Metal-to-insulator transition in Pt-doped TiSe₂ driven by emergent network of narrow transport channels

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Metal-to-insulator transitions (MIT) can be driven by a number of different mechanisms, each resulting in a different type of insulator—Change in chemical potential can induce a transition from a metal to a band insulator; strong correlations can drive a metal into a Mott insulator with an energy gap; an Anderson transition, on the other hand, due to disorder leads to a localized insulator without an energy gap. Here, we report the discovery of an alternative route for MIT driven by the creation of a network of narrow channels. Transport data on Pt substituted for Ti in 1T-TiSe₂ shows a dramatic increase of resistivity by five orders of magnitude for few % of Pt substitution, with a power-law dependence of the temperature-dependent resistivity $\rho(T)$. Our scanning tunneling microscopy data show that Pt induces an irregular network of nanometer-thick domain walls (DWs) of charge density wave (CDW) order, which pull charge carriers out of the bulk and into the DWs. While the CDW domains are gapped, the charges confined to the narrow DWs interact strongly, with pseudogap-like suppression in the local density of states, even when they were weakly interacting in the bulk, and scatter at the DW network interconnects thereby generating the highly resistive state. Angle-resolved photoemission spectroscopy spectra exhibit pseudogap behavior corroborating the spatial coexistence of gapped domains and narrow domain walls with excess charge carriers.

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Published in partnership with Nanjing University

npj Quantum Materials (2021)6:8; https://doi.org/10.1038/s41535-020-00305-2

INTRODUCTION

Pure 1T-TiSe₂, whose crystal structure is shown in Fig. 1a, undergoes a charge density wave (CDW) transition at $T_{\text{CDW}} = 200$ K with a $2 \times 2 \times 2$ charge order⁴. While the nature of this CDW has been a matter of debate for decades, many of the recent experimental studies favor the electronically driven CDW⁵-⁹, consistent with the theoretical description of excitonic insulator¹⁰,¹¹. Nevertheless, a transport study has found finite resistivity in polycrystalline TiSe₂ samples at low temperature¹², consistent with metallic behavior. The sensitivity of the low-temperature transport property on the synthesis condition¹³ suggests that the zero slope suggests that the temperature dependence follows a power-law behavior, without any exponential factor, as seen in Fig. 2b and the doping dependence in Fig. 2c.

The high sensitivity of resistivity to Pt substitution as well as the unusual temperature-dependent resistivity point toward a highly unusual insulating state. In this paper, we use a combination of electrical transport, angle-resolved photoemission spectroscopy (ARPES), and scanning tunneling microscopy (STM) to determine the mechanism for MIT in these compounds. Guided by the STM and ARPES data, we propose a model of narrow metallic channels on the domain walls of CDW, in an otherwise insulating background (see Fig. 1), which potentially provides explanations for the power-law temperature dependence of the resistivity, and points to an alternative path to obtain an MIT.

RESULTS AND DISCUSSION

Effects of Pt dopants

We find that Pt in 1T-TiSe₂ has two effects: (1) Our Hall measurements suggest that the Pt dopants introduce electron-like carriers to the system (see Supplementary Fig. 2). Usually, such carrier doping of a semimetal/semiconductor drives the system towards a metallic phase; this, however, is the opposite of what we find in 1T-PtxTi₁₋ₓSe₂. (2) Our DFT calculations find that it is energetically favorable for a Pt to substitute Ti rather than to intercalate. (See Supplementary Note 3.) Its t₂g orbitals have higher energy than the t₂g orbitals of Ti, thus acting as a local potential impurity. This Pt substitution is further corroborated by the shapes...
seen by examining the energy distribution curves (EDCs) in Fig. 3b, indicating the loss of long-range CDW correlation with doping. Interestingly, the 1T-TiSe₂ creates domain walls between different charge density wave (CDW) ordered domains. The CDW with ordering wavevector \( q = L \) supports at least four types of domains in-plane, related to each other by lattice translations. (Form factor of the CDW may introduce additional types of domains. See, e.g., ref. 73.)

