Emergence of charge density wave domain walls above the superconducting dome in 1T-TiSe$_2$

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Superconductivity in so-called unconventional superconductors is nearly always found in the vicinity of another ordered state, such as antiferromagnetism, charge density wave (CDW), or stripe order. This suggests a fundamental connection between superconductivity and fluctuations in some other order parameter. To better understand this connection, we used high-pressure X-ray scattering to directly study the CDW order in the layered dichalcogenide TiSe$_2$, which was previously shown to exhibit superconductivity when the CDW is suppressed by pressure$^1$ or intercalation of Cu atoms$^2$. We succeeded in suppressing the CDW fully to zero temperature, establishing for the first time the existence of a quantum critical point (QCP) at $P_c = 5.1 \pm 0.2$ GPa, which is more than 1 GPa beyond the end of the superconducting region. Unexpectedly, at $P = 3$ GPa we observed a reentrant, weakly first order, incommensurate phase, indicating the presence of a Lifshitz tricritical point somewhere above the superconducting dome. Our study suggests that superconductivity in TiSe$_2$ may not be connected to the QCP itself, but to the formation of CDW domain walls.

The term ‘unconventional superconductor’ once referred to materials whose phenomenology does not conform to the Bardeen–Cooper–Schrieffer (BCS) paradigm for superconductivity. It is now evident that, by this definition, the vast majority of known superconductors are unconventional; notable examples being the copper-oxide, iron-arsenide and iron-selenide high-temperature superconductors, heavy fermion materials such as CeIn$_3$ and CeCoIn$_5$, ruthenium oxides, organic superconductors, such as $\kappa$-(BEDT-TTF)$_2$X, and fullerides, and so on.

Despite their diversity in structure and phenomenology, the phase diagrams of these materials all exhibit the common trait that superconductivity resides near the boundary of an ordered phase with broken translational or spin rotation symmetry. For example, superconductivity resides near antiferromagnetism in CeIn$_3$ (ref. 3), near a spin density wave in iron arsenides$^4$, orbital order in ruthenates$^5$, and stripe and nematic order in the copper-oxides$^6$. The pervasiveness of this ‘universal phase diagram’ suggests that there exists a unifying framework—more general than BCS—in which superconductivity can be understood as coexisting with some ordered phase, potentially emerging from its fluctuations.

A classic example is the transition metal dichalcogenide family, MX$_2$, where M = Nb, Ti, Ta, Mo, and X = Se, S, which exhibits a rich competition between superconductivity and Peierls-like charge density wave (CDW) order$^7$. A recent, prominent case is 1T-TiSe$_2$, which under ambient pressure has CDW order below a transition temperature $T_{\text{CDW}} = 202$ K (ref. 8). This CDW phase can be suppressed either by intercalation of Cu atoms$^9$, or through the application of hydrostatic pressure$^{10}$, causing superconductivity to emerge. These studies indicate that the emergence of superconductivity coincides with a quantum critical point (QCP) at which $T_{\text{CDW}}$ goes to zero, suggesting that TiSe$_2$ exemplifies the universal phenomenon of superconductivity emerging near the suppression of an ordered state. However, until now, there has been no direct observation of the QCP, impeding efforts to understand the relationship between superconductivity and the suppression of CDW order.

A better understanding of this universal relationship requires a direct study of the CDW order parameter itself, through and beyond the QCP. Such a study would define the phenomenology and set constraints on what type of theory is needed to explain this pervasive phenomenon. For this purpose, we performed X-ray scattering experiments on the CDW order in TiSe$_2$ at low temperature and under hydrostatic pressure. Pressure is somewhat preferred to Cu doping as the former does not introduce non-stoichiometric disorder, allowing detection of quantum critical behaviour with the material nominally in its pristine state.

The origin of the CDW order in TiSe$_2$ has been the subject of debate. Explanations for its existence range from traditional Fermi surface nesting$^8$ to an excitonic insulator scenario$^9$ to an indirect Jahn–Teller effect$^{10}$, with the relative importance of electron–electron and electron–phonon interactions still in dispute$^{11-13}$. What is clear is that the CDW in TiSe$_2$ is a condensate of electron–hole pairs with nonzero total momentum, in which electron–electron interactions, the Peierls distortion and lattice pinning effects all play prominent roles.

X-ray experiments were carried out at the Cornell High Energy Synchrotron Source (CHESS) on TiSe$_2$ crystals mounted in a screw-driven diamond anvil cell (DAC) in a closed-cycle cryostat. Experiments were done without an analyser, the detector integrating over all scattered photon energies. In this case, the experiment measures an energy-integrated, equal time correlation function, $S(q)$, which is the Fourier transform of the time-averaged electron density correlator, incorporating both classical and quantum fluctuations$^{14}$. The lowest accessible temperature was 8.3 K, which was not low enough to enter the superconducting phase but was adequate to address the energy scale of the CDW, even close to the QCP.

