Evidence for chiral superconductivity on a silicon surface

Tin adatoms on a Si(111) substrate with a one-third monolayer coverage form a two-dimensional triangular lattice with one unpaired electron per site. These electrons order into an antiferromagnetic Mott-insulating state, but doping the Sn layer with holes creates a two-dimensional conductor that becomes superconducting at low temperatures. Although the pairing symmetry of the superconducting state is currently unknown, the combination of repulsive interactions and frustration inherent in the triangular adatom lattice opens up the possibility of a chiral order parameter. Here we study the superconducting state of Sn/Si(111) using scanning tunnelling microscopy, scanning tunnelling spectroscopy and quasiparticle interference imaging. We find evidence for a doping-dependent superconducting critical temperature with a fully gapped order parameter, the presence of time-reversal symmetry breaking and a strong enhancement in zero-bias conductance near the edges of the superconducting domains. Although each individual piece of evidence could have a more mundane interpretation, our combined results suggest the possibility that Sn/Si(111) is an unconventional chiral $d$-wave superconductor.

Superconductivity—dissipationless electrical conductivity in conjunction with perfect diamagnetism—is a profound manifestation of a macroscopic quantum phenomenon. Microscopically, supercurrents are carried by Cooper pairs whose pair wave functions become phase locked as they condense, like bosons, into a coherent macroscopic quantum state. In conventional superconductors, electron pairing is mediated by virtual phonon exchange. In this case, the relatively slow motion of ions provides a time-retarded effective attractive interaction that allows the electrons to overcome their mutual repulsion resulting in Cooper pairs with $s$-wave symmetry, where the composite spin and orbital angular momenta of the electrons are zero. Higher-angular-momentum states are typically driven by repulsive interactions, similar to cuprate superconductors with a high critical temperature ($T_c$). Here electron repulsion is minimized by imposing a nodal structure with a corresponding sign change in the superconducting wave function. More recent emphasis on topological
materials systems has raised expectations for the discovery of novel multicomponent order parameters that are topologically distinct from those of ordinary Cooper-pair condensates\textsuperscript{14–16}. Besides the microscopic nature of pairing interactions, the physics of these systems is dictated by broken symmetries such as crystal, spin rotation and time-reversal symmetries, although the experimental validation of intrinsically topological order parameters remains scant.

Superconductivity has recently been discovered in a system comprising one-third monolayer of Sn deposited on degenerately doped p-type Si(111) substrates\textsuperscript{16}. Its pairing symmetry, however, remains undetermined. This system is of particular interest because the undoped Sn monolayer is an antiferromagnetic single-band Mott insulator\textsuperscript{17–19} that becomes superconducting on hole doping, drawing interesting comparisons with high-$T_c$ cuprates\textsuperscript{3,20} with $d$-wave order parameters. The Sn layer, however, has triangular-lattice symmetry imposed by the Si(111) substrate. This geometry naturally allows for the existence of a chiral order parameter with topological edge states\textsuperscript{21–23}, if repulsive interactions dominate the pairing. The appearance of such an exotic order parameter is expected to furthermore depend on the electron correlation strength, shape of the Fermi surface and doping level\textsuperscript{22–24}. In particular, recent renormalization group calculations for the Sn/Si(111) system indicated a competition between chiral $d$- and $f$-wave instabilities and triplet $p$-wave instabilities, depending on the doping level and value of the nearest-neighbour Hubbard repulsion\textsuperscript{32}. At the same time, electron–phonon interactions, particularly to interfacial Si modes\textsuperscript{33}, could drive a conventional $s$-wave pairing\textsuperscript{34}.

Here we study the superconducting state of the Sn/Si(111) interface using scanning tunnelling microscopy (STM), scanning tunnelling spectroscopy (STS) and quasiparticle interference (QPI) imaging. Our observations reveal a strong doping dependence of a superconducting $T_c$, a fully gapped order parameter, the presence of time-reversal symmetry breaking and a strong enhancement in zero-bias conductance near the edges of the superconducting domains. Although each of these observations may have a mundane explanation, we discuss why we believe that a chiral $d$-wave scenario offers the most consistent interpretation of the measurements and theoretical modelling. Final confirmation, however, awaits experimental validation concerning the topological nature of the edge-state conductance.

At one-third monolayer coverage, the Sn adatoms form a ($\sqrt{3} \times \sqrt{3}$) superlattice on the Si(111) surface with one half-filled dangling-bond orbital per site and a Sn–Sn distance of 6.65 Å (Fig. 1a). All the other chemical bonds in the system are passivated. The non-interacting dangling-bond surface state has a bandwidth $W = 0.50$ eV (Fig. 1b), which is comparable to the onsite Hubbard interaction $U = 0.66$ eV of the dangling-bond orbitals\textsuperscript{16}. As such, the system is a Mott insulator with an upper Hubbard band (UHB) and lower Hubbard band (LHB) straddling the Fermi level (Fig. 1c).

Figure 1d shows an STM image of the triangular Sn adatom lattice. The Sn atoms are clearly resolved and well ordered. The dark point defects correspond to substitutional Si adatoms (most prevalent) and Sn adatom vacancies. Holes are introduced via modulation doping, using boron-doped Si substrates with different doping levels\textsuperscript{22–24} (Supplementary Note 1 and Supplementary Fig. 1) provide a discussion on dopant segregation). The hole concentration in the dangling-bond surface state is estimated from the spectral weight transfer in the tunnelling spectra, associated with the introduction of holes and formation of a quasiparticle peak in the Mott gap (Fig. 1b and Extended Data Fig. 1)\textsuperscript{25}.