### Pseudogap-like behavior observed in angle-resolved photoemission spectroscopy

To gain insight into the MIT in 1T-Pt₁₋ₓTiₓSe₂, we study the evolution of the single-particle spectral function of the doped single crystals from the metallic to the insulating regime using ARPES. Figure 3a, d show the energy-momentum intensity maps (EMIMs) \(^{15}\) around the L point for \( x = 0.1 \) and \( x = 0 \), respectively. The EMIM depicts the ARPES intensity as a function of one of the in-plane momentum components and electronic energy \( \omega \) referenced to the chemical potential \( \mu \), while keeping the other orthogonal in-plane momentum component fixed. Both samples show a hole-like band near the \( \Gamma \) point and its CDW shadow near the L point. Compared to that of the \( x = 0 \) sample, the shadow band of the \( x = 0.1 \) sample is much weaker and broader, indicating the loss of long-range CDW correlation with doping. Interestingly, the \( x = 0.1 \) sample shows suppression of the spectral weight at the Fermi level near the L point, which we discuss next.

The contrast between doped and undoped samples can be seen by examining the energy distribution curves (EDCs) in Fig. 3b, e, which show ARPES data as functions of \( \omega \) at a specific momentum. To detect energy gaps near \( \mu \), it is necessary to eliminate the effect of the Fermi function from the EDCs. This can be approximately taken into account by employing symmetrization technique \(^{16,17}\). A different method to accomplish this is to divide the EDCs by resolution-broadened Fermi function \(^{16,17}\). In order to compare results obtained from these two different techniques, we have conducted Fermi function division analysis of the EDCs from \( x = 0.1 \) sample at various temperatures, which are presented in Supplementary Fig. 6. These are similar to the data in Fig. 3b. For \( x = 0 \), the symmetrized EDCs (Fig. 3e) exhibit a peak at \( \mu \) at all measured temperatures implying the absence of any energy gap. The data for the \( x = 0.1 \) sample, (Fig. 3b) is markedly different. At higher temperatures of \( T \geq 103 \text{ K} \), the data show peaks at \( \mu \), indicating the absence of an energy gap. With decreasing temperature, however, the peaks of the symmetrized EDCs appear away from \( \mu \), implying gapped electronic excitations. It is to be noted that this energy gap is soft, meaning that there is finite spectral weight at \( \mu \) even at the lowest measured temperatures. This prompts us to refer to this energy gap as a pseudogap. We note that this pseudogap can be independently verified from the STM data as well (Fig. 4h), as we will show later.

The temperature evolution of the energy gap can also be investigated via leading-edge analysis of the ARPES data. To this end, we focus on Fig. 3c, where we compare the leading edges of the \( x = 0.1 \) sample and a polycrystalline gold sample at several temperatures (14, 73, and 103 K). Comparisons at several other temperatures (28, 43, 54, and 150 K) have been displayed in Supplementary Fig. 5 of Supplementary Note 4. Collectively, these figures show that the leading edge of the EDCs of the Pt-doped
sample \((x = 0.1)\) is shifted towards negative energy with respect to that of gold at each measured temperature below 103 K indicating the presence of an energy gap. This shift disappears for \(T \geq 103\) K, which evidences the absence of an energy gap.

Interestingly, ARPES data suggest that the pseudogap does not “close”, rather it gets “filled-up”. This can be seen by tracking the peak positions of the symmetrized EDCs as a function of temperature. For \(14\) K \(\leq T \leq 73\) K we find that the energy location of the peak of each symmetrized EDC is practically the same. There is, however, a monotonic increase in the spectral weight at \(\mu\) with increasing temperature from 14 K onward. Based on this, we speculate that it is the gradual increase in spectral weight at \(\mu\) with increasing temperature that plays a dominant role in the eventual disappearance of the pseudogap at higher temperatures. These observations are reminiscent of the temperature dependence of the pseudogap in underdoped cuprate high-temperature superconductors\(^{18,19}\). We, however, do not suggest that the pseudogap has the same origin in these two very different systems.

We can obtain an estimate for \(\bar{T}\) associated with the filling up of the pseudogap. To do this, we define a parameter \(L(T) \equiv 1 - \frac{I(T, \omega)}{I(T, \omega_{\text{peak}})}\), where \(I(T, \omega)\) is the intensity of the symmetrized EDC at \(\omega\), and \(\omega_{\text{peak}}\) is the energy at the peak of the symmetrized EDC. \(I(T, 0)\) is the intensity at \(\mu\). \(\bar{T}\) is then determined by the temperature at which \(L\) vanishes\(^{20,21}\). From Fig. 3f, \(\bar{T}\) is estimated to be \(\sim 90\) K, which is consistent with the observation of peaks at \(\mu\) in the symmetrized EDCs for \(T \geq 103\) K in Fig. 3b as well as with the leading edge comparison with Au shown in Fig. 3c.

