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Modification of two-dimensional charge density wave materials through electrochemical  
intercalation and interfacial interactions

by

Valerie S. McGraw

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor D. Kwabena Bediako, Chair

Professor Naomi S. Ginsberg

Professor James G. Analytis

Spring 2023



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## Abstract

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Charge density waves (CDWs) are periodic distortions in a crystal lattice which arise due to the instability of low-dimensional systems, including two-dimensional (2D) van der Waals (vdW) materials. 2D materials can be tuned through a variety of techniques: the creation of vdW heterostructures by stacking together different 2D materials can finely tune properties of the constituent materials and lead to novel behaviors; and electrochemical intercalation, whereby ions are inserted into the vdW gap, can allowed for controlled tuning of a material's charge carrier density. Both of these techniques for modifying 2D materials offer potential routes towards manipulation of their emergent CDW phases.

Chapter 1 of this dissertation contextualizes the study of CDW materials in terms of broader motivation, theoretical background, and a brief literature review. The integration of CDW materials into computer hardware could someday offer a solution to challenges in computing efficiency. Additionally, manipulation of the correlated electronic phenomena observed in CDW materials could also offer a route to high temperature superconductivity. The mechanisms underlying CDW formation include electron-electron coupling and electron-phonon coupling, which lead to periodic atomic displacements. CDWs can be seen in a variety of 1D and 2D materials, and external perturbations to these materials can be used to manipulate and suppress CDW transitions.

Chapter 2 discusses the creation of van der Waals heterostructures which interface the CDW material  $1T$ -TaS<sub>2</sub> and the non-CDW material  $1H$ -WSe<sub>2</sub>. Temperature-dependent electronic transport measurements show a suppression of the CDW transition temperature in  $1H$ -WSe<sub>2</sub>/ $1T$ -TaS<sub>2</sub> heterostructures compared to  $1T$ -TaS<sub>2</sub> and reveal the TaS<sub>2</sub> thickness-dependence of this effect. Raman spectroscopy measurements demonstrate that interfacial interactions in  $1T$ -TaS<sub>2</sub>/ $1H$ -WSe<sub>2</sub> lead to a significant decrease in intensity of signal from vibrational modes associated with the CDW lattice of  $1T$ -TaS<sub>2</sub>, as well as non-uniform shifts in vibrational frequencies in sufficiently thin samples. Along with Raman spectroscopy, photo-

luminescence spectroscopy is carried out with the aim of uncovering the mechanisms behind this CDW suppression, and indicates that charge transfer between the materials likely occurs; however, the exact nature of the interfacial interaction that leads to CDW suppression remains somewhat elusive.

Chapter 3 explores the modification of rare-earth tritelluride materials  $R\text{Te}_3$ , particularly  $\text{HoTe}_3$  by electrochemical intercalation.  $\text{HoTe}_3$  is synthesized, and characterization by Raman spectroscopy and electronic transport corroborate previous studies of  $R\text{Te}_3$  materials. Electrochemical studies are carried out, allowing the intercalation of  $\text{HoTe}_3$  by  $\text{Li}^+$  to be observed in-situ by optical microscopy, revealing a pattern of several distinct visual changes that occur in  $\text{HoTe}_3$  flakes upon intercalation. A concurrent optical microscopy and electronic transport measurement during intercalation suggests that these visual stages are accompanied by a transition to an increasingly insulating phase and/or possible sample degradation.

Together, these chapters demonstrate two distinct methods to modify 2D CDW materials and the use of multiple experimental techniques to analyze the effects of these modifications. The studies presented here contribute to a broader understanding of tunable properties in 2D CDW materials.