Figure 1e shows the normalized $dV/dI$ tunnelling spectra for excess hole concentrations of $p = 0.06$, 0.08 and 0.10, recorded at $T = 0.5$ K (the data for $p = 0.10$ are reported elsewhere\textsuperscript{25}). These spectra are representative of the superconducting density of states (DOS). Here we divided the raw tunnelling spectra by the normal-state $dV/dI$ spectrum obtained in a perpendicular 15 T magnetic field. This field is large enough to completely suppress the superconductivity for the $p = 0.08$ and 0.10 samples, which have upper critical field values of $H_{c2}(0.5 \text{ K})$ of 3 T (ref. 14) and 13 T, respectively (Extended Data Fig. 2). This procedure is a bit problematic for the $p = 0.06$ sample, where the upper critical field exceeds the magnetic-field capability of our instrument (15 T).

The Sn adatom lattice (Fig. 1a) is highly ordered, whereas the boron dopants are located in the silicon bulk. The superconducting DOS is, therefore, spatially uniform away from the localized point defects and edges of the ($\sqrt{3} \times \sqrt{3}$) domains. Figure 1f shows a series of spectra recorded at $T = 0.5$ K along the line segment shown in Fig. 1d. This level of homogeneity distinguishes Sn in the Si(111) system from, for example, complex oxides, which exhibit considerable electronic inhomogeneity, often in conjunction with various competing orders\textsuperscript{14,25}.

The normalized $dV/dI$ spectra of the $p = 0.08$ sample are plotted as a function of temperature (Fig. 1g). The gap feature persists up to about 8 K. Detailed Dynes fits\textsuperscript{26} of the spectra assuming $s$ and $d_{x^2−y^2}$ order parameter symmetries, as well as zero-bias conductance measurements as a function of temperature, consistently produce $T_c$ of about 7.6 ± 0.2 K with some evidence of superconducting fluctuations above $T_c$ (ref. 16, Extended Data Fig. 3 and Fig. 2a). A similar procedure for the $p = 0.10$ sample produces $T_c = 4.7 ± 0.3$ K (ref. 16), whereas $T_c$ of the $p = 0.06$ sample was difficult to ascertain because the spectra cannot be properly normalized ($H_{c2}(0.5 \text{ K}) = 15$ T). We conservatively estimate its $T_c$ to be around 9 K (Extended Data Fig. 2).

Fitting the $p = 0.08$ $dV/dI$ spectra with an $s$-wave gap produces a reasonable fit but with notable discrepancies near zero bias. Turning to potential chiral order parameters, we find that a chiral $d$-wave fit also agrees well with the data and even improves the fit at lower energies. A chiral $p$-wave gap clearly fails to describe the spectra, particularly at low energy (Fig. 2a). This failure occurs because any $p$-wave gap function must vanish at the $M$ point by symmetry. This point corresponds to the Van Hove singularity and lies close to the Fermi surface\textsuperscript{16,19}.

Therefore, it affects the gap substantially, producing pronounced shoulders in the DOS that are not experimentally observed. Other parameter symmetries such as extended chiral $p$-wave and nematic $d$-wave symmetries (that is, $d_{x^2−y^2}$ and $d_n$) do not fit the spectra either (Supplementary Note 2 and Supplementary Fig. 2) (a multigap order parameter can also be ruled out since this is a single-band system). Only $s$-wave and chiral $d$-wave symmetries produce good results, and it is not possible to conclusively discriminate between the two based on fitting alone.

Important details about the Fermi surface and order parameter symmetry can be obtained from spectroscopic STM imaging\textsuperscript{22}. Here one acquires a spatial map of the differential tunnelling conductance $g(r, V) = dI/dV(r, V)/dV$. Such $dI/dV$ maps typically reveal the presence of electronic standing waves as quasiparticles are elastically scattered by defects on the surface. The power spectrum of the differential conductance map—the QPI spectrum—then identifies the dominant scattering processes contributing to the standing-wave pattern. In itinerant systems, these typically correspond to scattering wavevectors connecting different $k$ points on constant-energy contours (corresponding to imaging bias) $q = 2k \pm G$, where $G$ is a reciprocal lattice vector of the ($\sqrt{3} \times \sqrt{3}$) adatom lattice.

Figure 2b,c shows the $T = 0.5$ K QPI spectra taken at ±5 meV bias ($p = 0.08$). Both spectra reveal the warped hexagonal Fermi contour of the normal state ($G = 0$), highlighted in magenta, along with several scattering replicas ($G \neq 0$), as indicated by the light-blue dumbbell-shaped contours\textsuperscript{22}. These spectra agree very well with previous calculations for the spectra in the normal state, and are fully consistent with the band structure for the Sn surface state\textsuperscript{22} (the presence of the quasiparticle band and its dispersion is inconsistent with an interpretation in terms of impurity band physics; Supplementary Note 3 and Supplementary Fig. 3). Real-space differential conductance maps at zero bias (Fig. 2d), that is, deep inside the superconducting gap, reveal the existence of very strong star-like scattering features centred at the various surface defects. The corresponding Fourier map (Fig. 2e) now reveals the presence of a flower-like feature centred at...
Our simulations reveal that the flower-like features only appear when time-reversal symmetry is broken. Such would be the case for non-magnetic scattering in a chiral superconductor, as simulated above, but it could also be due to magnetic scattering in an s-wave superconductor (Extended Data Fig. 5). In particular, the star-like scattering features in the real-space QPI maps are very similar to those observed for magnetic point scatterers in s-wave systems, and have been attributed to a focusing effect of magnetic bound states or Yu–Shiba–Rusinov (YSR) states due to Fermi surface anisotropy. To discriminate between the s-wave and d-wave scenarios, it is essential to establish the nature of defects on the surface.