The signature of a CDW in TiSe$_2$ is the existence of an order parameter reflection at a wave vector of (1/2, 1/2, 1/2), where the Miller indices $(H, K, L)$ represent a momentum transfer...
Figure 1 | Suppression of the charge density wave in TiSe$_2$ with temperature and pressure. a. Scans through the charge density wave (CDW) ordering vector showing suppression of CDW correlations with increasing pressure for (H, 1/2, 1/2). b. Small, residual CDW correlations observed in the normal state, both at high and low pressure. c. Pressure-dependence of the ratio $T_{CDW}/T(0)$, or the Landau coupling constant $g$, which in McMillan’s picture is proportional to the CDW coupling constant. d. Phase boundary delineating the ordered and disordered phases in the pressure-temperature plane. The $T_{CDW}$ values from ref. 1 are shown for comparison (the grey dashed line is an interpolation of the data). The points were found to fit well to a single power law over the entire region, $T_{CDW}(P) = T(0) - P/I_0^\beta$, with $\beta = 0.87 \pm 0.08$ (black dashed line), identifying the location of the quantum critical point at $P_c = 5.1 \pm 0.2$ GPa. Error bars on the temperature values represent the difference in reading between the cryostat cold finger and the top of the pressure cell. Error bars on the pressure values were determined by the energy resolution of the spectrometer used to monitor the ruby fluorescence lines. The range of fits consistent with these error bars were used to determine the error bars on $\beta$ and $P_c$.

$q = H \mathbf{b}_1 + K \mathbf{b}_2 + L \mathbf{b}_3$, where $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are basis vectors of the reciprocal lattice. We note that, unlike most other dichalcogenides such as NbSe$_2$ or TaS$_2$, the CDW in TiSe$_2$ at ambient pressure is always observed to be commensurate, with $H$, $K$, and $L$ having rational values at all temperatures$^{8,16,19}$, suggesting that lattice pinning plays a prominent role in its formation.

Confirming the conclusions of refs 1, 10, the CDW was found to be suppressed by hydrostatic pressure (Fig. 1a). The $T_{CDW}$ value fell to zero, indicating the absence of a quantum critical point at a pressure of $P_c = 5.1 \pm 0.2$ GPa. The pressure dependence of $T_{CDW}$ can be fitted well using a single power law, $T_{CDW}(P) = T(0) - P/I_0^\beta$, where $\beta = 0.87 \pm 0.08$ is an effective exponent characterizing the observed order parameter suppression (Fig. 1c). If one assumes that a Hertz–Millis picture of quantum critical scaling applies near the QCP (refs 20,21), this exponent $\beta \equiv \nu z$, where $\nu$ is the exponent of the correlation length and $z$ is the dynamical critical exponent. In mean field theory $\nu = 1/2$ and $z = 2$ for a CDW transition, implying $\beta = 1$, which is close to the measured value.

The complete phase diagram, showing the order parameter intensity, phase boundary and the location of the QCP, is shown in Fig. 2. In contrast to expectations based on refs 2,9,11, the QCP does not reside within the superconducting dome, which spans the range 2 GPa $< P < 4$ GPa, but lies more than a full GPa higher in pressure. This might seem to cast doubt on the presumed connection between CDW fluctuations and superconductivity. However, we will show below that the situation is more subtle.

Surprisingly, a trace quantity of CDW correlations was observed beyond the QCP. At $P = 5.9$ GPa a weak, resolution-limited CDW reflection is still present, whose integrated intensity is a factor of $10^4$ smaller than at ambient pressure. This temperature-independent feature was found to be present everywhere in the normal state of the $PT$ phase diagram, even above the classical transition at $P = 0$ (Fig. 1b). This suggests that our system is experiencing a weak, uniform, symmetry-breaking field that induces a trace amount of CDW correlations in the normal state.

Near the QCP one might also expect to observe quantum critical fluctuations, which should appear as power law tails in the correlation function, that is, $S(q) \propto q^{-(\nu z-1)}$, where $q$ is measured with respect to the ordering wave vector. However, unlike previous studies of the classical transition, in which such fluctuations are clearly visible$^{15}$, no tails were observed in our study of the quantum transition, even at high momentum resolution and close to the phase boundary. We attribute this behaviour, as well as the normal state feature above, to the presence of a small, internal strain gradient in the pressure cell, which for a CDW can act as a uniform, symmetry-breaking field that induces a trace amount of CDW correlations in the normal state.

Just as $T_{CDW}$ is suppressed by pressure, so too is the low-temperature value of the CDW integrated intensity, $I(0)$. This may provide insight into the pressure dependence of the interactions that drive the CDW. The CDW in TiSe$_2$ is believed to be rather strongly coupled, with $2\Delta \approx 7k_BT_{CDW}$ (ref. 7) and a normal state coherence length, $\xi_0$, of just a few lattice parameters$^{17}$. It was argued by McMillan$^{22}$ that, in this case, the ratio $T_{CDW}/I(0)$ is proportional
to the Landau coupling constant, $g$, which we plot in Fig. 1c. Although one might expect the coupling strength to decrease as the phase transition is approached, the trend in the ratio is the opposite, rising continuously up to $P = P_c$, McMillan’s mean field expression, which applies only to the ordered side of the transition where $T_{CDW}$ is nonzero, neglects disorder and quantum fluctuations and is too simplistic to accurately describe the region close to the QCP. Nonetheless, Fig. 1c suggests that the suppression of the CDW arises from some effect other than reduction in the coupling constant, such as changes in the commensurability or lattice stiffness.

