We thus conclude that the observed V-shaped gap (Fig. 2a) is the SC gap that opens at $T_c$ ~ 2.3 K on the surface of the CsV$_3$Sb$_5$. The V-shaped SC gap with nonzero LDOS at $E_c$ is strongly indicative of unconventional superconductivity. Moreover, the measured gap-to--$T_c$ ratio $2\Delta/k_BT_c$ ~ 5.2 puts the unconventional superconductor in the strong-coupling regime.

**Coexisting CDWs**

We next probe the spatial distribution of the off-diagonal long-range-ordered quantum states using the high-resolution STM/STS at an electron temperature of 300 mK, well below $T_c$. As the Cs atoms are unstable on the Cs-terminated surface and strongly affect the tip states, we perform the measurements on the Sb surface directly above the V Kagome plane (Fig. 1e). The STM topography (Fig. 3a) over a large 70 nm × 70 nm area (Methods) shows periodic modulations indicating the presence of CDWs. The corresponding Fourier transform after the Lawler–Fujita drift correction reveals, in addition to the atomic Bragg peaks (Fig. 3b), the pristine Sb lattice, two sets of new peaks (Fig. 3b). One set comprises six hexagonal wavevectors at $Q_{a_0} = (3n/3, n/3)$, corresponding to a $2a_0 \times 2a_0$ superstructure on the Sb surface. The other set is at uniaxial wavevectors marked by $Q_{4a_0} = (n+1/3, n/3)$, corresponding to unidirectional $4a_0$ modulations. These robust modulations are clearly visible in the topography (Fig. 3a, inset) and suggest the coexistence of superconductivity with $2a_0$ bidirectional and $4a_0$ unidirectional positional and rotational order (that is, a smectic state in the language of liquid crystals). The $dI/dV(r, V)$ conductance map at $V = -5$ mV shows three-field distributions (Fig. 3c) and the corresponding Lawler–Fujita drift-corrected Fourier transform (Fig. 3d) reveal the outstanding $Q_{a_0} = (n+1/3, n/3)$ peaks and the quasiparticle interference (QPI) patterns. The Bogoliubov QPI patterns in the SC state are notably different, but with certain unidirectional features similar to the normal-state QPI (ref. 14). Acquiring additional $dI/dV$ maps and Fourier transforms at different bias energies and over different regions (two examples are shown in Fig. 3e, f around the SC gap energy), we find that the two sets of peaks at $Q_{a_0} = (n+1/3, n/3)$ and $Q_{4a_0} = (n+1/3, n/3)$ are nondispersive in energy (Fig. 3g, Extended Data Fig. 2 and Supplementary Fig. 8). We thus conclude that $2a_0 \times 2a_0$ and $4a_0$ unidirectional CDWs coexist with superconductivity, giving rise to the smectic superconductor.

**3Q PDW with $4a_0/3$ period**

A striking feature of the $dI/dV$ maps, absent in the topography (Fig. 3b), is the new set of prominent peaks at hexagonal wavevectors $Q_{4a_0/3} = (n/3, n/3)$ in the Fourier transform (Fig. 3d). The 3Q peaks at $Q_{4a_0/3}$ are distinct from the uniaxial $Q_{4a_0}$, despite the overlap with a higher harmonic of $Q_{4a_0}$ along the $a_0$ direction. These peaks do not exist in the $dI/dV$ maps at energies much higher than the SC gap energy (Extended Data Fig. 3). They suggest an emergent $4a_0/3$ bidirectional 3Q electronic modulation without long-range charge order. The $Q_{4a_0/3}$ peaks are nondispersive at low energies around the...
SC gap (Fig. 3g), indicating the possible formation of a primary 3Q PDW. This is in contrast to the long-range CDWs at Q_{3q2} and Q_{3q4} that induce subsidiary PDWs at the same wavevectors in the SC condensate. The d/dV(t, V) map after Fourier filtering of atomic Bragg peaks at Q_{bragg} and noise from the small-q quasiparticle scattering (Supplementary Fig. 9) reveals the spatial pattern of the PDW (Fig. 3h). A hexagonal pattern of the bidirectional PDW with period 4a_{0}/3 (Supplementary Fig. 9) is clearly observed in the background of the 4a_{0} charge stripes.

