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Structure and control of charge density waves in two-dimensional 1T-TaS$_2$

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The layered transition metal dichalcogenides host a rich collection of charge density wave phases in which both the conduction electrons and the atomic structure display translational symmetry breaking. Manipulating these complex states by purely electronic methods has been a long-sought scientific and technological goal. Here, we show how this can be achieved in 1T-TaS$_2$ in the 2D limit. We first demonstrate that the intrinsic properties of atomically thin flakes are preserved by encapsulation with hexagonal boron nitride in inert atmosphere. We use this facile assembly method together with transmission electron microscopy and transport measurements to probe the nature of the 2D state and show that its conductance is dominated by discommensurations. The discommensuration structure can be precisely tuned in few-layer samples by an in-plane electric current, allowing continuous electrical control over the discommensuration-melting transition in 2D.

Significance

The ability to electrically control collective electron states is a central goal of materials research and may allow for the development of novel devices. 1T-TaS$_2$ is an ideal candidate for such devices due to the existence of various charge ordered states in its phase diagram. Although various techniques have been demonstrated to manipulate charge order in 1T-TaS$_2$, a fundamental understanding of the effects is still lacking, and the methods used are incompatible with device fabrication. By using both high-resolution transmission electron microscopy and electronic transport to investigate atomically thin 1T-TaS$_2$ samples, we clarify the microscopic nature of the charge ordered phases in the 2D limit and further control them by all-electrical means.


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is not observed in bulk crystals at this temperature. High-resolution electron microscopy and energy dispersive spectroscopy on fully suspended samples reveal a strong presence of oxidation as well as an amorphous layer on the surface (Figs. S1 and S2). The amorphous oxide (∼2 nm thickness) can be clearly seen atop both surfaces of the 1T-TaS₂ layers in cross section (Fig. 1C, Right). It is possible that oxidation leads to strong surface pinning, which destroys charge ordering in ultrathin samples. Recent resistivity measurements on exfoliated 1T-TaS₂ crystals have also reported the disappearance of CDWs in sufficiently thin flakes (5). It is not clear, however, whether these are intrinsic effects related to dimensionality or extrinsic consequences of oxidation.

To prevent surface oxidation, we exfoliated 1T-TaS₂ crystals within a nitrogen-filled glove box with under 2-ppm oxygen concentration. The flakes were protected by a capping layer of thin hexagonal boron nitride (hBN) before transfer out into the ambient environment (Methods). TEM diffraction performed on these protected samples reveals that CDW formation persists down to the lowest thicknesses measured (2 nm), as we discuss in detail in Fig. 4. This finding indicates that the absence of charge order in ultrathin, uncovered flakes is most likely caused by the effects of oxidation. The study and utilization of CDWs in 2D 1T-TaS₂ thus requires careful sample preparation in inert atmosphere.

The different structural phases of 1T-TaS₂ exhibit distinct electronic transport properties that may be exploited for device applications. In the main panel of Fig. 1B, we show temperature-dependent resistivity of a bulk crystal measured across the NC-C phase transition. Resistivity abruptly increases (decreases) by over an order of magnitude on entering the C (NC) phase. The hysteresis loop between cooling and warming defines the temperature region of metastability between the two phases and can be understood by a free energy picture (Fig. 1D). In a first-order transition, an activation barrier separates the stable energy minima corresponding to the NC and C states. With cooling from the NC phase, both the C state energy and the height of the barrier decrease with respect to the NC energy. When the C state has lower energy, the NC phase becomes metastable, but the system only transitions into the C phase when the activation barrier becomes comparable to the thermal energy. The situation is reversed when warming from the C phase. In oxidation-free 2D samples, this electronic transition is qualitatively unchanged.

Fig. 2A shows an example of hBN-encapsulated 1T-TaS₂ flakes before (Upper) and after device fabrication (Lower). To make electrical contact to the covered samples, we used a technique of edge metallization developed for graphene/hBN heterostructures (Methods) (16). A side-view device schematic is shown in the Inset of the lower panel. In the main panel of Fig. 2B (I = 0, black curve), we plot resistance as a function of temperature for a 4-nm-thick sample measured across the NC-C phase transition. The behavior is similar to that of the bulk crystal (Fig. 1B); however, the hysteresis region between cooling and warming is substantially widened, indicating that one or both of the CDW phases become more metastable.