ARPES data, therefore, reveal crucial information on the opening of a pseudogap at the chemical potential, which provides potential clues to the dramatic increase in resistivity with Pt-substitution, but also leaves us with some unanswered questions on the origin of the gap. Since the chemical potential shifts up into the conduction band with doping, a transition to a band insulator cannot be the origin of the gap. CDW is also unlikely to be the cause since the ordering is stronger in the undoped sample which is gapless at the chemical potential. In addition, we do not see evidence of hybridization of the conduction band with another band separated by the CDW wavevector. On the other hand, the fact that the gap fills up with increasing temperature suggests that it is a correlation-driven gap, which raises the question of why correlation effects in Pt-substituted TiSe\(_2\) are so different from the parent TiSe\(_2\).

Domain wall network revealed by scanning tunneling microscopy

To determine the origin of the pseudogap in 1T-Pt\(_{0.1}\)Ti\(_{1-x}\)Se\(_2\), we turn to local properties using STM. 1T-Pt\(_{0.1}\)Ti\(_{1-x}\)Se\(_2\) single crystals were cleaved at 80 K before being inserted into the STM head held at 4 K. From STM topography shown in Fig. 4a–c (also see Supplementary Note 5 and Supplementary Figs. 7–9), we find that the sample becomes increasingly disordered with the Pt doping, although the CDW survives as a short-range ordered state (Supplementary Fig. 9). Through selective inverse Fourier transform (explained in Supplementary Note 6), we can identify that the origin of the disorder is due to the increase in the domain wall density (see Fig. 5). This is consistent with the ARPES observation that the back-folded band becomes broader and weaker with Pt-doping.

The overall trend of the STM spectra with Pt doping can be seen in the typical STM spectra obtained far from impurities or domain...
walls for $x = 0, 0.02,$ and $0.1$ samples as shown in Fig. 4d. The U-shape of the spectra is consistent with the band gap of a semiconductor with a flat bottom representing the bulk indirect band gap between the p-states and d-states. Intrinsic doping leads to the Fermi energy $\mu$ being positioned close to the bottom of the conduction band for each of these $x$ values. A closer look at the density of states (Supplementary Fig. 11) indicates that for these pristine samples, the Fermi energy lies slightly inside the conduction band, resulting in metallic transport behavior. STM data show that the gap between the conduction and valence bands increases with increasing $x$ (dotted lines in Fig. 4d) which is consistent with ARPES data in Fig. 3a, d.

We now focus on the behavior of the local density of states (LDOS) in the $x = 0.1$ samples. An interesting picture emerges from our study of $dI/dV$ maps (measured at $V_{bias} = -20$ mV in the same area as the topography in Fig. 4c) that reveals regions with...
different density-of-states behaviors. In the larger area region within the domains denoted as 1 in Fig. 4f, g the density of states is close to zero around $\mu$ with the conduction band bottom seemingly shifted to higher energies. On the other hand, in the regions denoted by 2, 3, and 4, spatially correlated with the location of the domain walls as identified by the topography, we observe a finite density of states around $\mu$ with a small pseudogap. This suggests that there is a charge or spectral weight transfer from the domains to the domain walls.

The spatially averaged spectrum shown in Fig. 4h shows pseudogap, i.e., a depletion in the density of states relative to background on an energy scale of 30 meV around $\mu$, which is highlighted when a polynomial background is subtracted (see inset to Fig. 4h as well as Supplementary Fig. 10). Of importance is our observation that the energy scale of the pseudogap is comparable to the one observed by ARPES. Similar pseudogap features are not visible in the averaged spectra of the $x = 0$ samples (Supplementary Fig. 10). Based on this we can conclude that the pseudogap feature for $x = 0.1$ sample can be independently observed from STM and the associated energy scales qualitatively agree with the ARPES observations. In addition, STM provides a detailed local view that the Pt dopants disrupt the CDW and affects the local electronic spectra (see also Supplementary Note 5, and Supplementary Figs. 7–9). It is thus important to understand the role of the Pt dopants theoretically.