The most prevalent scattering defect on the surface is the substitutional Si adatom (replacing a Sn adatom). It shows up as a dark void in filled-state STM images and as a depressed adatom in the empty-state images (Extended Data Fig. 6). This observation indicates that the sp-like dangling-bond orbital of the Si atom is empty; also, because the adatom forms three covalent backbonds with the Si substrate, the Si adatom is expected to be non-magnetic. This is confirmed via first-principles density functional theory (DFT) total-energy calculations (which show that Si adatoms are placed 0.6 Å below the Sn adatoms) and by STM image simulations (Methods and Extended Data Fig. 6). In addition, spin-polarized DFT calculations (Methods) confirm the non-magnetic nature of this defect.

It is not possible to ascertain the nature of all the native defects on the surface (Extended Data Fig. 7a) and thus rule out any magnetic scattering contribution to the QPI pattern. We, therefore, created a new type of defect by depositing a tiny excess amount of (non-magnetic) Sn atoms at 120 K. STM images indicate that additional Sn adatoms are located at three-fold symmetric interstitial adatom sites, surrounded by three Sn adatoms of the two-dimensional host lattice (Extended Data Fig. 6). The excess Sn atoms easily move under the STM tip at tunneling biases in excess of ±0.8 V, indicating that they are weakly bound to the surface.

To elucidate the origin of flower-like features, we first simulated the QPI patterns for the s-wave and chiral d-wave order parameters using the T-matrix formalism and assuming non-magnetic scattering (Methods). Figure 3 shows the experimental QPI spectra of the p = 0.10 sample, along with the simulated spectra for the $d_{x^2−y^2}$ and $s$-wave state. The experimental pattern (Fig. 3b) is well reproduced in the simulations (Fig. 3c) (the theoretical features exhibit much more curvature because the calculations are based on non-interacting band dispersion, whereas experimental band dispersion has correlation-driven band renormalizations). Importantly, the flower is absent for the $s$-wave (both isotropic and anisotropic) pairing channel (Fig. 3d).

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Figure 2 | Low-temperature differential conductance and QPI spectra of the $(\sqrt{3} \times \sqrt{3})$ Sn surface ($p = 0.08$) on Si(111). a, Best fits of the low-energy normalized $dV/dI$ spectra at $T = 0.5$ K for different pairing symmetries. The inset shows a zoomed-in view of the zero-bias region. b–e, QPI images acquired at $V = -5$ mV (b) and $V = +5$ mV (c) beyond the superconducting gap. d, Real-space conductance map (r. c.), obtained at zero bias. The bright six-leaf features are scattering features from surface defects. e, Corresponding QPI spectrum (r. q.) obtained from the conductance map in d via Fourier transformation. The six dark-blue crosses in b, c and e indicate the Bragg peaks, whereas the coloured contours highlight the characteristic features in each QPI image.

Figure 4a plots the STS spectra across a substitutional Si defect, which reveals the existence of two in-gap states ($p = 0.08$). These states appear in pairs located symmetrically about the Fermi level reminiscent of YSR bound states, although the substitutional defect is non-magnetic. All the defects on the surface we have checked produce these YSR-like in-gap states at different energies, including the native vacancy defects, interstitial Si, excess Sn adatoms and various other defects (Extended Data Fig. 7). This is to be expected in a chiral $d$-wave scenario because both potential and magnetic defects are pair breaking $^{33,34}$. In the $s$-wave scenario, on the other hand, one would have to assume that all these defects are magnetic $^{35}$, which seems unlikely (Extended Data Fig. 5). Interestingly, the non-magnetic interstitial Sn adatoms produce the strongest star-like scattering features in real-space QPI maps and the most intense flower-like features in the corresponding power spectrum (Extended Data Fig. 7e–g). These enhanced scattering features near the excess Sn adatoms suggest that the $s$-wave scenario can be dismissed because time-reversal symmetry should not be broken in such a case. Alternatively, one might suggest that non-magnetic impurities are present in a magnetically ordered background, where they behave as magnetic impurities. Such a scenario, however, would require coexisting magnetism and superconductivity and point towards an unconventional order parameter (Supplementary Note 4).

Theory predicts $^{33,34}$ that the bound states of strong scatterers will be located deeper inside the gap compared with those of weaker scatterers. Indeed, we find that the substitutional Si defects produce in-gap states at $\pm 0.6$ meV, whereas interstitial Sn atoms produce states at $\pm 0.2$ meV. Note that the existence of gap states alone for each and every scattering defect is an indication of unconventional (that is, non-$s$-wave) superconductivity.

Our experimental measurements thus far point to a chiral $d$-wave superconducting state. To demonstrate that this pairing symmetry is consistent with the known electronic structure, we performed quantum Monte Carlo dynamical cluster approximation (DCA) method $^{36,37}$ calculations for the leading pairing instability of the $(\sqrt{3} \times \sqrt{3})$-Sn system. Here we consider a $3 \times 3$ triangular-lattice single-band Hubbard cluster embedded in a dynamical mean field and adopt parameters previously used to describe doped $^{33}$ and undoped $^{34} (\sqrt{3} \times \sqrt{3})$ Sn (Methods). Since our calculations are limited by the fermion sign problem, we focused on doping levels of $p = 0.05, 0.10$ and $0.15$, where we are able to access temperatures as low as $T = 6.59$ meV ($\beta T = 8$). For these parameters, the dominant superconducting instability indeed corresponds to degenerate $d_{x^2-y^2}$ and $d_{xy}$ order parameters at all the doping levels (Extended Data Fig. 8). These results are consistent not only with our observations but also several prior studies for the triangular-lattice Hubbard $^{35,36}$ and
ZBC) as a function of distance from the domain boundary. Each line is obtained from a conductance map (\( V = 0 \) mV), recorded at the indicated temperature. The first six curves are fitted with an exponential decay. 