Metastable phases of a CDW system are generally more susceptible to electronic perturbations, because CDWs directly couple to electric field (6–8, 17). In our device, we observe that continuous current flow stabilizes the NC phase at low temperatures. In Fig. 2B (main panel), we show ac resistance with temperature while also applying a continuous, in-plane dc current, starting at room temperature (300 K). As the dc current I is increased, the resistance at low temperature is monotonically lowered. Concomitant with this trend, the resistance jump resulting from the NC-C phase transition also decreases with increasing I. In the Inset, we plotted the ratio of the resistance difference between cooling and warming, ∆R, to resistance R in the more conducting state at T = 180 K, the temperature in the middle of the hysteresis region, as a function of the dc current level. For I = 35 μA (blue curve in main panel), the NC-C phase transition is completely absent. This measurement indicates that C phase formation in the current driven sample is very different compared with the zero-current, equilibrium condition. Current flow hinders the formation of the C phase and maintains the sample in the more conductive NC state at low temperature. We exclude Joule heating of the sample as a possible explanation by slowly turning off the current at low temperature and verifying that the resistance does not change. We also note that cooling and warming the sample again without dc current flow reproduces the original phase transitions (Fig. S3), indicating that the currents have not damaged the flake irreversibly.
Our observation suggests that it is possible to maintain the NC phase in a temperature region where it is not thermodynamically stable. We now show that the opposite phenomenon is also possible, i.e., we can drive a transition toward the thermodynamically stable state, if we apply an in-plane current after cooling or warming the sample in equilibrium. Fig. 2C shows the current induced phase transitions in the same device (4 nm thickness). Here, we start in the NC phase at room temperature and cool the sample down to 150 K without current flow. At this temperature, although the sample remains in the NC state, the NC phase is now metastable, and the C phase is the thermodynamically stable state. As we increase the voltage across the device (upper panel, dark green curve), the measured current through the device decreases in abrupt steps (marked by red arrows) when it reaches a critical current $I_c \sim 30$ μA (marked by red dashed line). On sweeping the bias current back to zero (light green curve), the device remains in a more insulating state. Warming up the sample after this point produces a temperature curve similar to the C phase, and a transition to the NC phase is observed. We have demonstrated that a bias current applied to the sample can be used to drive the metastable NC phase toward the thermodynamically preferred C state. The dashed green arrow in Fig. 2B marks the direction of this current-induced NC to C phase transition and a free energy schematic of this process is shown in the Inset of the upper panel of Fig. 2C.

Similarly, the metastable C state can also be driven toward the NC phase with current. Here, we start in the C phase at 50 K and warm up to 200 K. The sample remains in the C phase, but now the NC phase is the thermodynamic ground state. As shown in the lower panel of Fig. 2C, sweeping the voltage in this case results in a sharp increase in current and drives the sample toward the more conducting NC state. We have used the dashed orange arrow in Fig. 2B and the free energy picture in the inset of the lower panel of Fig. 2C to represent this opposite C to NC transition. Interestingly, both induced transitions occur when the current reaches about $I_c \sim 30$ μA, indicating that indeed current flow rather than electric field is the underlying mechanism that drives the transition. We repeated this measurement at various temperatures and initial conditions. In all cases, whenever the initial system is metastable, reaching a current threshold of 30 to 40 μA drives the system toward the thermodynamically stable state, regardless of device resistance. In contrast, we observe no induced transition up to 45 μA at 260 K, where a metastable phase ceases to exist.

Taken together, the results of Fig. 2 demonstrate that it is possible to electrically control the NC-C transition in 2D 1T-TaS$_2$, where the temperature region of metastability is significantly enhanced. A more detailed study of this phase transition in 2D samples, however, can provide a better understanding of our experimental observations. The key structural difference between the two CDW phases is the presence of the discommensuration network in the NC phase (Fig. 1B, red inset). The NC-C transition can then be interpreted as a discommensuration-melting transition, which can be significantly affected by dimensionality (18, 19). The discommensurations have a striking effect on the electronic transport properties in 1T-TaS$_2$. The NC phase is an order of magnitude more conductive than the C phase. If we assume that the interior of each commensurate domain has similar transport properties as the C phase, this then implies the discommensuration regions in the NC phase are at least 10 times more conductive than the domain interior (3). Such a view is supported by the fact that the atomic structure within the discommensurations is close to the high-temperature metallic phase (15). With this interpretation, we can use transport measurements to better understand the role of dimensionality on the discommensuration-melting transition.