Spatial modulations of SC at the PDW wavevector

To investigate the properties of the PDW and its effects on superconductivity, we measure the d/dV(t, V) spectra along a line cut parallel to the 4a_{0} stripes indicated in the topography (Fig. 3i). This direction corresponds to the q_{x} direction in reciprocal space (Fig. 3b), and thus avoids the 4a_{0} modulations due to the unidirectional charge order. The spatial evolution of the differential conductance (Fig. 3j) displays intricate modulations in the SC gap $\Delta(t)$, the coherence peak height at the gap edge and the zero-bias conductance. To extract quantitative information, we take the second derivative of each conductance curve: $D(t, V) = -d^2I/dV^2(t, V)$. The peaks in $D(t, V)$ along the cut (Fig. 3k) determine accurately the coherence peak locations (especially at negative bias) and the SC gap $\Delta(t)$, as in a recent study of the PDW modulation of the SC coherence in underdoped cuprates. The spatial modulation of the local SC gap $\Delta(t)$ (Fig. 3l), having an amplitude of the order of 7% of the average gap, is clearly visible with underlying periodicities. Its Fourier spectrum (Fig. 3j) displays pronounced peaks at $\frac{4}{3}Q_{bragg}$ associated with the PDW, in addition to the Bragg peak at $Q_{bragg}$ and the 2a_{0} CDW peak at $\frac{4}{3}Q_{bragg}$. The modulation of the SC gap further supports the identification of the $\frac{4}{3}Q_{bragg}$ peaks in the d/dV maps (Fig. 3e, f) with the 3Q PDW coupled to the SC condensate. More data, including the SC gap maps acquired in different regions exhibiting $Q_{3q4}a_{0}/3$ peaks in the Fourier transforms, are presented in Supplementary Figs. 10 and 11.

To demonstrate the modulation of the SC coherence by the PDW, we determine from the conductance spectrum (Fig. 3j) the coherence peak height at the gap edge: $P(t) = d/dV(t, +\Delta(t))$, the zero-bias conductance $G_{0}(t) = d/dV(t, 0)$ and the gap depth $H(t) = P(t) - G_{0}(t)$. The raw data for $P(t)$, $H(t)$ and $G_{0}(t)$ (Fig. 3m) display intriguing periodic modulations along the line cut. Remarkably, the modulations of the coherence peak $P(t)$ and zero-bias conductance $G_{0}(t)$ are out of phase (Fig. 3m and Supplementary Fig. 12a), leading to in-phase modulations of the coherence peak $P(t)$ and gap depth $H(t)$. As a higher coherence peak in STS usually reflects a higher superfluid density, the correlated modulations among $P(t)$, $H(t)$ and $G_{0}(t)$ amount to a concomitant deeper SC gap and less normal fluid density, demonstrating an unprecedented electronic density wave modulation of superconductivity. After filtering out atomic Bragg oscillations and small-q noise due to quasiparticle scattering from the raw data, the spatial modulation of the coherence peak height $P(t)$ and the SC gap depth $H(t)$ exhibit remarkable beating patterns of two primary frequencies corresponding to the leading bidirectional 4a_{0}/3 PDW and a weaker 2a_{0} CDW (Fig. 3n and Supplementary Fig. 12b). These results demonstrate that the emergent PDW involves both the superfluid and the normal fluid, such that the total electron density in the ground state is only weakly perturbed at the bidirectional $Q_{3q4}a_{0}/3$. 

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**Fig. 2** | V-shaped pairing gap and the Josephson effect observed using a SC STM tip on the Cs and Sb surfaces. a. Spatially averaged d/dV spectra obtained on the Cs and Sb surfaces over a 30 nm × 30 nm region with a small defect density at 300 mK, showing a particle–hole symmetric V-shaped gap near $E_{F}$ and nonzero LDOS at zero bias ($V = -2$ mV, $I = 1$ nA, $V_{sample} = 50$ μV). b. Colour map of temperature-dependent d/dV spectra obtained on the Cs surface, showing that the V-shaped gap reduces with increasing electron temperature and vanishes around -2.3 K (dashed white line; $V = -2$ mV, $I = 1$ nA, $V_{sample} = 50$ μV). c. Schematic diagram showing the Josephson STM on the CsV3Sb5 surface using a SC (Nb) tip. The modulation of the SC gap further supports the identification of the $\frac{4}{3}Q_{bragg}$ peaks in the d/dV maps (Fig. 3e, f) with the 3Q PDW coupled to the SC condensate. More data, including the SC gap maps acquired in different regions exhibiting $Q_{3q4}a_{0}/3$ peaks in the Fourier transforms, are presented in Supplementary Figs. 10 and 11.
Fig. 3 | STM topography, dI/dV map and linecut at 300 mK revealing CDW, PDW and spatial modulations of superconductivity on Sb surfaces.

a. The large-scale STM topography of the Sb surface (a) and the magnitude of the drift-corrected, two-fold symmetrized Fourier transform (b), showing wavevectors Q_{2*2} for 2 × 2 CDW and Q_{4*4} for 4a, unidirectional charge order (V = −10 mV, I = 500 pA). The inset in a shows a zoom-in of the outlined area, exhibiting an atomically resolved STM image (V = −5 mV, I = 1 nA).

c. dI/dV (V, −5 mV) map (c) and the magnitude of the drift-corrected, two-fold symmetrized Fourier transform (d), revealing new 3Q PDW modulations at Q_{3q/2} and Q_{3q/2} spatial modulation highlighted by the pink dashed line marking Q_{3q/2}. Black dashed lines in right panel denote the every quarter q spacing.