The spectra near the defect site exhibit two gap states at \( E_ \text{s} \). Spectrum recorded right on top of the defect is indicated by a triangle. The topographic image (Fig. 4b) shows a topographic map near a domain wall (vertical dashed line) between the superconducting \( \sqrt{3} \times \sqrt{3} \) \( \text{Sn} \) surface and the domain on the far-left side of the image (bright strip). 

Figure 4c-d shows the registry-aligned real-space conductance maps in the \((\sqrt{3} \times \sqrt{3})\) -wave pairing state, the details somewhat differ from theory. The simulated DOS of a chiral \( d \) superconductor, approaching the open edge of a cylinder (Methods). As in Fig. 4h, a spectrum from the centre of the cylinder is subtracted to highlight the contribution from the edge state to the total DOS inside the superconducting gap. The spectra in Figs. 4b-4j are vertically shifted for clarity.

Our experimental and theoretical results are far more consistent with chiral \( d \)-wave pairing. Such a pairing state should be characterized by a topological invariant \( \nu \), given by Chern number of 2 (Methods). As in Fig. 4h, a spectrum from the centre of the cylinder is subtracted to highlight the contribution from the edge state to the total DOS inside the superconducting gap. The spectra in Figs. 4b-4j are vertically shifted for clarity.

From the conductance map, we averaged the zero-bias conductance along the vertical direction and plotted it as a function of distance towards the interior (Fig. 4f). The data in the superconducting state are reasonably well described by an exponential decay (Fig. 4f, solid black lines), and we estimate that the decay length grows from \( \approx 3.8 \) nm at \( T = 0.5 \) K to \( \approx 12.8 \) nm at 6.0 K.

The increased zero-bias conductance can also be seen in the individual \( dI/dV \) spectra (Fig. 4h) taken along the line approaching the domain boundary. To highlight the DOS contribution emanating from the edge, we subtracted a \( dI/dV \) spectrum taken from deep in the bulk from the spectra in Fig. 4h (Fig. 4i). The data show that the superconducting coherence peaks shift to lower energies when the edge is approached, as indicated by the formation of the peak–dip structures at about \( \pm 2.2 \) mV in the subtracted spectra. At the same time, the spectral weight in the superconducting gap increases almost uniformly as a function of energy. This behaviour is consistent with an overlapping DOS from a linearly dispersing edge mode. To confirm this, we computed the chiral edge modes from a simple chiral \( d \)-wave mean-field model defined on a cylinder with open-boundary conditions (Methods and Extended Data Fig. 9). The simulated subtracted data, analogous to the data in Fig. 4i, are shown in Fig. 4j where they qualitatively reproduce the experimental data. We note, however, that our non-interacting model has some additional substructure in the DOS for the edge state, which arises from the spatial structure of the edge-state wave function. Although we also observe the substructure in the experimental spectra, the details somewhat differ from theory.

We expect that a detailed analysis of these features will require the inclusion of interactions in our edge-state model, which we leave for
future work. Although the enhanced zero-bias edge conductance is consistent with the presence of an edge mode, it is difficult to disentangle possible contributions from traditional coherence length effects (or inverse proximity effects\(^4\)). Also, the evidence does not imply that the edge-state conductance is topological in nature, which will be hopefully elucidated in future studies. Nevertheless, our combined results suggest the possibility that the hole-doped Sn/Si(111) Mott insulator system is an unconventional chiral d-wave superconductor.

The Sn/Si(111) system may not be unique. Many semiconductor surfaces and interfaces can be viewed as two-dimensional dangling-bond lattices or narrow-band systems that are inherently unstable towards structural distortion and electronic rearrangement\(^4\). The modulation doping approach employed in this study can probably unveil novel competing orders and/or topological phases on easily accessible semiconductor templates.

**Online content**

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at [https://doi.org/10.1038/s41567-022-01889-1](https://doi.org/10.1038/s41567-022-01889-1).

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Methods
Sample preparation
The hole-doped ($\sqrt{3} \times \sqrt{3}$)-Sn structure was grown on three heavily boron-doped p-type silicon substrates with nominal room-temperature resistivities of 0.002, 0.005 and 0.008 Ω cm. They correspond to surface hole-doping concentrations of 10%, 8% and 6%, respectively, due to differences in the amount of charge transfer from the bulk to the surface\(^7\). These substrates were annealed to 1,200 °C in an ultrahigh vacuum to prepare atomically clean Si surfaces. Sn atoms were deposited onto the clean surface from a thermal diffusion cell and the substrate temperature was maintained at around 600 °C. This procedure resulted in the formation of coexisting ($\sqrt{3} \times \sqrt{3}$)-Sn and (2$\sqrt{3}$ × 2$\sqrt{3}$)-Sn domains. The maximum size (without an internal domain boundary) of the ($\sqrt{3} \times \sqrt{3}$)-Sn superconducting domains on each substrate exceeded 200 × 200 nm\(^2\). A small amount of additional Sn atoms are deposited onto the surface when the sample is at 120 K, followed by a fast transfer to the STM measurement stage at a lower temperature. Additional details can be found elsewhere\(\textsuperscript{10}\).

