Controlling many-body states by the electric-field effect in a two-dimensional material

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To understand the complex physics of a system with strong electron–electron interactions, the ideal is to control and monitor its properties while tuning an external electric field applied to the system (the electric-field effect). Indeed, complete electric-field control of many-body states in strongly correlated electron systems is fundamental to the next generation of condensed matter research and devices1–2. However, the material must be thin enough to avoid shielding of the electric field in the bulk material. Two-dimensional materials do not experience electrical screening, and their charge-carrier density can be controlled by gating. Octahedral titanium diselenide (1T-TiSe2) is a prototypical two-dimensional material that reveals a charge-density wave (CDW) and superconductivity in its phase diagram3, presenting several similarities with other layered systems such as copper oxides3, iron pnictides4, and crystals of rare-earth elements and actinide atoms5. By studying 1T-TiSe2 single crystals with thicknesses of 10 nanometres or less, encapsulated in two-dimensional layers of hexagonal boron nitride, we achieve unprecedented control over the CDW transition temperature (tuned from 170 kelvin to 40 kelvin), and over the superconductivity transition temperature (tuned from a quantum critical point at 0 kelvin up to 3 kelvin). Electrically driving TiSe2 over different ordered electronic phases allows us to study the details of the phase transitions between many-body states. Observations of periodic oscillations of magnetoresistance induced by the Little–Parks effect show that the appearance of superconductivity is directly correlated with the spatial texturing of the amplitude and phase of the superconductivity order parameter, corresponding to a two-dimensional matrix of superconductivity. We infer that this superconductivity matrix is supported by a matrix of incommensurate CDW states embedded in the commensurate CDW states. Our results show that spatially modulated electronic states are fundamental to the appearance of two-dimensional superconductivity.

The charge-carrier density—or equivalently, the Fermi energy—strongly controls phase transitions in correlated systems. Traditionally, charge-carrier density can be controlled by doping, that is, by chemical modification of the material. Unfortunately, the alteration of the system’s chemical composition leads to the unavoidable introduction of disorder. In strongly correlated systems, owing to their exponential sensitivity to the local electronic environment, disorder can have a profound impact that masks the intrinsic many-body behaviour6. Hence, there is a growing need to change the charge-carrier density of strongly correlated systems without chemical means. The application of an electric field is one of the ‘cleanest’ ways (that is, it tends not to introduce disorder) to address many-body states because it is intrinsically homogeneous. However, electric fields are screened by the bulk material in three-dimensional metals, making their use difficult.

The Fermi energy not only controls the number of electric carriers (electrons or holes) but also the screening of external electric fields and internal electron–electron interactions7. In two-dimensional (2D) systems the electrons move in a plane while the electric field propagates in three-dimensional space. Hence, 2D electrons are unable to screen electric fields, external or their own. Therefore, we chose to work with a 2D material, TiSe2, of nanometre-scale thickness, and we used an ionic gel electrolyte gate to apply the electric field. In addition, the flake of TiSe2 was encapsulated by a 2D dielectric, hexagonal boron nitride, to avoid external disorder and chemical oxidation and degradation caused by both air and the electrolyte.

Electrical transport measurements under electric-field-induced doping enabled us to construct the phase diagram shown in Fig. 1. Electron doping suppresses the CDW transition from 170 K to 40 K and superconductivity appears with a dome that peaks at 3 K. We show that the emergence of superconductivity is directly associated with the inhomogeneous electronic states that correspond to a periodic structure of the amplitude and phase shifts of the superconductivity order parameter. This periodic structure must be stabilized and pinned to the lattice, so we can infer the presence of an incommensurate CDW (ICDW) matrix surrounding commensurate CDW (CCDW) regions.

TiSe2 nanosheets with thicknesses of 10 nm or less were prepared by mechanical exfoliation of a high-quality single crystal (Extended Data Fig. 1). The device fabrication and measurement details are described in Methods and Supplementary Information. In Fig. 2a we sketch the electric-field double layer transistor device used in our experiments; Fig. 2b shows a typical top-gate sweep at 285 K and the variation of the electron density as measured by the Hall effect (see Methods and Extended Data Fig. 2a, b). Using an electrolyte top gate and an electrostatic doped-Si bottom gate we could control the electron density up to about 1015 cm−2 and thereby explore the phase diagram of this 2D material.