Emergent network of narrow transport channels
The substituted Pt acting simply as scattering centers for the charge carriers does not explain the extreme sensitivity of transport property to doping. The Pt dopants, however, can provide a pinning potential for the commensurate CDW. Following the argument by Imry and Ma$^{22}$, two dimensions is the lower critical dimension for commensurate order with a random field. This suggests that in TiSe$_2$, which is a layered system with weak interlayer coupling, Pt dopants can strongly disrupt the long-ranged CDW order. This is consistent with the large heterogeneity in the LDOS measured by STS in the doped samples (Fig. 4c, f, g),
and also provide a possible explanation for the dramatic impact of doping on transport.

The large resistance increase and the transition to an insulating phase suggest a model in which the introduction of Pt in TiSe₂ produces an irregular network of channels as shown by the STM images. Our DFT calculations indicate a large potential difference between Ti and a Pt impurity that substitutes for Ti. The effect of such an impurity on a CDW material is akin to a stone impacting a glass surface and producing cracks. While the understanding of the precise mechanism for the creation of domain walls is left for a future study, our results paint a picture of the consequences of having domain walls after Pt substitution. The STM LDOS indicates that the charge within the self-doped TiSe₂ moves into the domain walls creating a large full gap inside domains and a weaker pseudogap within the domain wall. Thus dc transport occurs primarily via the network of domain walls with the resistance being dominated at the interconnects.

The power-law \( p(T) \) has previously been observed in (quasi-) one-dimensional systems\(^{35–38} \) and was interpreted as due to Luttinger liquid physics. In such a scenario, the power-law suppression of the LDOS should be due to the tunneling of an electron into a system in which the elementary particles are not electrons but fractionalized charge and spin bosonic collective modes. In spite of the suppressed LDOS, the resistance of a clean Luttinger channel vanishes at zero temperature\(^{39} \), except for the contact resistance. This is a singular example of the role of vertex corrections in strongly modifying the transport behavior from that reflected in the single-particle Greens function and LDOS. The observed resistivity \( \rho \sim T^{-\beta} \) in this case then should arise from strong scattering at the interconnects of the network of Luttinger channels created in Pt-substituted TiSe₂—a Luttinger liquid junction formed between intersecting channels can lead to a diverging resistance\(^{40} \).

Networks of metallic domain walls have previously been observed in Cu-intercalated TiSe₂\(^{41} \), and also in other contexts: integer quantum Hall systems\(^{42} \), magnetically ordered systems\(^{43} \), nearly commensurate charge density wave systems\(^{44} \), and also recently in moiré systems\(^{45–48} \) with periodic networks determined by the moiré pattern. Remarkably, power laws have also been observed in the mass transport through a network of dislocations in solid \(^{3} \)He generated by a pressure difference\(^{49} \), suggesting a more ubiquitous occurrence of the network of narrow channel transport. The mechanism for the generation of networks is system-specific—disorder, quench, dislocation, etc. Nevertheless, the transport properties at temperatures below the domain gap scale are determined by the electronic structure of the network, as well as its connectivity. A recent theoretical work shows that a network of Luttinger channels supports a stable insulating fixed point with power-law temperature dependence\(^{50} \).

Let us point out that Luttinger liquid network is not the only explanation for the power-law-like temperature dependence. Another possible mechanism for an insulating behavior with power-law temperature dependence is the “rare chain hopping”\(^{51–56} \), which describes the transport behavior of percolating channels whose resistivity is controlled by the connectivity to the network. It leads to a much weaker \( T \) dependence compared to variable range hopping, which may appear as a power law in a limited temperature range. Nevertheless, the formation of one-dimensional conduction channels is a crucial ingredient in the rare chain hopping model.

In summary, through a collective study of transport, ARPES, and STS, we argue that the low energy insulating behavior in Pt-doped TiSe₂ arises as a result of an interplay between electron correlation and disorder, and is governed by an emergent network of CDW domain walls behaving as narrow channels of low energy transport (see Fig. 1c–e).

Going further, it would be interesting to study whether the MIT mechanism discussed here applies to other systems with CDW. Immediate questions specific to TiSe₂ are how unique is the effect of Pt, and whether other substitutions act similarly. Our preliminary investigations with other substitutions indicate a much smaller increase of resistivity, by less than an order of magnitude, as opposed to the five orders of magnitude increase with Pt.