STM/STS measurements
The STM data were acquired using a cryogenic STM (Unisoku) that can cool the sample and tip to 400 mK in the presence of a perpendicular magnetic field of up to 15 T. Differential conductance spectra $dI/dV$ or their spatial maps $g(r, V)$ were acquired using lock-in detection with a typical modulation voltage of $V_{mod} = 0.14$ mV and a typical modulation frequency of 673 Hz. A typical $g(r, V)$ map consists of 272 × 272 pixels measured over a 56 × 56 nm\(^2\) surface area. The QPI images are then produced by calculating the power spectral density of the Fourier transforms of the real-space conductance map $g(r, V)$.

STS fits
We fit the normalized $dI/dV$ spectra (Fig. 2a) with DOS $N_s(\omega)/N_0(\omega)$, where $N_s(\omega) = \text{Im} \text{Im}_0(\omega)$ denotes the DOS in the superconducting (normal) state. Here

\[
\hat{\mathcal{G}}(\mathbf{k}, \omega) = \frac{(\omega + i\Gamma) + c(\mathbf{k})f_\tau + (\Delta(\mathbf{k}) + i\Delta(\mathbf{k}))}{(\omega + i\Gamma)^2 - (\mathbf{c}(\mathbf{k}))^2 - (\Delta(\mathbf{k}))^2}
\]

(1)

is the non-interacting Green’s function in Nambu space, $f_\tau$ are Pauli matrices, $c(\mathbf{k})$ is the bare-band dispersion and $\Delta(\mathbf{k})$ parameterizes the superconducting gap function in Nambu space $\Delta(\mathbf{k}) = [c_{\uparrow}^\dagger, c_{\downarrow}^\dagger]$. Note that for the chiral $p$-wave case, the vector direction $\mathbf{d} = \hat{z}$.

To model the Sn surface state, we adopted the tight-binding model derived from another work\(\textsuperscript{11}\), which is derived from ab initio electronic structure calculations. The band dispersion is

\[
e(\mathbf{k}) = -2t_1 \cos (k_x a) + 2 \cos (\frac{\sqrt{3}}{2} k_y a) \cos (\frac{1}{2} k_x a) - 2t_1 \cos (\frac{\sqrt{3}}{2} k_y a) + 2 \cos (\frac{\sqrt{3}}{2} k_x a) \cos (\frac{1}{2} k_y a) - 2t_1 \cos (2k_x a) + 2 \cos (k_x a) \cos (\frac{\sqrt{3}}{2} k_y a) - 4t_2 \cos (\frac{\sqrt{3}}{2} k_y a) + \cos (\frac{\sqrt{3}}{2} k_x a) + \cos (\frac{\sqrt{3}}{2} k_y a) - 2t_1 \cos (2\sqrt{3}k_x a) + 2 \cos (3k_x a) \cos (\sqrt{3}k_y a) - \mu
\]

(2)

where $t_1 = 52.7$ meV, $t_2 = 0.3881t_1$, $t_3 = 0.1444t_1$, $t_4 = -0.0228t_1$, $t_5 = -0.0318t_1$ and $\mu = -0.017$. Note that we adjusted the chemical potential to put the Van Hove singularity of -7.1 meV below $E_F$ (ref. \textsuperscript{14}).

To model the normal state, we set $\Delta(\mathbf{k}) = 0$. To model an $s$-wave superconductor, we set $\Delta(\mathbf{k}) = \Delta_0 r_1$. To model the chiral $p$- and $d$-wave cases, we set $\Delta(\mathbf{k}) = \frac{\Delta_0}{2} (t_1 + it_2) + \frac{\Delta_0}{2} (t_1 - it_2)$, where $\Delta_0 = 2\Delta_0 \left[ \beta_0(\mathbf{k}) + \beta_0^*(\mathbf{k}) \right]$ (ref. \textsuperscript{42}),

\[
\beta_0(\mathbf{k}) = \sqrt{3} \sin \left( \frac{\sqrt{3} t_0 a}{2} \right) \cos \left( \frac{k_x a}{2} \right)
\]

and $\beta_0^*(\mathbf{k}) = \sin (k_x a) + \cos \left( \frac{\sqrt{3} t_0 a}{2} \right) \sin \left( \frac{k_x a}{2} \right)$

for chiral $p$-wave pairing, and

\[
\beta_0(\mathbf{k}) = (k_x + \Delta_0 r_1)
\]

and $\beta_0^*(\mathbf{k}) = \sqrt{3} \sin \left( \frac{\sqrt{3} t_0 a}{2} \right) \sin \left( \frac{k_x a}{2} \right)$

for chiral $d$-wave pairing. We have also fit the spectra with nematic $d$-wave order parameters (Supplementary Note 2) and found that they are unable to reproduce the experimental spectra.

We then fit the theoretical DOS to the STS data treating $\Delta_0$ and $\Gamma$ as fitting parameters. The best fits (Fig. 2a) are obtained with $(\Delta_0, \Gamma) = (1.88, 0.290), (0.76, 0.081)$ and $(0.54, 0.170)$ for the $s$-, chiral $p$- and chiral $d$-wave cases, respectively, in units of millielectronvolts.

QPI calculations
The QPI spectra are calculated using the Born approximation to the $T$-matrix formalism, with a single point-like potential located at the origin. The Fourier transform of the modulation in the electron density is given by

\[
\delta n(\mathbf{q}, \omega) = \frac{1}{N} \sum_{\mathbf{k}} \text{Tr} \left[ \frac{1}{2\pi} \text{Im} \left[ (t_0 + t_3) \hat{\mathcal{G}}(\mathbf{k}, \omega) \hat{\mathcal{V}}(\mathbf{k}, \mathbf{q}, \omega) \right] \right]
\]

(3)

where $\hat{\mathcal{G}}(\mathbf{k}, \omega)$ is the Green’s function given by equation (1); $\hat{\mathcal{V}}$ is the impurity potential; and $c(\mathbf{k})$ and $\Delta(\mathbf{k})$ are the bare-band dispersion and superconducting order parameter, respectively. We considered both magnetic ($\hat{\mathcal{V}} = V_{ext}$) and non-magnetic ($\hat{\mathcal{V}} = V_{ext}$) scatterers, whose strengths are parameterized by $V_{ext}$. For the superconducting gap, we considered many different pairing symmetries, as parameterized above (Extended Data Fig. 5).