Variation of the charge-carrier density n leads to strong variations of the sheet resistance R_S of the device, as shown in Fig. 2c, d. At low charge-carrier densities, one can clearly see a peak in the resistivity versus temperature. The CDW transition temperature10, T_{CDW}, corresponds to the inflection point of the resistance and was also measured by using the Hall effect (Extended Data Fig. 2c), to detect the reconstruction of the Fermi surface. On increasing the charge-carrier density, T_{CDW} decreases from 170 K to 40 K before becoming undetectable at around n = 7.5 × 10^{14} cm^{-2}.

On increasing the electron density we observe the superconductivity state, as shown in Fig. 2d. The superconductivity transition temperature, T_c, increases from 0 K at the quantum critical point (QCP) at n = 1.2 × 10^{14} cm^{-2} up to approximately 3 K at an optimal density of n = 7.5 × 10^{14} cm^{-2}. We note that this is exactly the density at which the CDW signal vanishes, indicating a scenario of two competing orders11. A further increase in density suppresses T_c, giving rise to the formation of a superconductivity dome, as shown in Fig. 1 together with representations of the inferred structure in each region of the phase diagram (discussed below).

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When the superconducting coherence length $\xi(T)$ becomes larger than the sample thickness close to $T_C$, we expect the material to behave as a 2D system and the superconducting transition is anticipated to be of the Kosterlitz–Thouless (K–T) type with vortex–antivortex unbinding\(^{15}\). One of the trademarks of the K–T transition is the broadening of the resistance with lowering of the temperature, as shown in Fig. 2d.

For the K–T transition the resistivity is expected to scale with the coherence length as:

$$\xi(T) \approx a \exp\left(-\frac{b}{\sqrt{\left|T - T_{K-T}\right|}}\right)$$

where $T_{K-T}$ is the K–T transition temperature, and $a$ and $b$ are material parameters. The experimental result reproduces this relation close to $T_{K-T}$ as shown in Fig. 3a for a charge-carrier density of $n = 2.67 \times 10^{14}$ cm\(^{-2}\). We also observe current–voltage scaling\(^{13}\) in the superconductivity phase ($V \propto I^{\alpha}$) with $\alpha = 0.5$ for $n = 5.9 \times 10^{14}$ cm\(^{-2}\) at the lowest temperature (Extended Data Fig. 3a). By fitting to equation (1), the K–T transition temperatures can be extracted for each doping level. In Fig. 3b we show the behaviour of $T_{K-T}$ close to the QCP as a function of electron density. Quantum critical scaling\(^{14}\) predicts $T_{K-T} \propto (n - n_c)^{z}$, where $z$ is the dynamical exponent and $\nu$ is the correlation length exponent. As shown in Fig. 3b and Extended Data Fig. 3b and c, we find $2\nu \approx 2/3$. The same scaling was observed in other systems\(^{15-17}\), and indicates that the superconductivity transition is of the classical three-dimensional XY or, equivalently, 2D quantum universality class\(^{16,17}\).