More broadly, our finding that the CDW domain walls provide one-dimensional channels of transport has implications for other CDW systems. In the Cu-intercalated TiSe₂ where superconductivity and the incommensurate CDW are observed around the same doping\(^{37} \), the domain walls could play a major role by channeling electrons into these narrow channels and thereby enhance correlation effects for superconductivity and magnetism. As was pointed out in ref. \(^{49} \), when the superconductivity coexists with the CDW close to commensurate-incommensurate transition, the network of domain walls can lead to percolative superconductivity.

**METHODS**

**First-principles calculation**

The first-principles band structure and the partial density of states (pDOS) of pure TiSe₂ and PtSe₂ were calculated using the modified Becke–Johnson potential\(^{50} \) as implemented in the WIEN2k package\(^{51} \). Spin–orbit coupling was not included in the calculation throughout this paper. For simplicity in these calculations, we used the experimental lattice constants \( a = 3.537 \) Å and \( c = 6.007 \) Å for TiSe₂\(^{52} \) and \( a = 3.7278 \) Å and \( c = 5.0813 \) Å for PtSe₂\(^{53} \) with the fixed internal coordinate \( c_{se} = 0.25 \) where Ti or Pt is placed on the c = 0 plane.

For the energy comparison between different Pt positions, we optimized the crystal structures using the DFT-D3 energy functional\(^{50} \) as implemented in the Vienna ab initio simulation package\(^{64–66} \). Calculations for the cases (2) and (3) employed the \( 6 \times 6 \times 2 \) supercell.

For the calculation of the onsite energies of the Wannier orbitals, we calculated the band structure of PtTi₁₋ₓSe₂ using the \( 3 \times 3 \times 2 \) supercell, and then extracted the Wannier functions of the Pt-e₉ + Ti-e₉ model using the WIEN2k, WIEN2WANNIER, and WANNIER90 softwares\(^{66–68} \). We omitted the maximal localization procedure. The crystal structure was fixed throughout the calculations for simplicity.

**Growth**

Single crystals of Pt₁₋ₓTiₓSe₂ were grown by chemical vapor transport using excess Se as the transport agent. Stoichiometric amounts of Pt and Ti, as well as Se power with approximately 50% excess Se by mass were sealed in evacuated quartz tubes of approximately 6 inches in length and 0.5 inches in diameter. Samples were heated in a gradient furnace for ten days minimum at a gradient of 900–1100 °C then cooled to room temperature. Reported doping amounts in this study are for nominal compositions.

**ARPES**

Temperature-dependent ARPES measurements on undoped and Pt-doped 1T-TiSe₂ single crystals were performed using a Scienta R4000 electron analyzer at the SIS beamline of Swiss Light Source, Paul Scherrer Institute, Switzerland. The measurements were performed using plane-polarized light with 45 eV photon energies \( (h\nu) \). The energy and momentum resolutions were approximately 10–20 meV and 0.0055 Å⁻¹, respectively.

**STM**

The experiment was performed in an ultrahigh vacuum (UHV) system with a base pressure lower than \( 10^{-10} \) mbar and at a temperature of ~4 K. The samples were cleaved at room temperature and immediately inserted into the STM scanner at 4 K. Differential conductance (dI/dV) spectra were acquired using a standard lock-in technique.

**DATA AVAILABILITY**

All relevant data are available from the corresponding author upon reasonable request.
ACKNOWLEDGEMENTS
K.L. and N.T. acknowledge support from National Science Foundation (NSF) Grant No. DMRF-1629382. J.C., C.L.H., and E.M. acknowledge support from NSF Grant No. DMRF-1629374. D.I., Z.W., and V.M. acknowledge support from NSF Grant No. DMRF-1629098. J.L., J.Z., M.S., J.M., M.Y., and U.C. were supported by the Sino-Swiss Science and Technology Cooperation Grant No. IZLCCZ-170075. R.A. acknowledges the financial support of Japan Society for the Promotion of Science Kakenhi Grant No. 16H06345.

AUTHOR CONTRIBUTIONS
K.L. and N.T. performed theoretical modeling. J.C., C.L.H., and E.M. grew the crystals and performed the transport measurements. D.I., Z.W., and V.M. performed the STM measurements. J.L., J.Z., M.S., J.M., M.Y., and U.C. performed the ARPES measurements. M.O. and R.A. performed the DFT calculations.

COMPETING INTERESTS
The authors declare no competing interests.

ADDITIONAL INFORMATION
Supplementary information is available for this paper at https://doi.org/10.1038/s41535-020-00305-2.

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