*To past, present, and future members of UAW 2865 and 5810.*

*Solidarity forever.*

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# Chapter 1

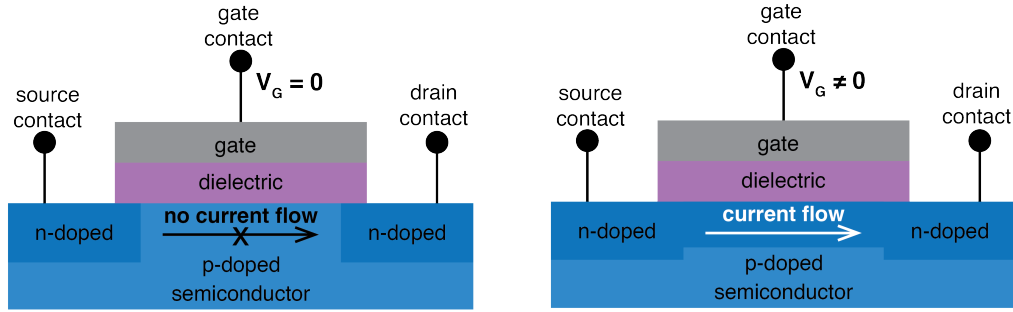
## Introduction

### 1.1 Background

#### Two-dimensional materials

The isolation of graphene from bulk graphite in 2004 sparked a rapidly growing interest in the fascinating properties that can emerge in atomically-thin materials.[1] Graphene possesses high carrier mobilities, thermal conduction, transparency, and flexibility, making it attractive for a variety of technological applications, ranging from computing, sensing, energy storage, and catalysis.[2, 3] The isolation of graphene was possible due to the crystal structure of graphite: graphite is a 2D van der Waals material, wherein atoms within a given layer are held together by covalent bonds, while only weak van der Waals forces bond together separate layers. Following the discovery of graphene, the principle of isolating single (or few) layers from van der Waals materials led to an ever-expanding family of new 2D materials, many of which possess markedly different properties from their bulk analogues. The rich array of available 2D materials provides the opportunity to combine individual layers of different materials into new heterostructures, inspiring the (perhaps overused) metaphor of stacking layers of materials together like Lego bricks. Heterostructures can combine different materials that possess entirely different electronic and/or optical properties from one another to create a new material that exhibits completely distinct behaviors from those of their individual constituent materials.

Due to their “quasi-2D” nature, even bulk van der Waals materials can exhibit phenomena that are not typically observed in bulk, three dimensional materials. One such phenomenon is the tendency for an atomic lattice to undergo periodic distortions known as charge density waves (CDWs) below a transition temperature  $T_{\text{CDW}}$ . The following sections discuss broader motivation for the study of CDW materials, details of CDW formation, notable developments in the history of CDW materials, and experimental techniques used to study CDW materials.



**Figure 1.1:** Schematic of a field-effect transistor. On the left, the transistor is shown in its OFF state, where no gate voltage is applied, and no current flows between the source and drain. The diagram on the right shows the transistor in its ON state, where a gate voltage  $V_G$  is applied, creating an electric field in the dielectric layer, and changing the charge carrier density in the semiconducting channel such that current can flow between the source and drain.

## Motivation for the study of charge density wave materials

### Moore's Law: the end of an era

The energy usage and material resources required to meet our growing demand for computer chips and increasingly complex computing tasks will be both monetarily and environmentally costly. Current computer hardware utilizes field-effect transistor (FET) technology, wherein electric fields control the flow of current through a digital logic circuit. Figure 1.1 shows the basic structure of a FET, which consists of a semiconductor channel between two doped regions, called the source and drain, which are connected to the external circuit. The channel is made of a semiconducting material such as Si or GaAs, and it is doped to create an excess of electrons or holes. The FET also has a third electrode, called the gate, which is separated from the channel by an insulating dielectric layer, such as  $\text{SiO}_2$ . When a voltage is applied to the gate, it creates an electric field that modulates the charge carrier concentration in the channel, controlling the flow of current through the device and creating the on/off states required for digital logic.[4]