A. Energy dependence of the Fourier linecuts along the q_{1} (top) and q_{2} (bottom) directions as a function of energy, showing non-dispersive ordering vectors at Q_{1q/2}, Q_{3q/2} and Q_{3q/2} (green curve) and Q_{3q/2} (pink curve), showing consistency with Bragg-filtered modulations of P(r) and H(r).
The observation of the PDW at \( \mathbf{Q}_{\text{pdw}} = \mathbf{Q}_{3q-4a}/3 \) in the superconductor is consistent with the existence of a shallow roton minimum at the same wavevector \( \mathbf{Q}_{\text{roton}} = \mathbf{Q}_{3q-4a}/3 \) in the dynamical density–density response function of the superfluid (Extended Data Fig. 4). The roton gap protects the superfluid from crystallization, allowing only short-ranged charge density correlations. The 3Q PDW is described by an inhomogeneous order parameter \( \Delta_{\text{pdw}}(r) = \sum_\alpha \Delta_{\alpha Q_\alpha}^s(\mathbf{Q}_\alpha^s, \mathbf{r} - \mathbf{Q}_\alpha) \), where \( \Delta_{Q_\alpha}^s(\mathbf{Q}_\alpha, \mathbf{r}) = \Delta_\alpha \cos(\mathbf{Q}_\alpha^s \cdot \mathbf{r} - \phi_\alpha) \), and \( \mathbf{Q}_\alpha = 1q, 2q, 3q \), are the momenta corresponding to \( \mathbf{Q}_{3q-4a}/3 \) in the 3Q directions and \( \phi_\alpha \) is a relative phase. Below \( T_c \), it couples to the uniform SC condensate \( \Delta_0 \). Thus, the intertwined density wave order has the character of delocalized Cooper pair excitations and localized charge excitations. To stress this distinction, we refer to this novel quantum state as a roton PDW, without implying direct observation of roton excitations, which may be visible in the conductance spectrum at higher energies through mode coupling. In this scenario, the low-energy excitations involve both gapless quasiparticles and roton PDW excitations. As a roton is a bound vortex–antivortex pair\(^{25,26}\), the roton PDW can be viewed as a commensurate hexagonal vortex–antivortex lattice (Extended Data Fig. 4) from the zeroes in the complex PDW order parameter \( \Delta_{\text{pdw}}(\mathbf{r}) \) that coexists with the uniform component of the SC order parameter \( \Delta_0 \). Such an unconventional SC state necessarily breaks the time-reversal symmetry, exhibiting spontaneous phase windings associated with \( \Delta_{\text{pdw}}(\mathbf{r}) \) and unconventional SC vortices\(^{26,27}\). The roton PDW provides a qualitative explanation for our observations. The low-energy states inside the V-shaped SC gap (Fig. 2a) are composed of both localized vortex–antivortex core states and itinerant nodal quasiparticles contributing to the observed thermal transport\(^{16}\). The spatial modulation of the coherence peak height and zero-bias conductance can be accounted for by those in the local superfluid density and the anti-correlated normal fluid density on the vortex–antivortex lattice (Extended Data Fig. 4) under weak modulations of the SC gap.

**PDW as a ‘mother state’ and emergent pseudogap**

We further investigate the nature of the PDW by applying a magnetic field along the c axis. The magnetic-field-dependent \( d/dV \) spectra on the Sb surface away from field-induced vortices show that the SC gap is gradually reduced with increasing field and vanishes at about 2 T (Supplementary Fig. 13). At 0.04 T, we observed SC vortices (Supplementary Fig. 14). Figure 4a centres on a vortex in the hexagonal vortex lattice. In the vortex halo marked in Fig. 4a, we obtain the \( d/dV(r, \mathbf{r} - 5 \text{ mV}) \) map (Fig. 4b). The Fourier transform shows that the 3Q PDW at \( \mathbf{Q}_{3q-4a}/3 \) survives in the vortex halo, with split peaks (Fig. 4c).
In contrast to the cuprates, where the $8\alpha_0$ PDW appears only in the vortex halo with suppressed but nonzero superconductivity, the $4\alpha_0/3$ PDW is strong enough to emerge both in the vortex halo and in the fully fledged superconductor in zero field. When the magnetic field is raised to 2 T, the SC gap disappears and superconductivity is suppressed at 300 mK (Supplementary Fig. 13). The $dI/dV(−5\text{ mV})$ map and the Fourier transform (Fig. 4d, e) show that, while the QPI pattern changes substantially, all of the density wave peaks remain within the $Q_{\text{pdw}}$, associated with the $4\alpha_0/3$ PDW. With superconductivity removed by the magnetic field, these coexisting density waves define a ‘zero-temperature’ pseudogap phase with a suppression of the LDOS over $±5\text{ meV}$ in the spatially averaged $dI/dV$ spectrum shown in Fig. 4h. In contrast to the $1×4$ and $2×2$ CDW peaks that exist at all energies, the nondispersive $Q_{\text{pdw}}$ peaks are visible only in the energy range of the pseudogap ($±5\text{ meV}$) and are absent at higher energies (Extended Data Fig. 3). This suggests an intriguing possibility that the observed $4\alpha_0/3$ 3Q PDW is a ‘mother state’ responsible for the pseudogap, as proposed in theories of the cuprates. A Ginzburg–Landau analysis (see Methods “Discussions of PDW as a ‘mother state’”) shows that, owing to the hexagonal symmetry, the 3Q PDW induces a secondary 3Q CDW of identical period, giving rise to an intertwined electronic order at $Q_{\text{pdw}}$ as the ‘mother state’ responsible for the pseudogap. We have identified the PDW pseudogap with the energy of the peak in the LDOS near 5 mV in the SC state at 300 mK (Methods and Extended Data Fig. 5) and acquired the pseudogap map, which indeed exhibits spatial gap modulations with Fourier peaks at the PDW vector $Q_{\text{pdw}}$.