DFT calculations
Plane-wave DFT calculations were implemented using the QUANTUM ESPRESSO open-source computer code\(\textsuperscript{47}\). We have used the Perdew–Burke–Ernzerhof exchange–correlation functional\(\textsuperscript{48}\) and the ultrasoft pseudopotentials provided by the code\(\textsuperscript{49}\). The energy cutoff for the plane waves is 40 Ry. Although DFT cannot capture the Mott state of the ($\sqrt{3} \times \sqrt{3}$)-Sn system, it accurately captures the ground-state structure\(\textsuperscript{47}\). We employed a ($9 \times 9$) supercell with 6 Si layers and 27 Sn adatoms in $T_1$ positions. In total, there are 594 atoms in the unit cell. To simulate the substitutional Sn defect, we replaced one of the 27 Sn adatoms with a Si atom. Based on the experimental results, the interstitial Sn adatom is placed at the centre of an equilateral triangle formed by three adjacent Sn atoms of the original ($\sqrt{3} \times \sqrt{3}$)-Sn surface. Hence, the total number of Sn atoms is 28 (Extended Data Fig. 6). The bottom two Si layers and H layer are fixed in these simulations. The ($9 \times 9$) first Brillouin zone was sampled with a $2 \times 2$ Monkhorst–Pack grid\(\textsuperscript{50}\) and the geometry is relaxed until the forces are lower than 0.001 Ry Bohr\(^{-1}\). In the total-energy minimized geometry, the Sn atoms forming the triangle are located -0.2 Å above the atoms of the ($\sqrt{3} \times \sqrt{3}$)-Sn layer. The additional Sn adatom at the centre of the triangle is located -0.11 Å above the ($\sqrt{3} \times \sqrt{3}$)-Sn layer, that is, -0.09 Å below its nearest neighbours.

STM image simulations
The simulated STM images for both defect structures were calculated using the Keldysh–Green function formalism\(\textsuperscript{51}\) together with the FIREBALL local-orbital DFT Hamiltonian\(\textsuperscript{43}\). This procedure has
been successfully used in many works before\textsuperscript{35}. In our simulations, a standard W tip is placed at a distance of 5 Å above the surface, and images were generated for tunnelling parameters close to the experimental conditions. In Extended Data Fig. 6, we show the experimental and simulated images side by side, showing excellent agreement for the chosen tunnelling parameters. The STM images can be correlated to the different atomic heights and the projected DOS on different atoms. The projected DOS on the interstitial Sn adatom, calculated with the local-orbital DFT code, is shown in Extended Data Fig. 6.

### Code availability

The DCA++ code used for this project is available via GitHub at https://github.com/CompFUSE/DCA. The QUANTUM ESPRESSO code can be obtained from https://www.quantum-espresso.org/. The FIREBALL code is available via GitHub at https://github.com/fireball-QMD. Codes for performing the QPI and edge-state calculations are available via Zenodo at https://doi.org/10.5281/zenodo.7249821.

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Author contributions
F.M. and X.W. contributed equally to this work. F.M., X.W., C.C. and K.D.W. prepared the samples and performed the STM experiments. P.M. and T.A.M. performed the DCA calculations. J.S. and J.W.F.V. performed the edge-state calculations. C.G. and J.O. performed the DFT calculations and STM image simulations. S.J. performed the QPI calculations. S.J. and H.H.W. conceived and supervised the project and wrote the manuscript with input from all the authors.

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The authors declare no competing interests.

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Extended Data Fig. 1 | Spectral features of the ($\sqrt{3} \times \sqrt{3}$)-Sn surface grown on two different Si wafers and estimates of the hole concentration. a $dI/dV$ spectrum of the $p = 0.08$ surface at 0.5 K, featuring the lower Hubbard band (LHB), quasi-particle peak (QPP), and upper Hubbard band (UHB). b $dI/d(V/I)$ spectrum obtained from the spectrum in panel a, fitted with six Gaussian peaks. From the fitting, we find that the area under the QPP represents 16.1% of the total spectrum, excluding the peak on the far left which represents the contribution of the silicon valance band. This area fraction converts to a hole doping level of 8.05%, i.e., $p = 0.08$; See Ref. 18 for more details. c $dI/d(V/I)$ spectrum of the ($\sqrt{3} \times \sqrt{3}$)-Sn surface (0.5 K), subject to the same fitting analysis as in b. The area fraction of the QPP is 12.1%, which corresponds to hole doping level of 6.05% ($p = 0.06$). Gaussians are used only for the purpose of spectral area determination.
Extended Data Fig. 2 | Tunneling spectroscopy of the superconducting state. 

**a** STM image ($V_s = -2$ V, $I_t = 0.01$ nA) of the $p = 0.08$ surface with neighboring (competing) $\sqrt{3} \times \sqrt{3}$-Sn and $(2\sqrt{3} \times 2\sqrt{3})$-Sn domains. The former is superconducting while the latter is semiconducting. 