Historically, developments in computing technology have followed Moore's Law, an observation that the number of transistors on a microchip doubles every two years. This trend has held true for several decades and has resulted in a remarkable increase in computing power and enabled countless new technologies. However, there are several limitations to Moore's Law that are becoming increasingly apparent as technology advances. The ability to rapidly increase the number of transistors on a chip necessitates increasingly small components, which is now reaching its physical limit as transistors approach the atomic scale.[5] A related observation, Koomey's Law, states that the energy efficiency of computing doubles every 1.5 years. This has allowed for the continued growth of computing power despite the limitations of Moore's Law.[6] However, as the amount of data being processed increases, the

energy required to move that data between processing units and memory also increases. As the limitations of current trajectories in computer hardware become increasingly apparent, our continued technological demands require new paradigms in energy-efficient computing.

### CDWs to the rescue

CDW materials offer an exciting possible alternative to traditional silicon transistor technology. CDW materials undergo phase transitions due to electronic instabilities whereby periodic lattice distortions occur, which are often accompanied by abrupt changes in resistance/conductivity due to the opening of an energy gap. These transitions may allow for modulation between resistance states with low-energy stimuli. CDW distortions are most commonly seen in low-dimensional, anisotropic, materials, which will be explained in greater detail in the following section. The goals of achieving precise tuning and sufficient on/off current ratios between phases have motivated interest in CDW materials among researchers.

Additionally, the correlated electronic behaviors governing the CDW can also give way to superconductivity, further motivating the study of these materials. Current applications of superconductivity, mainly the generation of high magnetic fields, require cryogenic cooling due to very low critical temperatures for superconductivity. The ability to realize high-temperature superconductivity is a major area of research, as superconducting materials that can operate at, or near, room temperature could usher in vast technological advancements such as zero-loss energy transmission in electrical power grids, and the creation quantum bits to store information in quantum computing. Because there exist open questions in the study of CDW and superconducting phase transitions, experiments which probe the modulation of CDW behavior can provide useful insight into precise manipulation of correlated electronic phases towards the application of CDW materials. While the specific CDW systems that are the focus of this dissertation will not likely be implemented in any future technologies, they contribute to a richer understanding of CDW behavior in 2D materials.

## 1.2 Mechanisms of charge density wave formation

CDW distortions arise primarily as a result of electron-electron and electron-phonon interactions. This section aims to synthesize (and simplify) the underlying principles from chemistry and physics that describe the CDW transition. To begin, it is helpful to consider atomic distortions from a molecular chemistry perspective. In the simplest model, we can think of two H atoms, each with one electron. At infinite distance, the electrons both occupy degenerate 1s atomic orbitals. As the atoms are moved closer together, the 1s orbitals will hybridize to form  $\sigma$  bonding and antibonding molecular orbitals, which are lower (bonding) and higher (antibonding) in energy than the atomic orbitals. Both electrons can occupy the  $\sigma$  bonding orbital, lowering the total electronic energy of the system. We next consider the Jahn-Teller effect, commonly seen in octahedral metal-ligand complexes. Jahn-Teller distortions can cause non-uniform elongation or compression of metal-ligand bonds due to splitting

in energy levels of the  $t_{2g}$  and  $eg$  d-orbitals. This breaking of symmetry and degeneracy will lower the energy of the system by pairing electrons in lower-lying orbitals.

## Instability in low-dimensional systems

Next, we use tight-binding theory to understand the instability of a 1D chain of electrons. The following explanation is adapted from Steven H. Simon's *Oxford Solid State Basics* [4] and Reference [7]. We consider an infinite 1D line of equally-spaced atoms, each with 1 electron. With one electron per orbital, electrons can “hop” between orbitals, making this system metallic. Tight-binding theory gives us the energy vs. wavevector dispersion relation:

$$E(k) = \epsilon_0 - 2t \cos(ka) \quad (1.1)$$

where  $E$  is energy,  $k$  is the wavevector,  $a$  is the lattice constant,  $\epsilon_0$  is the energy of an electron at a given atomic site, and  $t$  is the hopping term which describes the energy involved with moving an electron between neighboring atomic sites. Next, we examine the consequences of moving alternating atomic sites by some amount  $\pm\delta x$ . The lattice constant is doubled to  $2a$ , and the hopping parameter  $t$  will no longer be equivalent for an electron hopping between its two neighboring sites. For hopping along the short and long distances, respectively, we have:

$$\begin{aligned} t_{short} &= t(1 + \Delta) \\ t_{long} &= t(1 - \Delta) \end{aligned} \quad (1.2)$$

where  $\Delta$  is the energy for an electron to sit at any given atomic site in this distorted configuration, and it will be proportional to  $\delta x$ . For a half-filled band, there are two equivalent, but distinct, possibilities: (1) an atom at position  $n$  is moved by  $+\delta x$ , an atom at position  $n + 1$  is moved  $-\delta x$ ,  $n + 2$  by  $+\delta x$ , ..., or (2) an atom at position  $n$  is moved by  $-\delta x$ , an atom at position  $n + 1$  is moved  $+\delta x$ , etc. This leaves us a degenerate pair of states, one filled and one unfilled, causing the energy of the filled/unfilled states to be lowered/raised by  $\Delta$ , opening a gap at the Fermi energy. This is known as a Peierls distortion, and it is schematically illustrated in Figure 1.2.

The distortion of a 1D chain will lead to a redistribution of charge density; if we assume a uniform charge density throughout an undistorted chain, such that

$$\rho(\vec{r}) = \rho_0 \quad (1.3)$$

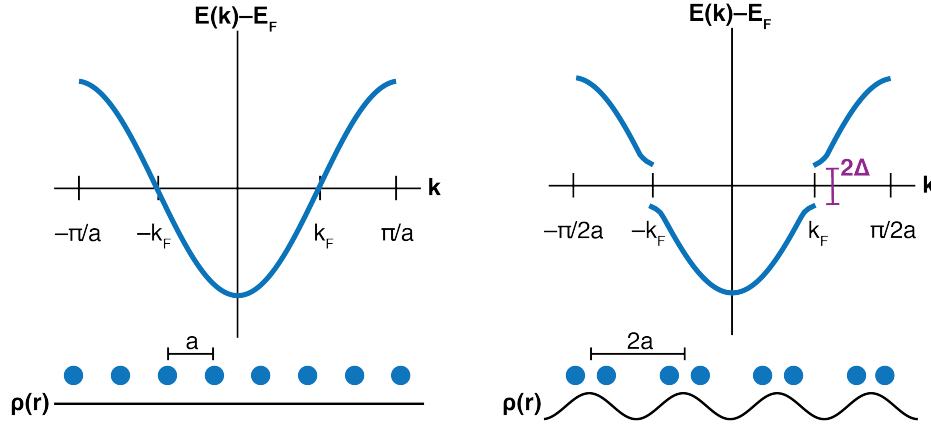
we can then express the charge density of a periodically distorted system as:

$$\rho(\vec{r}) = \rho_0 + \rho_1 \cos(2\vec{k}_F \cdot \vec{r} + \varphi) \quad (1.4)$$

where  $\varphi$  is a phase factor.<sup>1</sup> This redistribution of charge density is also illustrated at the bottom of Figure 1.2.

---

<sup>1</sup>An important consequence of this phase factor is that for an ideal CDW material it imparts the ability for



**Figure 1.2:** Plots of the dispersion relation  $E(k)$  vs  $k$  for an undistorted (left) and Peierls-distorted (right) 1D chain of 1-electron atoms, showing an energy gap of magnitude  $2\Delta$  opening on the right. Schematics showing the charge density as a function of real space  $r$  are included below. Adapted from Reference [7].