Finally, we warmed up the sample to the normal state above $T_c$ and acquired $dI/dV$ maps (Fig. 4f) in the same range at 4.2 K. The corresponding Fourier transform (Fig. 4g) shows modified QPI patterns from the SC state at 300 mK (Fig. 3d) due to the closing of the SC gap. The PDW peaks at $Q_{\text{pdw}}$ are more diffused, but clearly present, demonstrating that the PDW and the intertwined electronic order persist to the normal state. The spatially averaged $dI/dV$ spectrum at 4.2 K (Fig. 4h) indeed exhibits a broad incoherent normal-state pseudogap correlated with the primary PDW over the energy range $±5\text{ meV}$. The comparison of the averaged $dI/dV$ spectra (Fig. 4h) obtained in different states including the SC state at 0 T, the vortex halo at 0.04 T, the ‘zero-temperature’ pseudogap state at 2 T and 300 mK, and the normal-state pseudogap phase at 4.2 K reveals a rather consistent and enlightening picture of the interplay between superconductivity, the primary PDW, the intertwined density waves and the pseudogap with striking analogy and distinction to the physics of the high-$T_c$ cuprates.

The $dI/dV$ map and Fourier transform (Fig. 4f, g) indicate that $2\alpha_0 \times 2\alpha_0$ CDW and $4\alpha_0$ unidirectional charge order persist above the SC transition. The properties of the CDWs in the normal state, discussed in more detail in the Methods together with our density functional theory (DFT) calculations (Extended Data Fig. 6 and Supplementary Figs. 15 and 16), are in good agreement with the recent STM work. The angle-dependent magnetoresistance measurements reveal a two-fold resistivity anisotropy (Extended Data Fig. 7) with a sharp onset below $50\text{ K}$, which matches well with the onset temperature $T_{\text{strip}}$ of the $4\alpha_0$ stripes detected by STM. This suggests an incipient rotational-symmetry-breaking bulk electronic state below $T_{\text{strip}}$, which can be either a quasi-three-dimensional (3D) $4\alpha_0$ stripe phase with interlayer coupling, or a different state that manifests as the $4\alpha_0$ unidirectional charge order on the Sb-terminated surface of CsV$_3$Sb$_5$.

Unconventional superconductivity can arise in model calculations from local and extended electron correlations on the kagome lattice. We stress, however, that the physics discovered here goes well beyond CsV$_3$Sb$_5$ being another candidate unconventional superconductor. It embodies a set of highly provoking quantum electronic states and excitations that show striking analogies and distinctions and may hold the common set of keys to resolve some of the outstanding issues in the cuprate high-$T_c$ superconductors, including smectic electronic liquid crystal states, the interplay among PDW, CDW and intertwined electronic order, and their impact on the pseudogap phenomenon and unconventional superconductivity. Our findings provide groundwork and insights for future studies on how the unconventional SC state, the roton PDW and the coexisting charge order originate microscopically from the correlated $Z_2$ topological kagome bands, and on the prospects of emergent topological superconductivity in AV$_3$Sb$_5$.