The temperature dependence of the sheet resistance can be written as $R_s = R_{so} + CT^\nu$ (where $R_{so}$ is the residual resistance at 3 K), which decreases monotonically with charge-carrier density as shown in Fig. 3c, in accordance with the above conclusion regarding the Harris criterion. In an ordinary metal (or Fermi liquid) we expect $\alpha = 2$, independent of doping. Nevertheless, in Fig. 3c we find $1 < \alpha < 2$ (Extended Data Fig. 4a, b) over the entire phase diagram. Notice that at around $n = 7.5 \times 10^{14}$ cm\(^{-2}\), $\alpha \simeq 1.5$ extends down to temperatures close to the superconductivity transition, which would seem to indicate the presence of another QCP, owing to suppression of the CDW, inside the superconductivity dome. In what follows we show that this is not the case.
The presence of the competing orders in this 2D system has striking consequences for the electronic transport. In Fig. 4a we show the magnetoresistance as a function of magnetic field for a density of \( n = 5.9 \times 10^{14} \text{ cm}^{-2} \). The magnetoresistance in the superconductivity phase is positive, as expected, but we clearly observe the presence of plateaus and oscillations in the data. By taking the derivative of the magnetoresistance, \( dR/dB \), in Fig. 4b we observe that these features are temperature-independent and have well defined periods. The periodicity in magnetic field reflects a spatial periodicity given by the cyclotron equation, \( \ell = (\Phi_0/2B)^{1/2} \), where \( \Phi_0 = h/(2e) \approx 2.068 \text{ T nm}^2 \) is the flux quantum and \( B \) is the magnetic field periodicity. We have analysed the magnetoresistance data as a function of electron density (or gate voltage). (Magnetoresistance data for other electron densities are shown in Extended Data Fig. 5.) One can see a clear trend in the data (as shown in Fig. 4c): the length scale decreases monotonically with electron density from \( \ell(n) \approx 450 \text{ nm at } n \approx 1.3 \times 10^{14} \text{ cm}^{-2} \) to \( \ell(n) \approx 170 \text{ nm at } n \approx 5.9 \times 10^{14} \text{ cm}^{-2} \). The magnetoresistance oscillates periodically with magnetic field \( B \) and temperature \( T \), which displays temperature-independent periodic oscillations. c, Derived magnetoresistance oscillating period \( B_M \) and the corresponding length scale \( D_{\text{CDW}} \). Error bars define the 90% confidence interval. d, Charge-carrier-density-dependent two-terminal conductance \( dR/dV \) shows the ZBCP, indicating non-\( s \)-wave superconducting pair symmetry. Charge-carrier density \( n = C \times 10^{14} \text{ cm}^{-2} \), where \( C \) is indicated by the colour; see legend.
and non-Fermi-liquid behaviour, strongly indicates that the CDW plays a part.

We now consider how local variations of the CDW can stabilize the superconductivity matrix. The CDW corresponds to a spatial modulation of the charge density \( \rho = \Delta(r)e^{-iQ \cdot r} \), where \( \Delta \) is the CDW order parameter, \( r \) is the position in the 2D plane and \( Q \) is the CDW ordering vector. On the basis of symmetry alone, the Ginzburg–Landau free energy for \( \Delta \) can be written as

\[
F = \int d^2 r \left\{ a(\Delta)^2 + b(\Delta)^4 + c(\Delta)^6 \right\} + \frac{1}{2m^*Q^2} \left[ |Q \cdot (\nabla - iQ) \Delta|^2 + \kappa |Q \times \Delta|^2 \right]
\]

(2)

where \( a, b, c, m^* \) and \( \kappa \) are phenomenological parameters that determine the energy scale for the spatial variation of \( \rho \). Variations in the amplitude \( \Delta \) are energetically very costly because the CDW has to be locally destroyed. However, variations in the CDW phase are energetically allowed and can be expressed as

\[
\Delta(r) = \Delta_0 \exp \left[ \frac{\mathbf{K} \cdot (\mathbf{r} - \mathbf{r}(r))}{2} \right]
\]

(3)

where \( \Delta_0 \) is the CDW order parameter in the uniform CCDW phase, \( \mathbf{K} \) is a reciprocal lattice vector in the direction of \( Q \), \( \theta(r) \) is a spatially varying phase and we have included the known CDW wavevector for TiSe\(_2\) (1/2, 1/2, 1/2). When \( \theta = \pi n \) (where \( n \) is an integer) we again have a CCDW, whereas if \( \theta = Q \cdot r \) we have an ICDW. For illustrative purposes, we assume that the variation in \( \theta(\mathbf{x}) \) is one-dimensional in nature and substitute equation (3) into equation (2) to obtain

\[
\delta F = \int d\mathbf{x} \frac{1}{2} \left[ \partial_\theta (\theta(x) - 1)^2 - g |1 - \cos(2\theta(x))| \right]
\]

(4)

where \( g \) depends on the Ginzburg–Landau parameters and \( x = |\mathbf{K}|/2 - Q \cdot \mathbf{r} \) is the dimensionless length scale. The last equation reflects how the free energy changes locally with the phase. Minimizing equation (4) with respect to \( \theta \) we obtain

\[
\frac{d^2 \theta}{dx^2} = -2g \sin(2\theta)
\]