Our understanding of the Peierls distortion tells us that we expect an energy gap to open at the Fermi wavevector, leading to a redistribution in charge density. Next, we describe further factors underlying the instability of systems of electrons in 1D. The following is adapted from Grüner's *Density Waves in Solids*. [8] To begin, we consider a  $d$ -dimensional electron gas interacting with a time-independent potential,  $\phi(\vec{r})$  which has the form

$$\phi(\vec{r}) = \int_q \phi(\vec{q}) e^{i\vec{q} \cdot \vec{r}} d\vec{q} \quad (1.5)$$

Working within the framework of linear response theory, which describes the response of a system to an external perturbation, we express the rearrangement of charge density in terms of an induced charge:

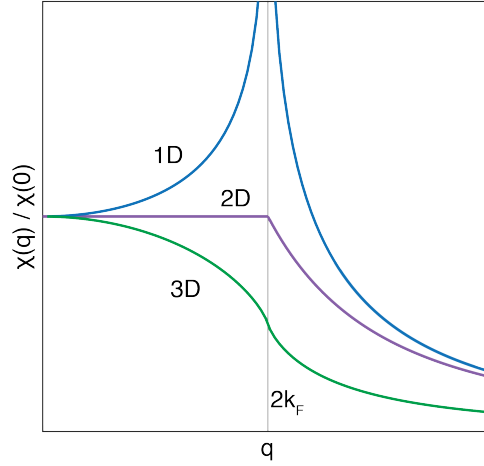
$$\rho^{\text{ind}}(\vec{r}) = \int_q \rho^{\text{ind}}(\vec{q}) e^{i\vec{q} \cdot \vec{r}} d\vec{q} \quad (1.6)$$

and we relate the applied potential to the rearrangement of charge density through the Lindhard response function  $\chi(\vec{q})$ , which is used to describe the interaction of an electric potential with electrons in a solid. We have:

$$\rho^{\text{ind}}(\vec{r}) = \chi(\vec{q}) \phi(\vec{q}) \quad (1.7)$$

---

a CDW to traverse along the direction of  $\vec{q}$ ; a moving CDW will carry current through the material, which can lead to superconductivity. Although we will not give further consideration to these phenomena in our mathematical description of CDWs, we will discuss experimental realizations of current flow through, and emergent superconductivity in, CDW materials in following sections.



**Figure 1.3:** Evaluation of the Lindhard response function in 1D, 2D, and 3D.

with

$$\chi(\vec{q}) = \int \frac{d\vec{k}}{(2\pi)^d} \frac{f_k - f_{k+q}}{\epsilon_k - \epsilon_{k+q}} \quad (1.8)$$

where  $d$  is the number of dimensions,  $\epsilon$  is the energy at a given wavevector, and  $f_k$  represents the Fermi function

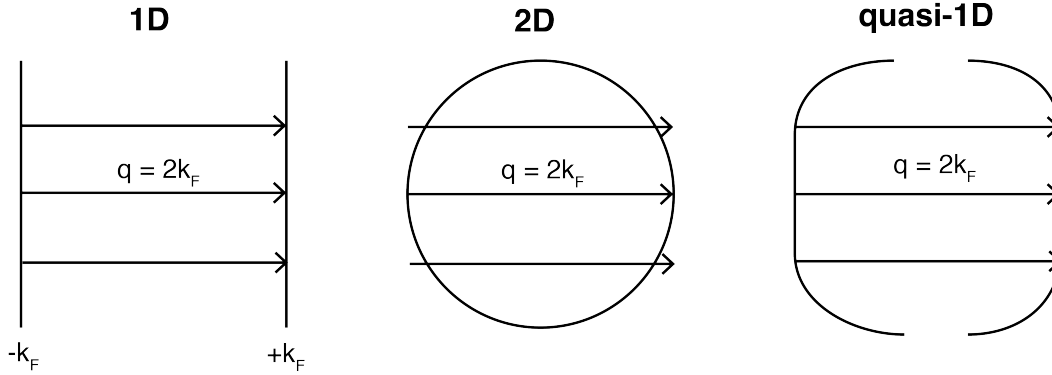
$$f(\epsilon_k) = \frac{1}{1 + e^{(\epsilon_k - \epsilon_F)/k_B T}} \quad (1.9)$$

Evaluating  $\chi(\vec{q})$  provides useful insight into the disparate responses of one-, two-, and three-dimensional electron gases to an applied potential, which becomes important as we consider the interactions of electrons with atomic potentials in an extended solid. Figure 1.3 shows plots of  $\chi(q)$  vs.  $q$ . In 3D, the function varies smoothly with  $q$ ; there is a singularity in its derivative at  $2k_F$ . In contrast, the 1D function diverges at  $2k_F$ .