As the number of 1T-TaS$_2$ layers decreases, the resistivity change corresponding to the NC-C phase transition evolves in a continuous manner down to 2 nm thickness in environmentally protected samples. Fig. 3D shows resistivity as a function of temperature for four hBN-covered 1T-TaS$_2$ flakes, all measured using...
a 1 K/min sweep rate. Their thicknesses are 2, 4, 6, and 8 nm as determined using an atomic force microscope. For comparison, we show data from an unprotected, 20-nm-thick flake, which exhibits characteristics similar to the bulk crystal, indicating that the effects of oxidation are less pronounced in thicker samples. The temperature hysteresis associated with the phase transition between cooling and warming is substantially increased in thinner samples, consistent with our earlier observations of the device in Fig. 2A. The progressive widening of the hysteresis loop continues down to the 4-nm-thick device, below which there is no longer a detectable transition. A guide to the eye for the expansion of this metastable region is shown by the colors in Fig. 3A. In the upper panel of Fig. 3B, we plot $\Delta T = T_{\text{c,warm}} - T_{\text{c,cool}}$ as a function of flake thickness, where $T_{\text{c,warm}}$ and $T_{\text{c,cool}}$ are the experimentally observed NC to C or C to NC transition temperature during the warming or cooling process, respectively. Here, $T_c$ is determined by the temperature at which the first derivative peaks in the temperature sweep. $\Delta T$ is 60 K for the 20-nm flake, slightly larger than that for the bulk crystal (40 K), and grows to 120 K for the 4-nm device. In the same panel, we also plot the average temperature $T_{\text{c,avg}} = (T_{\text{c,warm}} + T_{\text{c,cool}})/2$ of the transition. $T_{\text{c,avg}}$ does not change substantially with thickness and remains between 180 and 190 K, which then implies that lower dimensionality does not stabilize either the NC or C phase. Instead, the NC (C) phase becomes increasingly metastable during cooling (warming) for thinner samples, indicating that the size of the energy barrier separating the NC and C phases increases (Fig. 1D).

Although $\Delta T$ increases when sample thickness is reduced, the resistivity jump associated with the phase transition decreases with decreasing thickness. In the bottom panel of Fig. 3B, we plot the resistivity difference $\Delta \rho$ between cooling and warming at $T = 180$ K, normalized to $\rho$ in the more conductive state as a function of flake thickness. The closed circles are extracted directly from the data in Fig. 3A, whereas the open squares are corrections due to the effects of contact resistance (Fig. S4). For the 20-nm device, resistivity changes by an order of magnitude. The change is smaller for thinner devices and disappears completely for the 2-nm device, which indicates that more conducting NC discommensurations persist at low temperatures for thinner samples, consistent with the larger energy barriers required to remove them. Also, the resistivity jump becomes less abrupt, which is a reflection that the phase transition has slowed, as larger energy barriers generally act also to impede the kinetics of a phase transition. A simple circuit model presented in Fig. 3C allows us to connect the measured resistance jump in the NC-C transition, $\Delta R$, with the estimated density of discommensurations $1/d$ left in the low temperature phase. We assume that the device resistance at low temperature is dominated by conduction through a random network of discommensuration channels (shown as white lines), which is generally sensitive to the particular microstructure formed. However, for device sizes much larger than $d$, we find the resistance with discommensuration channels would be $R \sim p_{\text{DC}} d$, where $p_{\text{DC}}$ is the resistivity per unit length of each discommensuration channel.