**Online content**

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31. Berg, E., Fradkin, E. & Kivelson, S. A. Charge-4e superconductivity from pair-density-wave order in certain high-temperature superconductors. Nat. Phys. 5, 830–833 (2009).
32. Lee, P. A. Amperean pairing and the pseudogap phase of cuprate superconductors. Phys. Rev. X 4, 031017 (2014).
33. Agterberg, D. F. et al. The physics of pair-density waves: cuprate superconductors and beyond. Annu. Rev. Condens. Matter Phys. 11, 231–270 (2020).
34. Liu, X., Chong, Y. X., Sharma, R. & Davis, J. C. S. Discovery of a Cooper-pair density wave state in a transition-metal dichalcogenide. Science 372, 1447–1452 (2021).
35. Landau, L. On the theory of superfluidity. Phys. Rev. 75, 884–885 (1949).
36. Feynman, R. P. in Progress in Low Temperature Physics Vol. 1 (ed. Gorter, C. J.) 17–53 (Elsevier, 1955).
37. Feynman, R. P. & Cohen, M. Energy spectrum of the excitations in liquid helium. Phys. Rev. 102, 1189–1204 (1956).
38. Nozières, P. Is the roton in superfluid 4He the ghost of a Bragg spot? J. Low Temp. Phys. 137, 45–67 (2004).
39. Edkins, S. D. et al. Magnetic field–induced pair density wave state in the cuprate vortex halo. Science 364, 976–980 (2019).
40. Dai, Z., Zhang, Y.-H., Senthil, T. & Lee, P. A. Pair-density waves, charge-density waves, and vortices in high-Tc cuprates. Phys. Rev. B 97, 174511 (2018).
41. Yu, S. L. & Li, J. X. Chiral superconducting phase and chiral spin-density-wave phase in a Hubbard model on the kagome lattice. Phys. Rev. B 85, 144402 (2012).
42. Kiesel, M. L., Platt, C. & Thomale, R. Unconventional Fermi surface instabilities in the kagome Hubbard model. Phys. Rev. Lett. 110, 126405 (2013).
43. Wang, W. S., Li, Z. Z., Xiang, Y. Y. & Wang, Q. H. Competing electronic orders on kagome lattices at van Hove filling. Phys. Rev. B 87, 115135 (2013).

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Single-crystal growth of CsV,Sb, sample

Single crystals of CsV,Sb, were grown from Cs liquid (purity 99.98%), V powder (purity 99.9%) and Sb shot (purity 99.999%) via a modified self-flux method. The mixture was placed in an alumina crucible and sealed in a quartz ampoule under an argon atmosphere. The mixture was heated to 1,000 °C and soaked for 24 h, and subsequently cooled at 2 °C h⁻¹. Finally, the single crystal was separated from the flux and the residual flux on the surface was carefully removed by Scotch tape. Except for the sealing and heat treatment procedures, all of the preparation procedures were carried out in an argon-filled glove box to avoid the introduction of any air and water. The obtained crystals have a typical hexagonal morphology with a size greater than 2 × 2 × 0.3 cm³ (Supplementary Fig. 1) and are stable in air.

Sample characterization

The X-ray diffraction pattern was collected using a Rigaku SmartLab SE X-ray diffractometer with Cu Ka radiation (λ = 0.15418 nm) at room temperature. Scanning electron microscopy and energy-dispersive X-ray spectroscopy were performed using a HITACHI S5000 with an energy-dispersive analysis system, Bruker XFlash 6|60. Magnetic susceptibility was determined by a SQUID magnetometer (Quantum Design MPMS XL-1). The SC transition of each sample was monitored down to 2 K under an external magnetic field of 1 Oe. Both in-plane electrical resistivity and Hall resistivity data were collected on a Quantum Design Physical Properties Measurement System.

Surface determination

The weak bonds between Cs and Sb2 layers offer a cleave plane and make it possible to have both Cs-terminated and Sb-terminated surfaces. At the interface of the two surfaces, we can clearly identify the atomic structures on both the top and bottom surfaces using high-resolution STM. We find that the lattice in the bottom layer shows a honeycomb configuration, which matches that of the Sb2 layer, while the top surface shows a hexagonal lattice with a spacing of 1 nm, which is about 3 times larger than the lattice constant of the pristine Cs surface (Extended Data Fig. 1).

STM/STS

The samples used in the experiments are cleaved at room temperature (300 K) or low temperature (78 K) and immediately transferred to an STM chamber. Experiments were performed in an ultrahigh-vacuum (1 × 10⁻¹⁰ mbar) ultralow-temperature STM system equipped with a 9-2-2 T magnetic field. The electronic temperature in the ultralow-temperature STM system is calculated by subtracting the lattice contribution to the electronic temperature. Repeating the procedure hundreds of times, the exposed Sb surface can be as large as 150 nm × 80 nm (Supplementary Fig. 15).

Drift correction and two-fold symmetrized Fourier transform

To eliminate the STS-tip drift effect from the topography and d/dV map, we apply the well-known Lawler–Fujita algorithm, after subtracting a second- or third-degree polynomial background, and obtain a set of displacement fields and drift-corrected topography. The so obtained displacement fields are then applied to the simultaneously measured d/dV maps in the same field of view as the topography. To reduce background noise, we also apply the two-fold symmetrization along the axis perpendicular to the q, direction in the Fourier transform in Figs. 3b, d and 4c, e, g.