**b** STM tunneling spectra of the superconducting phase for $p = 0.08$. 

**c** Temperature dependent $dI/dV$ spectra measured in zero B-field. 

**d** Zero bias conductance (ZBC) extracted from panel b. The ZBC increases with the B-field and saturates at ~13 T. 

**e** ZBC extracted from normalized $dI/dV$ (most of the data are shown in Fig. 1e). The ZBC increases with temperature and saturates around 7.8 K. The normal state spectra in b and c exhibit minor suppression of the conductance near zero bias, which is due to the slow dissipation of the tunneling charge from the surface into the bulk, see Ref. 56 for more details. Such effect becomes more significant for the $p = 0.06$ sample in panel f. 

**f** Tunneling spectra from the $p = 0.06$ surface. 

**g** Field dependent $dI/dV$ spectra measured at $0.5$ K. 

**h** Temperature dependent $dI/dV$ spectra measured in zero B-field. 

**i** $dI/dV$ spectra normalized by dividing the spectra in panel g with the corresponding spectra in panel h (same temperature), except for the $0.5$ K and $2.0$ K data in panel g, for which we used the $3.0$ K data in panel h so as to avoid division by the very small signal at zero bias. Note the persistence of the gap feature up to $9.0$ K. 

**j** ZBC extracted from panel i. The ZBC increases with B-field and does not saturate at $15$ T. 

**k** ZBC extracted from panel i. The ZBC increases with temperature and saturates around $9.0$ K. 

measured in at $15$ T.
Extended Data Fig. 3 | Fitting of the tunneling spectra. To fit the full $T$-dependence, we performed a Dynes-like fit of the $\frac{dI}{dV}$ spectra while adopting an angular-dependent gap function $\Delta(\theta)$ as parameterized in Ref. 15. (The results obtained using this approach are consistent with those obtained by fitting the full momentum-dependence Green’s function in the superconducting state, see Fig. 2.) a–c Fitting results for the $p = 0.08$ system, assuming $s$-wave and $d_{x^2-y^2}$ order parameters. The $s$-wave and $d_{x^2-y^2}$ + id$_{xy}$ wave fits only reveal minor differences. d Extracted values of $\Delta_0$ as a function of temperature. e The corresponding temperature dependence of the broadening parameter $\Lambda$. Error bars in d and e are estimated in a way similar to Ref. 15.
Extended Data Fig. 4 | Experimental QPI results. **a–e** QPI data and processing procedures. **a** STM image ($V_s = 0.1 \text{ V}, I_t = 0.1 \text{nA}$) of a ($\sqrt{3} \times \sqrt{3}$)-Sn surface ($\rho = 0.1$) with several surface defects appearing as dark spots. **b** Corresponding $dI/dV$ image at $T = 0.5 \text{ K}$. The bright star-like features are centered at the defect locations in panel **a**. The power spectrum of panel **b**, symmetrized and rotated in panel **d**. The central region is subsequently suppressed to enhance the high frequency features, as shown in panel **e** (see Ref. 18 for more details). **f–h** show 4, 3, and 2 sets of QPI results obtained from ($\sqrt{3} \times \sqrt{3}$)-Sn surfaces for $\rho = 0.1, 0.08,$ and $0.06$, respectively. Each column shows QPI images obtained in a fixed spatial region but with different biases, as indicated on the left. The measurement temperatures are labeled above each column, and data are shown for temperatures above and below $T_c$. The central flower leafs only appear when the sample is in superconducting state and when the measurement bias is within the superconducting gap (within ±1.5 mV, ±2.2 mV, and ±3.6 mV, in **f, g, and h**, respectively). These QPI images are enclosed by the dashed red rectangles. Panel **f** shows QPI results obtained at $T = 5 \text{ K}$ (slightly larger than $T_c = 4.7 \text{ K}$ for this sample), or at 0.5 K in an 8 T B-field ($H_{c2} = 3 \text{ T}$). These data have a significantly reduced flower leaf feature, which could come from superconducting fluctuations. In panel **g**, the “0.5 K ($< T_c$)” data are QPI results obtained from a sample with interstitial Sn adatoms, deposited at 120 K. The presence of interstitial Sn considerably enhances the flower-leaf features at the center of the Brillouin zone.
Extended Data Fig. 5 | Simulated QPI spectra for different gap symmetries and scattering centers. The top and bottom rows show results for nonmagnetic ($\hat{V} = V_0 \hat{\tau}_3$) and magnetic ($\hat{V} = V_0 \hat{\tau}_0$) scatterers, respectively, with $V_0 = 100$ meV. Results are shown in the superconducting state assuming s-wave (left column), chiral $p + ip$ (middle column), and $d + id$ (right column) order parameters. The spectra are calculated at a bias voltage of 1 meV. In each case, the magnitude of the gap $\Delta_0$ and smearing parameter $\delta$ are obtained from fits of the $dI/dV$ spectra shown in Fig. 2a (see Methods). Note the absence of the central flower-leaf feature for non-magnetic scattering combined with the s-wave order parameter.
Extended Data Fig. 6 | Experimental and simulated STM images of the substitutional Si and interstitial Sn adatom defects.  
a–d Experimental (\(I_t = 0.1\) nA) and simulated STM images for the substitutional Si defect. The Si atom is invisible in filled state images, indicating that there are no occupied dangling bond states to tunneling from. The Si atom is visible in empty state images, but the atom appears to be dim due to its smaller covalent radius.  
e–h Experimental STM images (\(I_t = 0.1\) nA) of the interstitial Sn adatom defect center. Panel e reveals three very bright adatoms that are part of the regular (\(\sqrt{3} \times \sqrt{3}\))–Sn lattice. The interstitial Sn atom is located at the center of this cluster and cannot be imaged within the accessible bias range, as the adatom moves at higher biases.  
i–m Simulated STM images. Note the slightly increased brightness of the Sn atoms indicated by the blue arrows in panel g. This subtle effect is captured by the theory simulation in panel k.  