We can further substantiate the microscopic picture presented above by providing atomic structural analysis based on TEM. As before, the CDW structure is preserved by environmentally controlled hBN encapsulation. In Fig. 4A, we show diffraction images taken from two 1T-TaS$_2$ flakes of different thicknesses (12 and 2 nm). To highlight their temperature dependence, we have overlaid the diffraction patterns for each flake at 295 K (red peaks) and 100 K (blue peaks), our lowest achievable temperature. Ta Bragg peaks are again connected by a dashed triangle. Multiple scattering from hBN creates additional discernable peaks. The CDW peaks have been circled for easy identification. Although the peaks circled in gray appear qualitatively similar for

![Figure 3](image-url) Dimensional dependence of phase transition—electron transport. (A) Thickness evolution of temperature-dependent resistivity around NC-C phase transition measured on hBN-covered ultrathin samples and 20-nm-thick flake. (B) Average transition temperature and temperature hysteresis (Upper) and normalized resistivity difference (Lower) between cooling and warming as a function of sample thickness. Open squares are corrections from contact resistance (Fig. S4). Hysteresis widens and resistivity difference decreases in thinner samples, whereas average transition temperature remains constant. Resistivity change can be used to estimate the discommensuration density $1/d$ at low temperature. (C) Circuit model of discommensuration network.
both flakes, only the thicker flake displays additional peaks (circled in blue) at 100 K, indicating that it makes the transition to the C phase (compare with blue panel in Fig. 1A), whereas the thinner flake remains in the NC phase. This observation is consistent with our transport data as larger energy barriers in thinner samples require lower temperatures to realize the C phase.

The movement of the gray-circled peaks with cooling (denoted by arrows, Fig. 4A) can be understood more quantitatively with reference to the zoom-in schematic shown in Fig. 4B (Upper Right). The position of this CDW peak is related to the periodicity $D_{NC}$ of the NC domains (Upper Left) by a simple geometric expression (14): $D_{NC} = a/\sqrt{(2\pi\Delta\phi/(360)^2 + (\Delta \lambda/\lambda_{C})^2)}$, where $\Delta\phi$ is the difference in degrees between $\phi$ and $\phi_C = 13.9^\circ$, and $\Delta \lambda$ is the difference between the apparent wavelength averaged over many domains and $\lambda_{C} = \sqrt{13a}$. Thus, as the domain size grows, the NC peaks move closer to the C phase positions. We explicitly measured the position and angle of the CDW wave vectors for these two samples at several different temperatures during cooling to determine the domain period $D_{NC}$ using the expression above. The results are plotted in the lower panel of Fig. 4B. For comparison, we also reproduce STM results obtained by Thomson et al. on the surface of a bulk crystal (14). For bulk samples, $D_{NC}$ grows steadily from 60 to 90 Å on cooling from 340 to 215 K and then jumps to an arbitrarily large value on transition into the C phase at ~180 K. At the same time, the width of the discommensuration regions remains relatively constant (~22 Å) in all of the NC phase (13). As with our transport results, we find that reducing sample thickness suppresses the NC to C phase transition to lower temperatures during cooling and slows the CDW domain growth rate during the transition. For both of the thin flakes, the initial domain size at room temperature is similar to that of the bulk crystal ($D_{NC} \approx 60-70$ Å). $D_{NC}$ increases slightly upon cooling in the NC phase. For the 12-nm flake, the C phase is formed between 100 and 150 K, whereas the 2-nm flake remains in the NC phase even at 100 K. Its domain size here is much larger ($D_{NC} \sim 500$ Å), however, indicating that the phase transition has begun to take place. This result is in clear contrast to bulk samples where the transition is abrupt.

Our transport and TEM measurements both indicate that reduced dimensionality increases the energy barrier separating the NC and C CDW phases and thus widens the metastable region of the phase transition. The transition into the C phase involves melting or removal of the NC discommensuration network. Microscopically, energy barriers to discommensuration motion have been attributed to the presence of defects or impurities in the material, which act to pin them locally (20). Even in nominally pure CDW samples, clusters of localized defects have been observed by STM (21, 22), where the distance between defects is on the order of ~10 nm. In bulk 1T-TaS$_2$, the interlayer stacking of NC domains make the discommensurations walls extended planar objects (15, 23), which are generally more difficult to pin. In two dimensions, however, the discommensurations become lines, which may be more easily immobilized. We have constructed a model of the discommensuration pinning for a 2D system of thickness $t$ (Fig. S5). We find that in the ultrathin limit where $t$ is smaller than the mean distance between impurities, the pinning energy for a discommensuration plane scales as $E_{pin} \sim t^{-2/3}$, corresponding to a cross-over from collective weak pinning to strong individual pinning. These strong pinning centers stabilize the NC discommensuration network at low temperatures during cooling and will also hinder the nucleation and growth of discommensurations when warming from the C phase, thus increasing the temperature region of metastability for both CDW phases in accordance with our experimental observation.