DFT calculations

All calculations were performed within the DFT as implemented in VASP (the Vienna Ab-initio Simulation Package). The exchange–correlation functional was treated within the generalized gradient approximation as parametrized by Perdew–Burke–Ernzerhof. The cutoff energy for the plane-wave basis set is 300 eV. The zero-damping DFT-D3 van der Waals correction is employed in all of the calculations. Spin–orbit coupling is considered in the band structure calculations. k-meshes of 9 × 9 × 6 and 6 × 6 × 6 are used for calculating electronic structures of the pristine phase and 2 × 2 CDW phase, respectively. The phonon dispersions are calculated (without spin–orbit coupling) by using the phonopy code within a 3 × 3 × 2 supercell for the pristine structure and 2 × 2 × 2 supercells for 2 × 2 CDW phases.

Discussions of PDW as a ‘mother state’

The magnetic field experiments in Fig. 4 raise an intriguing question of whether the observed 4a₀/3 bidirectional PDW is a ‘mother state’ responsible for the pseudogap. The concept of a ‘mother state’ PDW was proposed in theories of the cuprates, where the 8a₀, PDW is strong enough to produce a half-period 4a₀ modulation in the vortex halo, and while fluctuating above Tc, it induces a secondary 4a₀, CDW responsible for the pseudogap behaviour. We argue that the 4a₀/3 bidirectional PDW may indeed be a ‘mother state’, but under a different incarnation. In the Ginzburg–Landau theory, in addition to coupling to a SC condensate Dc, if available, the products of a robust PDW order parameter and itself can generate an intriguing set of electronic order parameters. Among them, the induced CDWs are given by ψQ0=Q(r)=(ΔQ0(r)ΔQ0(r)+h.c.) and ψQs=Qs(r)=ΔQs(r)ΔQs(r)+ΔQs(r)ΔQs(r), in our notations defined in the main text. In the hexagonal zone, the half-period CDW ψQ0 has wavevectors 2Q0=3Q0fflag, which are not new but coincide with the existing peaks of the 2a₀ × 2a₀ CDW in the second zone. More
surprisingly, because of the hexagonal symmetry, the induced CDW $\Psi_{Q_0}$ has a wavevector $Q_0 = Q_0^\alpha - Q_0^\beta$, which is identical to one of the three PDW wavevectors $Q_0 = \pm 3a_0/2$. This remarkable result suggests that the 3Q PDW with period $4a_0/3$ induces a secondary 3Q CDW of identical period, giving rise to an intertwined electronic order at $Q_0 = 3a_0/4$ as the ‘mother state’ responsible for the pseudogap.

Spatial modulations of the PDW pseudogap

We have obtained the Fourier transforms of $d/dV(r, -5 \text{ mV})$ maps taken at different temperatures and observed that, as the temperature is reduced, the PDW peak intensity at $Q_0 = 3a_0/2$ormalized by the Bragg peak intensity at $Q_{\text{Bragg}}$ in the same direction increases substantially below the SC transition temperature $T_{\text{c}} = 2.5 \text{ K}$ following the onset of the coupling to the SC condensate. This suggests the possibility of identifying the pseudogap energy scale and detecting the pseudogap modulations in the SC state.

To this end, we first acquire a spatially averaged conductance spectrum over a region at 300 mK below $T_{\text{c}}$. The spectrum exhibits several peaks in the energy range between 1 mV and 6 mV (Extended Data Fig. 5a). These peaks are also visible in the corresponding bottom curve in Fig. 4h, which are broadened possibly owing to averaging over a much larger field of view beyond the coherence length. We find that only the peak located near 5 meV remains prominent above $T_{\text{c}}$, and exhibits periodic spatial modulations as shown in the linecut in Extended Data Fig. 5b. We thus identify the peak located near 5 meV as the PDW pseudogap peak with its energy position defining the pseudogap size ($\Delta^*$) (Extended Data Fig. 5a). Then, we acquire the pseudogap map $\Delta^*(r)$, which displays spatial modulations of the pseudogap size, having an amplitude of the order of 12% of the averaged pseudogap (Extended Data Fig. 5c). In the Fourier transform of $\Delta^*(r)$, the peaks at the PDW vector $Q_0 = 3a_0$ can be clearly observed (Extended Data Fig. 5d). This further demonstrates our observation of the $3a_0/3$ bidirectional PDW as a ‘mother state’ responsible for the pseudogap, which coexists with the SC gap below $T_{\text{c}}$ by coupling to the SC condensate and is detectable by STM.