(5)

the differential equation for the pendulum (\( x \) plays the part of ‘time’), which has periodic solutions with period \( \ell_{\text{ICDW}} \approx \pi(4/2 - Q) \). These spatially periodic variations of the phase represent Neél-like domain walls of ICDW between CCDW regions with different phase where \( \ell_{\text{ICDW}} \) is the thickness of the domain wall. McMillan described\(^{25} \) how these defects allow a uniform CCDW with slowly varying phase to break apart into domains of CICW separated by ICDW domain walls that have more rapidly varying phases. The domain wall density is \( \pi/4 \) to match the homogeneous ICDW state.

A full solution to this problem in 2D is lacking, but we speculate that domain walls form a periodic matrix illustrated schematically in Fig. 1; blue CCDW regions with constant phases are embedded in a periodic ICDW matrix. We note that a similar structure was observed in 1T-TaS\(_2\), in which the ICDW state exists at ambient conditions\(^{24} \). The self-organizing principle is that repulsive interactions occur between domain walls owing to higher-order terms in the free energy\(^{23} \). Therefore the ICDW domains will form a matrix, breaking the CCDW into domains with fixed area, as required by the Little–Parks effect.

As shown by ref. 23, ICDW dynamic phase fluctuations—that is, phonon modes of the ICDW (not the lattice)—can exist in these domain walls. It is conceivable that these ICDW phonons induce superconductivity pairing and localize Cooper pairs in one-dimensional regions of the 2D system. Another intriguing aspect of our results is displayed in Fig. 4d, which shows the point-contact conductance spectra measured at each density, in which we observe a clear zero bias conductance peak (ZBCP) in the superconductivity state. Extended Data Fig. 6 shows its temperature and magnetic field dependence at a density of \( n = 2.1 \times 10^{14} \text{ cm}^{-2} \). ZBCPs are observed in a wide range of unconventional superconductors and are understood to arise by Andreev reflection from a Cooper pairing potential having an internal phase shift of the superconductivity order parameter\(^{25} \). These results are therefore in stark contrast to the experimentally determined single-gap \( s \)-wave superconductivity observed in the Cu-intercalated Cu\(_{12}TiSe\(_2\) (ref. 26). It is unlikely that our 2D samples would develop a superconductivity order parameter that is qualitatively distinct from that of Cu\(_{12}TiSe\(_2\) (for example, \( d \)-wave). The existence of the ZBCP therefore suggests that, together with the spatial modulation of the superconductivity amplitude (which is demonstrated by the Little–Parks effect), there may also be a modulation of the superconductivity phase, although the correspondence between the amplitude variation and the phase variation cannot be determined from our measurements.

The observed state in 1T-TiSe\(_2\) bears some similarity to the pair density wave (PDW) superconducting CDW phases. However, further experiments are required to substantiate the PDW hypothesis. Although one-dimensional PDW states have attracted more attention within the context of the copper oxide superconductors\(^{27} \), more general PDW states having phase and amplitude variations in 2D are expected to be possible\(^{28} \).

The coexistence of CCDW and ICDW was first observed by recent X-ray measurements of TiSe\(_2\) at pressures close to where the superconductivity phase was expected\(^{29} \). ICDW domain walls with a periodicity along the \( c \) axis of \( \sim 300 \text{ nm} \) were observed, similar to the length scale determined in this experiment. While the periodicity was most pronounced along the \( c \) axis, a weak in-plane signal of incommensurability was observed that might correspond to the electronic microstructure observed here in the superconducting order (Abbamonte, P., personal communication, 15 January 2015).