m (9 × 9) supercell used in the DFT calculations for the interstitial Sn adatom defect. Sn adatom and Si substrate atoms are shown in green and gold, respectively. The interstitial Sn atom is placed near the center of the (9 × 9) unit cell, as indicated by the red arrow.  

n Experimental \(dI/dV\) spectra recorded on top of the interstitial adatom (red) and far away from the interstitial location (blue). The latter reveals the characteristic LHB/QPP/UHB features (see Extended Data Fig. 1). The strong peak at about -0.35 eV corresponds to the triangular adatom feature in panels a, e. It is captured by the DFT calculation (black line). The peak at +1.25 eV in the theoretical DOS mainly consists of the (empty) 5p orbitals of the interstitial adatom. Simulated images at this bias indeed visualize this atom (not shown), but it cannot be imaged at this tunneling bias.
Extended Data Fig. 7 | Tunneling spectra (0.5 K) measured at defect locations on the superconducting ($\sqrt{3} \times \sqrt{3}$)Sn surface (p=0.08) and corresponding QPI data. a STM image ($V_s=0.02$ V, $I_t=0.1$ nA) showing several intrinsic surface defects. S1, S2 and S3 are substitutional Si defects and V1 is a Sn vacancy, as judged by the appearance of a hole for a wide range of positive and negative tunneling biases (images at other biases are not shown). Defects with unknown structures are labelled On, with $n=1 \sim 6$. b Tunneling spectra of the V1 and On defects in panel a. c Tunneling spectra of the interstitial Sn adatom defects A1, A2, and A3; see Supplementary Fig.. All defects produce a pair of in-gap states. The substitutional Si defects (S1, S2, and S3) exhibit a well defined double-peak structure at ± 0.6 meV. Interstitial Sn adatoms (A1 and A2) also possess a double peak structure, but with smaller energy splitting (± 0.2 meV). The A3 defect appears to have a single (unresolved) peak structure. d STM image ($V_s=-0.5$ V, $I_t=0.1$ nA) of a the ($\sqrt{3} \times \sqrt{3}$)Sn surface with interstitial Sn defects (indicated by arrows) and other intrinsic defects, mostly substitutional Si or adatom vacancies. e Corresponding dI/dV image obtained at a sample bias of $V_s=-0.4$ mV. The interstitial Sn defects produce the strongest scattering features in the real space conductance maps, as compared to those of other intrinsic defects. f, g compares the QPI spectra from the same ($\sqrt{3} \times \sqrt{3}$)Sn surface with and without adsorbed Sn defects. $I_{FC}$ represents averaged scattering intensities for the segment of the Fermi contour enclosed by the magenta rectangle, while the averaged intensity for the flower leaf features near the center of the Brillouin zone (enclosed by the red rectangle) is represented in units of $I_{FC}$. The relative scattering intensity of the flower leaf feature is strongest for the surface with the interstitial Sn adatoms defects.
Extended Data Fig. 8 | The leading (degenerate) eigenvectors of the Bethe–Salpeter equation for the triangular lattice Hubbard model. a, b The momentum space structure of the leading eigenvectors, which show a pairing symmetry consistent with $d_{x^2-y^2} + id_{xy}$ pairing. The size and color of the dots indicate the magnitude and sign of the eigenvector at the momentum points of the $3 \times 3$ cluster. The green hexagon shows the boundaries of the first Brillouin zone. c The doping dependence of the leading eigenvalues at an inverse temperature of $\beta = 8/t_c$. 
Extended Data Fig. 9 | Magnetic vortices of the superconducting $\sqrt{3} \times \sqrt{3}$-Sn surface observed at 0.5 K. a-e Magnetic vortices for the $p = 0.08$ sample. a Topographic STM image. b, c $dI/dV$ maps obtained with a tunneling bias inside the superconducting gap with a B-field of 1 T and 3 T, respectively. d $dI/dV$ spectra measured along the line crossing a magnetic vortex in panel c. e ZBC obtained from panel d with an exponential fit for determining the superconducting coherence length $\xi$. f-i Magnetic vortices for the $p = 0.06$ sample. f Topographic image. g $dI/dV$ map obtained with a tunneling bias inside the superconducting gap with a B-field of 4 T. This sample exhibits a very low zero bias $dI/dV$ signal, presumably due to the very high series resistance of this lightly doped sample at 0.5 K. Therefore the vortex features are only resolved away from zero bias. h $dI/dV$ spectra measured along the line crossing a magnetic vortex in panel g. i $dI/dV$ (-1.5 mV) along the line indicated in panel g with an exponential fit for determining the superconducting coherence length.
Extended Data Fig. 10 | Electronic band dispersion for a chiral d-wave superconductor in the presence of edges. Results were obtained by considering a mean-field $d_{x^2-y^2} + id_{xy}$ order parameter on a triangular lattice. The edge state spectrum is obtained by solving the tight-binding Hamiltonian on a cylinder, with open boundary conditions along the $y$-direction and periodic boundary conditions along the $x$-direction. Momentum $k_x$ remains a good quantum number and the resulting spectrum is shown here for a system of 400 chains (labeled by $n$) stacked in the $y$ direction and a $k$-mesh of 400 points. To clearly show the edge states here we computed the spectrum for $\Delta_0 = 1.5$ meV. As expected for a chiral d-wave superconductor with Chern number $C = \pm 2$, two chiral linearly dispersing in-gap states exist on each edge.