Discussions of CDW in normal state

The $d/dV$ map and Fourier transform (Fig. 4f, g) indicate long-range $2a_0 \times 2a_0$ CDW and $4a_0$ unidirectional charge order in the normal state above the SC transition. These can be seen directly from the atomically resolved STM topography over large areas and the $d/dV$ maps measured at different bias energies with nondispersive $Q_0 = 3a_0$ and $Q_0 = 4a_0$ peaks shown in the Extended Data Fig. 6. We find that the pinning of the $4a_0$ unidirectional charge order is weak as it can be spatially manipulated by the tip-induced electric field. As the STM tip scans along one lattice direction, the positions of the stripes can be spatially shifted along the same direction. Occasionally, the distance between two neighbouring stripes changes from $4a_0$ to $2a_0$ (Supplementary Fig. 15). The properties of the $2a_0 \times 2a_0$ CDW and the $4a_0$ unidirectional charge order in the normal state are in good agreement with the recent STM work over a wide range of temperatures. Our DFT calculations find that the 3D $2 \times 2 \times 2$ CDW arises from phonon softening and electron–phonon coupling in all AV$_2$Sb$_3$ (ref. 13). The phonon spectrum showing mode softening in CsSbB$_3$ is reproduced in Supplementary Fig. 16, together with a comparison of the large-energy-scale $d/dV$ spectrum and the DFT band structure. Combining the theory and experiments, we believe the $2 \times 2$ CDW order is robust and extends from the SC ground state all the way up to $T_{\text{c}} \sim 94 \text{ K}$ (ref. 14). However, we find that the electron–phonon coupling-mediated superconductivity alone, obtained by solving the McMillan equation in the reconstructed lattice structure, cannot describe the observed strong-coupling superconductor.

The $4a_0$ unidirectional charge order also does not emerge in the electron–phonon coupling picture alone and is most likely also driven by electron correlations, given that it onsets at a substantially lower temperature (~50 K) below the $2a_0 \times 2a_0$ structural transition at $T_{\text{c}}$. While X-ray scattering experiments have observed the bulk $2 \times 2 \times 2$ CDW order, the $4a_0$ charge order has not been detected within the current resolution, leaving the issue of whether or in what form the rotation symmetry breaking $4a_0$ axial CDW exists in the bulk. As STM/STS cannot answer this question, we performed angular-dependent magnetoresistance measurements and clearly observed the twofold symmetry with the anisotropy axis along one of the lattice directions (Extended Data Fig. 7). Surprisingly, the onset of the resistivity anisotropy below ~50 K matches well with the onset temperature $T_{\text{anis}} \sim 50 \text{ K}$ of the $4a_0$ charge order detected by STM. This finding suggests an incipient rotational-symmetry-breaking bulk electronic state below $T_{\text{anis}}$, which can be either a quasi-3D form of the $4a_0$ stripes with interlayer coupling, or a different state that manifests as the $4a_0$ stripes on the 5b−terminated surface of the kagome metal CsV$_3$Sb$_5$.

Data availability

Data measured or analysed during this study are available from the corresponding author on reasonable request.

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Author contributions

H.-J.G. designed the experiments. H.-J.G., H.B., Y.X., G.Q., Z.H., Y.Y., C.S. and G.L. performed STM experiments with guidance from H.-J.G. and H.Y.Z. and H.L. prepared samples. C.Q.G. and Z.T. also participated in sample preparation. X.D., J.Y., H.Y., S.M., H.Z. and G.L. performed STM experiments with guidance from H.-J.G. and H.Y. Z.Z. and H.L. performed STM experiments with guidance from H.-J.G. and H.Y.

Competing interests

The authors declare no competing interests.

Additional information

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Extended Data Fig. 1 | Detailed STM characterization of the Sb and Cs surfaces. a, Top panel: a typical STM image showing a step edge of Cs surface. Bottom panel: line profile along the white dotted arrow in a, indicating that the height of the step edge is ~0.95 nm, which is consistent with the calculated interlayer distance (Vin = -1 V, It = 0.1 nA). b, Atomically-resolved STM image of Cs surface, showing a hexagonal lattice with a period of 1.0 nm, which is \sqrt{3} times larger than the lattice constant (a = b = 0.55 nm, see Fig. S1a). (Vin = -500 mV, It = 0.5 nA). c, Atomically-resolved STM image of Sb surface, showing a honeycomb lattice. The periodicity of the honeycomb lattice is about 0.56 nm, which agrees with the bulk lattice constant (a = b = 0.55 nm, see Fig. S1a). d, Atomically-resolved STM image of an interface between the top Cs and bottom Sb surfaces (same as in Fig. 1d). The atomic model is overlaid on the image, showing that each Cs atom sits on top of the Sb honeycomb center (Vin = -500 mV, It = 0.5 nA). e, FFT of d showing the Cs \sqrt{3} \times \sqrt{3} R30° reconstruction relative to the Sb 1 × 1 lattice. f, g Top panels: schematics showing STM manipulations to expose the bottom Sb surface. Bottom panels: STM images of Cs surface before (f) and after (g) STM manipulation, respectively, showing the freshly-obtained bottom Sb surface highlighted by the white dotted square (Vin = -500 mV, It = 0.5 nA).
Extended Data Fig. 2 | STM topography and dI/dV maps over a 40 nm × 40 nm region at 300 mK. a, Topography, dI/dV maps and the intensity of the drift-corrected Fourier transforms at the sample bias from -2 mV to 0 mV, respectively. Each map consists of 500 pixels × 500 pixels. b, Energy dependence of the Fourier line cuts along the three directions of the hexagonal zone. (V' = 5 mV, I' = 2 nA, Vmod = 0.5 mV).
Extended Data Fig. 3 | Absence of $4a_0/3$ in high energy $dI/dV$ maps at 300 mK.