In summary, we studied samples of TiSe\(_2\) a few nanometres in thickness and tuned the material through the CDW and superconductivity phases using the electric-field effect. This technique allowed us to study in great detail the QCP in the material and classify its universality class. We also identified the interplay between superconductivity and CDW through the formation of an inhomogeneous many-body state which we identify with the localization of Cooper pairs along a matrix of incommensurate dislocations surrounding regions of CCDW. We conjecture that the superconductivity has in its origin in the coupling of the McMillan phonon modes of the ICDW with the electrons. These results open up opportunities for electric-field tuning of many-body states in condensed matter research.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

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1. Ueno, K. et al. Electric-field-induced superconductivity in an insulator. Nature Mater. 7, 855–858 (2008).
2. Bollinger, A. T. et al. Superconductor–insulator transition in La\(_2\)Sr\(_y\)CuO\(_4\) at the pair quantum resistance. Nature 472, 458–460 (2011).
3. Yu, Y. et al. Gate-tunable phase transitions in thin flakes of 1T-TaSe\(_2\). Nature Nanotechnol. 10, 270–276 (2014).
4. Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nature Nanotechnol. 7, 699–712 (2012).
5. Shen, K. M. & Davis, J. C. S. Cuprate high-\( T_c \) superconductors. Mater. Today 11, 24–1 – 21 (2008).
6. Stewart, G. R. Superconductivity in iron compounds. Rev. Mod. Phys. 83, 1589–1652 (2011).
7. Stewart, G. R. Heavy-fermion systems. Rev. Mod. Phys. 56, 755–787 (1984).
8. Castro-Neto, A. H. & Jones, B. A. Non-Fermi-liquid behavior in U and Ce alloys: criticality, disorder, dissipation, and Griffiths-McCoy singularities. Phys. Rev. B 62, 14975–15011 (2000).
9. Kotov, V. N., Uchoa, B., Pereira, V. M., Guinea, F. & Castro Neto, A. H. Electron-electron interactions in graphene: current status and perspectives. Rev. Mod. Phys. 84, 1067–1125 (2012).

10. Fisher, M. E. & Langer, J. S. Resistive anomalies at magnetic critical points. Phys. Rev. Lett. 20, 665–668 (1968).

11. Castro Neto, A. H. Charge density wave, superconductivity, and anomalous metallic behavior in 2D transition metal dichalcogenides. Phys. Rev. Lett. 86, 4382–4385 (2001).

12. Minnhagen, P. The two-dimensional Coulomb gas, vortex unbinding, and superfluid-superconducting films. Rev. Mod. Phys. 59, 1001–1066 (1987).

13. Reyren, N. et al. Superconducting interfaces between insulating oxides. Science 317, 1196–1199 (2007).

14. Sachdev, S. Quantum Phase Transitions (Cambridge Univ. Press, 1999).

15. Caviglia, A. D. et al. Electric field control of the LaAlO3/SrTiO3 interface ground state. Nature 456, 624–627 (2008).

16. Parendo, K. A. et al. Electrostatic tuning of the superconductor-insulator transition in two dimensions. Phys. Rev. Lett. 94, 197004 (2005).

17. Aubin, H. et al. Magnetic-field-induced quantum superconductor-insulator transition in Nb1.23Si1.788. Phys. Rev. B 73, 094521 (2006).

18. Mason, N. & Kapitulnik, A. Superconductor-insulator transition in a capacitively coupled dissipative environment. Phys. Rev. B 65, 220505 (2002).

19. Yazdani, A. & Kapitulnik, A. Superconducting-insulating transition in two-dimensional a-MoGe thin films. Phys. Rev. Lett. 74, 3037–3040 (1995).

20. Harris, A. B. Effect of random defects on the critical behaviour of Ising models. J. Phys. Chem. 7, 1671 (1974).

21. Tinkham, M. Introduction to Superconductivity (McGraw-Hill, 1975).

22. McMillan, W. L. Theory of discommensurations and the commensurate-incommensurate charge-density-wave phase transition. Phys. Rev. B 14, 1496–1502 (1976).

23. McMillan, W. L. Time-dependent Landau theory of charge-density waves in transition-metal dichalcogenides. Phys. Rev. B 12, 1197–1199 (1975).

24. Burk, B., Thomson, R. E., Zettl, A. & Clarke, J. Charge-density-wave domains in 1T-TaS2 observed by satellite structure in scanning-tunneling-microscopy images. Phys. Rev. Lett. 66, 3040 (1991).

25. Kashiwaya, S. & Tanaka, Y. Tunnelling effects on surface bound states in unconventional superconductors. Rep. Prog. Phys. 63, 1641–1724 (2000).