To investigate this possibility, we employed a novel, precision technique for measuring the degree of commensurability of the CDW. The difficulty in such a measurement is referencing the wave vector of the CDW to a Bragg reflection of the underlying lattice. In the case of TiSe$_2$, there is no Bragg reflection close to the CDW, so any small geometric misalignment propagates into large errors in the values of $(H, K, L)$.

To overcome this difficulty, we performed scattering experiments at two photon energies simultaneously. An X-ray source with diffractive optics always contains harmonics, that is, a small percentage of photons with precisely half the wavelength, in our case a tiny fraction of 36 keV photons in our nominally 18 keV beam. Rather than filtering out the harmonics, we employed an energy-proportional detector to measure both energies in parallel, allowing simultaneous measurement of the $(H, K, L)$ and $(2H, 2K, 2L)$ points in momentum space. This allowed us to reference $in situ$ the CDW correlations near $(1/2, 1/2, 1/2)$ to the Bragg reflection at $(1, 1, 1)$, eliminating errors due to misalignment, temperature drifts and so on. This measurement was performed at a selection of points across the phase diagram, at pressures near and below the superconducting dome. The results are summarized in Fig. 3, with labels ‘C’ or ‘IC’ added to the corresponding points in Fig. 2.

Consistent with past X-ray studies, at low pressures the CDW was found to be commensurate to within the experimental resolution of a few thousandths of a reciprocal lattice unit (r.l.u.). This was true even for the anomalous normal state peak observed above $T_{CDW}$ (Fig. 1b). Surprisingly, however, at $P = 3$ GPa — directly above the superconducting dome — weak incommensurate behaviour was observed at the level of $2 \times 10^{-3}$ r.l.u. At the lowest temperatures the CDW is commensurate, but IC behaviour emerged as the temperature was increased, becoming most pronounced near the phase boundary at $T = 90$ K. The incommensurability was largest along the $L$ direction (Fig. 3), suggesting that the IC behaviour may be attributed to phase slips in the stacking of the CDW order along the $c$ axis, separated by a distance $\sim 1/0.002 = 500$ lattice parameters. Although it was not possible to perform this measurement at every point in the phase diagram, observation of IC behaviour is sufficient to establish the existence of a Lifshitz multicritical point, analogous to behaviour in helical ferromagnets, somewhere in the region above the superconductivity dome.

The transition from C to IC CDW order may be weakly first order. Although the effect lies near the limit of our resolution, the transition appears to exhibit a coexistence region for $25$ K $< T < 50$ K, in which both C and IC phases are present (Fig. 3). A first-order character would make this C/IC transition similar to those in other dichalcogenides, such as $1T$-TaSe$_2$ (ref. 25) and $1T$-TaS$_2$ (ref. 26).

Our study has significant bearing on the existing picture of CDW melting and the emergence of superconductivity in TiSe$_2$. First, the

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**Figure 2** Summary pressure–temperature phase diagram of TiSe$_2$. a, Broad phase diagram showing charge density wave (CDW) ordered, normal state and superconducting phase boundaries. The green colour scale indicates the integrated intensity of CDW correlations, including both the C and IC components. The superconducting $T_{SC}$ value, reproduced from ref. 1 has been exaggerated by a factor of five for visibility. Points where the precise commensurability was measured are labelled C, I or C/I, indicating commensurate, incommensurate or coexistence, respectively. b, Zoom-in on the region exhibiting the transition between commensurate and incommensurate order (grey dashed rectangle in a).
existence of an IC phase suggests that the natural wave vector of the CDW, which is set by the Fermi surface topology, shifts from the commensurate point as the energy bands adjust with pressure. This destabilizes the CDW by reducing the energy saved from the lattice pinning potential. We note that this view is not dependent about 450 μm in diameter. The pressure was calibrated by measuring the fluorescence of a small ruby chip placed in the sample beside the TiSe₂ crystal.

X-ray experiments. Experiments were carried out at the C1 beam line at CHESS with a 4 K diffractometer. To simultaneously measure scattering at (0.5, 0.5, 0.5) and (1, 1, 1), an energy-proportional scintillation counter was fitted into two independent single-channel analysers to bin the 18 keV and 36 keV photons into separate scaler channels.

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Author contributions
Y.I.J. and P.A. designed the experiment. Y.I.J., K.D.F. and P.A. built the experimental 
apparatus. Y.I.J., X.M.C., K.D.F., G.A.P., Y.G., J.C.T.L., J.G. and P.A. performed the X-ray 
experiments. S.Y., Y.I.J. and S.L.C. grew the crystals. Y.I.J., P.G., G.J.M., S.L.C., T.C.C., E.F. 
and P.A. analysed and interpreted the data. P.A. wrote the paper.

Additional information
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Competing financial interests
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