a, Large-scale STM image (60 nm × 60 nm) of the Sb surface obtained at the temperature below $T_c$ (300 mK), where a unidirectional charge order is visible ($V_s = -20$ mV, $I_t = 2$ nA). b, The magnitude of drift-corrected Fourier transform of a, showing clearly the $Q_{3q-2}$ CDW and $Q_{1q-4}$ stripe CDW peaks. c, d $dI/dV$ mapping (1024 pixels × 1024 pixels) over the same region at -20 mV and the corresponding magnitude of drift-corrected Fourier transform ($V_s = -20$ mV, $I_t = 2$ nA, $V_{mod} = 0.2$ mV). d, f $dI/dV$ mapping (1024 pixels × 1024 pixels) over the same region at -30 mV and the corresponding magnitude of drift-corrected Fourier transform ($V_s = -30$ mV, $I_t = 2$ nA, $V_{mod} = 0.2$ mV).
Extended Data Fig. 4 | Schematic illustration of the roton-PDW. Top panel: the roton dispersion and roton minimum at $Q_{\text{roton}} = Q_{3\text{roton}}$ in the reciprocal lattice. Bottom panel: the 3Q roton-PDW at $Q_{\text{PDW}} = Q_{\text{roton}}$ forming a commensurate vortex-antivortex lattice (red, blue and yellow circles) that spatially modulates the tunneling conductance spectra along a line cut.
Extended Data Fig. 5 | Spatial map of pseudogap and $Q_{3q-4a/3}$ modulations. 

a, Spatially-averaged $dI/dV$ spectrum obtained below $T_c$, exhibiting several peaks in the energy range between 1 mV and 6 mV ($V_s = -10$ mV, $I_t = 1$ nA, $V_{mod} = 0.05$ mV). The PDW pseudogap peak located near 5 mV is labelled as $P$. 
b, Waterfall and color plot of a $dI/dV$ line cut, showing spatial modulations of the peak $P$ ($V_s = -3.7$ mV, $I_t = 1$ nA, $V_{mod} = 0.05$ mV). 
c, Spatial gap map of $\Delta^* (\mathbf{r})$, showing the spatial modulations of the pseudogap ($V_s = -3.7$ mV, $I_t = 1$ nA, $V_{mod} = 0.05$ mV). 
d, Fourier transform of the pseudogap map showing peaks at the PDW vectors $Q_{3q-4a/3}$ circled in magenta.
**Extended Data Fig. 6** | Charge ordered normal state in CsV₃Sb₅ above \( T_c \).

**a, b** Large-scale STM topography of Sb surface obtained at 4.2 K and the magnitude of drift-corrected Fourier transform, showing \( 2a_0 \times 2a_0 \) and \( 4a_0 \) striped CDW peaks at wave vectors \( \mathbf{Q}_{3q-2a} \) and \( \mathbf{Q}_{1q-4a} \) (\( V_s = -90 \text{ mV}, I_t = 2 \text{nA} \)).

**c, d** \( dI/dV \) mapping of **a** at 20 mV and the magnitude of drift-corrected Fourier transform, respectively (\( V_s = -90 \text{ mV}, I_t = 2 \text{nA}, V_{\text{mod}} = 0.5 \text{ mV} \)). **e**. Energy dependence of the Fourier line cuts along \( \mathbf{q}_a \) directions, showing that peaks at \( \mathbf{Q}_{3q-2a} \) and \( \mathbf{Q}_{1q-4a} \) at 4 K are non-dispersive (\( V_s = -90 \text{ mV}, I_t = 2 \text{nA}, V_{\text{mod}} = 0.5 \text{ mV} \)).
Extended Data Fig. 7 | Normal state angular-dependent magnetoresistance.

**a.** Schematic of the in-plane resistance measurement under a 5 T magnetic field by rotating the sample along c axis of the single crystal. **b.** Angular plot of the normalized anisotropic magnetoresistance \( \Delta R / R_{\text{min}} = R(\theta) - R_{\text{min}} \), showing two-fold symmetry at the temperature below \(~50\) K. \( \theta \) is defined in **a.** **c.** Temperature dependence of the angular-dependent \( \Delta R / R_{\text{min}} \) of at the angle of \( 28^\circ \), showing the onset of two-fold rotational symmetry below \( T^* \sim 50 \pm 10 \) K.