26. Li, S. Y., Wu, G., Chen, X. H. & Taillefer, L. Single-gap s-wave superconductivity near the charge-density-wave quantum critical point in Cu2TiSe3. Phys. Rev. Lett. 99, 107001 (2007).

27. Fradkin, E., Kivelson, S. A. & Tranquada, J. M. Theory of intertwined orders in high temperature superconductors. Rev. Mod. Phys. 87, 457 (2015).

28. Agterberg, D. F. & Tsunetsugu, H. Dislocations and vortices in pair-density-wave superconductors. Nature Phys. 4, 639–642 (2008).

29. Joe, Y. I. et al. Emergence of charge density wave domain walls above the superconducting dome in 1T-TiSe2. Nature Phys. 10, 421–425 (2014).

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Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to A.H.C.N. (phycastr@nus.edu.sg).
METHODS

Crystal growth and quality verification. TiSe₂ single crystals were grown in two steps by the chemical vapour transport method. First, polycrystalline TiSe₂ was prepared by mixing high-purity titanium powder (from Alfa Aesar, 99.999%) and selenium powder (from Alfa Aesar, 99.999%) in a stoichiometric ratio and heating the mixture at 800 °C for 3 days in a vacuum-sealed (10⁻⁶ Torr) silica tube. Second, the polycrystalline powder was loaded into a two-zone tube furnace together with the transport agent I₂ at a concentration of 5 mg cm⁻². The polycrystalline powder was then heated to 670 °C and single crystals of TiSe₂ were collected at 600 °C over a period of 10 days.

The quality of the bulk single crystals was confirmed by X-ray diffraction and temperature-dependent Raman spectroscopy, as shown in Extended Data Fig. 1a and b. Further energy dispersive X-ray spectroscopy verified the stoichiometric composition of the crystals.

Device fabrication and characterization. TiSe₂ was exfoliated in a pure argon atmosphere by Scotch tape onto a SiO₂ (300 nm)/Si wafer and examined under high-resolution optical microscopy. The non-uniformity in thickness can be discriminated by cross-correlation of the colour with atomic force microscopy measurements of the height. Flakes with uniform thickness of around 10 nm or less and a long bar shape were selected for the device fabrication. Electrodes for transport measurements were fabricated by standard electron beam lithography techniques using a polymethylmethacrylate (PMMA) positive resist, followed by deposition of Ti (10 nm)/Au (65 nm). Thin crystals (one to three layers) of commercial hexagonal boron nitride were transferred onto the nanosheets within the argon atmosphere; the role of hexagonal boron nitride is to protect the TiSe₂ from degradation by both oxidation and damage by the electrolyte gate.

Atomic force microscopy results show that the surface is clean (as shown in Extended Data Fig. 2b), with a roughness within ±1 nm, which may result from the non-uniform thickness of the TiSe₂ flake.

Electrical transport measurements were performed both in a 4He cryostat and in a 3He/4He dilution cryostat. Electrical transport measurements were performed using standard alternating-current (a.c.) lock-in amplifier and direct-current (d.c.) techniques, and resistance-versus-temperature and field measurements were performed using currents of 10−100 nA to avoid Joule heating.

The ion gel solution was prepared by mixing the triblock copolymer polystyrene-poly(methylmethacrylate)-polystyrene (PS-PMMA-PS) and the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) into an ethyl propionate solvent (weight ratio of polymer to ionic liquid to solvent is 0.79:3.90:15). After covering the device with ion gel droplets by drop casting, the device as shown in Extended Data Fig. 2a was loaded into the cryostat and kept at room temperature and high vacuum for one hour to remove residual water from the electrolyte. Afterwards, resistance was measured against gate voltage to characterize the capability of the ion gel; a typical electrolyte gate sweep is shown in Fig. 1b.

The charge-carrier density doping by the ionic gate can be derived from the Hall-effect measurement both at high (285 K) and low (3 K) temperature; the former is shown in Extended Data Fig. 3c, and the latter is used to construct the phase diagram because the latter has a better direct correlation with the superconducting dome. Although the hexagonal boron nitride passivation prevents the accumulation of ions directly at the surface of TiSe₂, this was not found to reduce the capacity of the gate much, as demonstrated by our results and those of a recent work.