By using this microscopic understanding of the NC-C phase transition in 2D samples, we may further elucidate the role of dc current in the measurements of Fig. 2 B and C. When the sample is cooled in equilibrium starting in the NC phase, the activation barrier between the NC and C states is continuously lowered, and therefore discommensurations are driven away and domain size grows steadily. Near the transition temperature, the small barrier can then be overcome with sufficient current flow, which depins the discommensurations to form the C phase ground state (Fig. 2C). On the other hand, when the sample is cooled out of equilibrium in the presence of a large dc current, it is likely that the domain size does not grow—the activation barrier remains large and the small-domain NC state persists on cooling to the lowest temperatures (Fig. 2B). The dc current is thus effectively a way to control the activation barrier between the NC and C phases.

Although a spatially resolved study is still needed to fully understand these effects, our results have both clarified the nature of the 2D state in 1T-TaS$_2$ and demonstrated clear electrical control over the NC-C phase transition in ultrathin samples, further establishing the material’s relevance for device applications. We also expect our environmentally controlled techniques to be applicable for the study of other 2D transition-metal dichalcogenides that may be unstable under ambient conditions (24).

**Methods**

**Synthesis of 1T-TaS$_2$.** High-quality single crystals of 1T-TaS$_2$ were grown by the chemical vapor transport (CVT) method with iodine as a transport agent. The high-purity Ta (3.5 N) and S (3.5 N) were mixed in chemical stoichiometry and...
heated at 850 °C for 4 d in an evacuated quartz tube. The harvested TaS
powders and iodine (density: 5 mg/cm³) were then sealed in an another quartz tube and heated for 2 wk in a two-zone furnace, in which the source
zone and growth zone were fixed at 900 °C and 800 °C, respectively. The tubes were rapidly quenched in cold water to ensure retaining of the
1T phase.

Device Assembly and Fabrication. We exfoliated thin 1T-TaS² flakes onto SiO₂/Si wafers inside a N₂-filled glovebox containing below 2 ppm O₂ conzen-
tration. Outside the glovebox we separately exfoliated single-crystal hBN
flakes onto SiO₂/Si using a polydimethylsiloxane (PDMS) stamp covered with
polypropylene carbonate (PPC), we picked up thin hBN (<30 nm thickness)
via the method described in Wang et al. (16). This sample was then moved
inside the glovebox. To prepare the 1T-TaS₂ for TEM study, we used the hBN
to again pick up 1T-TaS₂ in situ and then transfer the hBN/1T-TaS₂ stack onto
a TEM chip with a SiN membrane. The chip was then moved outside of the
glovebox and cleaned in acetone, followed by isopropanol.

To prepare 1T-TaS₂ for transport studies, we again exfoliated flakes on
SiO₂/Si inside the glovebox. hBN was used to cap 1T-TaS₂ in a manner similar
to that described above. First, electron beam resist (950PMMA A6, thickness
~300 nm) was used as an etch mask to define the device channel. The pattern
was written using a 30-keV electron beam lithography system with an
exposure dosage between 300 and 450 μC/cm². Afterward, the stack was
etched in an Oxford ICP 80 system using plasma generated from a mixture of
O₂ and CHF₃ gases with a flow rate of 4 and 40 sccm, respectively. This etch
leaves 1T-TaS₂ exposed at the edges of the channel. We found a 1-min etch
time can completely etch away flakes under 10 nm thickness.

A subsequent lithography step was then used to pattern metal electrodes
contacting the 1T-TaS₂ edge. We performed a second identical etch immedi-
ately before metal evaporation (1 nm Cr/50 nm Au) to expose a new edge

SEM/TEM. The conventional TEM experiments, including electron diffraction,
were conducted on a FEI T12 Bio-Twin operating at 80 keV. Temperatures as low
as ~97 K were accessible using a cryogenic specimen stage. A high vacuum en-
vironment and the microscope’s fixed cryo-shields prevented accumulation of ice
on the specimen when held at low temperatures. High-resolution scanning TEM
images were collected on a FEI Tecnai F20 transmission electron microscope
operating at 200 keV with a probe forming semiangle of roughly 9.6 mrad and a
high-angle annular dark-field detector at a camera length of 150 mm.

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