2D superconducting properties and the K–T transition. As discussed in the main text, the superconducting transition under different fixed perpendicular magnetic fields was measured. Extended Data Fig. 3b shows the magnetoresistance plot for a charge-carrier density of \( n = 2.67 \times 10^{14} \text{cm}^{-2} \) (see Extended Data Fig. 3b). By using finite size scaling with the formula \( R_\text{c}/R_\text{c} = F(\Delta B - B_0)T^{-1/2} \), where \( R_\text{c} \) and \( R_\text{c} \) are two fitting parameters and \( F(\Delta B - B_0) \) is an arbitrary function with \( F(0) = 1 \) (ref. 38), the data are expected to collapse into two sets of lines, with a certain \( z \) value. As displayed in Extended Data Fig. 3c, the data collapse for \( z \approx 2.3 \), which confirms the previous result.

Magnetoresistance oscillations at other doping levels. The magnetoresistance oscillation is observed when we sweep a perpendicular magnetic field at different temperatures in the superconducting state. From the QCP point \( n = 1.2 \times 10^{14} \text{cm}^{-2} \) to the near-optimum doping \( n = 5.9 \times 10^{14} \text{cm}^{-2} \), the oscillations can be observed for all doping levels. However, these oscillations can only be clearly observed for certain temperatures \( T_0 \) and magnetic fields \( B_0 \), whereas \( T_0 \) and \( B_0 \) values increase with increasing doping. For instance, for \( n = 1.3 \times 10^{14} \text{cm}^{-2} \), \( T_0 = 0.3 \text{K} \) and \( B_0 = 0.06 \text{T} \); for \( n = 2.7 \times 10^{14} \text{cm}^{-2} \), \( T_0 \) increases to 0.4 K and \( B_0 \) increases to 0.13 T, as one can see from Extended Data Fig. 4. Although \( T_0 \) and \( B_0 \) values as well as the periods of oscillation \( B \) depend on doping level, the amplitude of the magnetoresistance oscillation does not monotonically depend on doping levels. We find that the oscillating amplitude for doping levels of \( 1.3 \times 10^{14} \text{cm}^{-2} \) and \( 5.9 \times 10^{14} \text{cm}^{-2} \) is larger than that for other doping levels we measured. One can clearly see more contrast or sharpness for the periodic straight lines in Fig. 4b and Extended Data Fig. 5c than in Extended Data Fig. 5d. The stronger magnetoresistance oscillations at these doping levels could be related to the enhanced Cooper-pair phonon interaction, aroused by strong quantum fluctuation.

Temperature dependence of the sheet resistance. We plot the temperature dependence of the sheet resistance between 3 K and 100 K with the doping level ranging from 4 × 10¹⁴ cm⁻² to 13 × 10¹⁴ cm⁻² as shown in Extended Data Fig. 5a and b. By taking the temperature derivative \( d(\log(z))/d(T) \), we extract at each doping as a function of the temperature.

At doping levels away from the optimal doping, \( 7.5 \times 10^{14} \text{cm}^{-2} \), we observe Fermi-liquid behaviour at low temperatures below \( T_{C,DW} \). At the optimal doping level an exponent of 3/2 is observed over a wide range of temperature; this exponent is similar to the one observed in MnsB. As described in the main text, microscopic fluctuations of the order parameters from those of a CCDW to those of an ICDW gives rise to this temperature dependence.

Point-contact conductance spectroscopy. Point-contact conductance spectroscopy of the normal-superconducting junction between Au/Ti and TiSe₂ was performed by the two-terminal a.c. + d.c. method, whereby the d.c. voltage is modulated with an additional a.c. voltage, such that the derivative \( dV/dI \) can be measured at the first harmonic by a current preamplifier and standard lock-in amplifier techniques.

The contacts were patterned by standard electron beam lithography using a PMMA positive resist. The development of the resist is performed in air to allow the oxidation of the contact region such that the contacts (despite not being nanoscale) are in the so-called ‘soft’ contact regime that has been successfully applied to pnictide and copper oxide superconductors. In this regime spectroscopic information can be obtained because the transport is primarily through multiple point-like pinholes whose individual dimension is smaller than the mean free path in the contact.

REFERENCES

30. Di Salvo, F. J., Moncton, D. E. & Waszczak, J. V. Electronic properties and superlattice formation in the semimetal TiSe₂. Phys. Rev. B 14, 4321–4328 (1976).
31. Holy, J. A., Woo, K. C., Klein, M. V. & Brown, F. C. Raman and infrared studies of superlattice formation in the semimetal TiSe₂. Phys. Rev. B 16, 3628–3637 (1977).
32. Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. Science 306, 666–669 (2004).
33. Mayorov, A. S. et al. Micrometer-scale ballistic transport in encapsulated graphene at room temperature. Nature Lett. 11, 2396–2399 (2011).
34. Meyer, T. J. et al. Highly flexible MoS₂ thin-film transistors with ion gel dielectrics. Nat. Nanotechnol. 12, 4013–4017 (2012).
35. Gallagher, P. et al. A high-mobility electronic system at an electrolyte-gated oxide interface. Nature Commun. 6, 6437 (2015).
36. Rayen, N. et al. Superconducting interfaces between insulating oxides. Science 317, 1196–1199 (2007).
37. Fisher, M. P. A. Quantum phase transitions in disordered two-dimensional superconductors. Phys. Rev. Lett. 65, 923–926 (1990).
38. Pfeiffer, C., Julian, S. R. & Lonzarich, G. G. Non-Fermi-liquid nature of the normal state of itinerant-electron ferromagnets. Nature 414, 427–430 (2001).
39. Daghero, D. & Gonnelli, R. S. Probing multiband superconductivity by point-contact spectroscopy. Supercond. Sci. Technol. 23, 043001 (2010).

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Extended Data Figure 1 | Characterization of the high quality of single-crystal TiSe₂. a, X-ray diffraction of both single-crystal and powder TiSe₂ sample. The inset shows the as-grown TiSe₂ single crystal. b, Raman spectroscopy pattern at both high temperature and low temperature. The two main phonon modes, $E_g$ and $A_{1g}$, are distinct, whereas only below $T_{CDW}$ are the peaks corresponding to CDW phonon mode detectable. The inset displays the unit cell of the TiSe₂ lattice and the main phonon mode vectors.
Extended Data Figure 2 | The Hall bar device and its characterization by Hall effect measurement. a, Optical microscope picture. b, Atomic force microscope picture of the Hall bar device. c, Temperature dependence of the charge-carrier density measured by the Hall effect at different top gate voltages, $V_{TG}$. Scale bar, 5 μm.
Extended Data Figure 3 | Characterization of the K–T transition. a, The current–voltage power-law fit for $n = 5.9 \times 10^{14} \text{ cm}^{-2}$ at different temperatures is consistent with the behaviour of the 2D K–T transition. b, Temperature-dependent magnetoresistance of the superconducting transition at different fixed perpendicular magnetic fields for $n = 2.67 \times 10^{14} \text{ cm}^{-2}$. c, The magnetoresistance data in b collapses into two sets of lines by so-called finite size scaling.
Extended Data Figure 4 | The $R$ versus $T$ power-law fit indicates the existence of strong quantum fluctuation. 

a, Temperature dependence of the sheet resistance for different doping levels. 
b, The data shown in a is plotted on a log–log scale.
Extended Data Figure 5 | The magnetoresistance oscillation for charge-carrier densities of $1.3 \times 10^{14}$ and $2.7 \times 10^{14}$ cm$^{-2}$. a, c, Perpendicular magnetic-field-dependent magnetoresistance measured at different temperatures. b, d, Plots of $dR_s/dB$ against $B$ and $T$ for $n = 1.3 \times 10^{14}$ cm$^{-2}$ and $n = 2.7 \times 10^{14}$ cm$^{-2}$, respectively.
Extended Data Figure 6 | The conductance measured for a charge-carrier density of $2.1 \times 10^{14}$ cm$^{-2}$. a, Magnetic field dependence at 0.1 K. b, Temperature dependence at zero magnetic field. a.u., arbitrary units.