To better understand the divergent behavior in 1D, we must consider the particular Fermi surface topology for an electron gas of a given dimension. The Fermi surface of a 1D electron gas consists of just two discrete points along a 1D wavevector, with a filled and unfilled state separated by  $q = 2k_F$ . The 2D and 3D Fermi surfaces are a circle and sphere, respectively, with diameter  $2k_F$ ; along a given dimension in  $k$ -space, there will be exactly 2 points (one pair of states) separated by  $q = 2k_F$ . Returning to our expression for  $\chi(\vec{q})$  (Equation 1.8), we see that the mathematical driving force behind the divergence in 1D is pairs of degenerate states where  $\epsilon_k = \epsilon_{k+q}$ , with one filled and one empty state. For the 1D Fermi surface there exists a high density of such pairs,<sup>2</sup> causing  $\chi(\vec{q})$  to diverge. It then follows that the lower density of these pairs of states in 2D and 3D will eliminate the divergent response. The divergent response in 1D leads to a phenomenon called Fermi surface nesting wherein parallel

<sup>2</sup>Neighboring states on the 1D Fermi surface will necessarily be separated by  $2k_F$  because the Fermi surface only contains points at  $+k_F$  and  $-k_F$





**Figure 1.4:** Schematic of Fermi surfaces for a 1D, 2D, and quasi-1D electron gas, showing portions connected by wavevector  $q = 2k_F$ .

points on the Fermi surface will “nest” into one another, creating a periodic distortion in the lattice (i.e., a CDW) that varies the charge density with period

$$\lambda = \frac{\pi}{k_F} \quad (1.10)$$

For an electron gas in 2D and 3D, whose Fermi surfaces are a circle and sphere, respectively, the choice in  $q$ -direction considered thus far can be arbitrary when evaluating  $\chi(\vec{q})$  along a given axis due to their highly symmetric nature. In real materials with different Fermi surface topologies, nearly-perfect Fermi surface nesting can occur along a given axis when there exist parallel portions of the Fermi surface, opening an energy gap at that particular section of the Fermi surface and driving CDW distortions along specific axes. This is depicted in Figure 1.4, which shows the Fermi surfaces of a 1D and 2D electron gas, as well as a 2D Fermi surface with parallel sections which are able to give way to quasi-1D behavior, allowing Fermi surface nesting to occur. While Fermi surface nesting can be the primary driving force behind CDW transitions in some materials, strong Fermi surface nesting is not predicted in some CDW materials. In such cases, electron-phonon interaction is understood to be the driving force for the CDW transition.

## Electron-phonon coupling

The following is also adapted from Grüner.[8] We next consider how electron-phonon interaction can lead to CDW formation. We again will start with a 1D electron gas, but will now include interactions with vibrations of an ionic lattice in our description, and we will use principles of Mean Field Theory to calculate the phonon spectrum for this ideal 1D metal. Some basic assumptions are made for simplicity: most notably, we are considering a system with only small ionic displacements from equilibrium, and we are ignoring terms that arise from effects at the Brillouin zone edge, which we can assume to be far from  $k_F$  (recalling

that we are mainly interested in the behavior at the Fermi surface). We write the Frölich Hamiltonian in second-quantization notation:

$$H = \sum_k \epsilon_k a_k^\dagger a_k + \sum_q \hbar \omega_q b_q^\dagger b_q + \sum_{k,q} g_q a_{k+q}^\dagger a_k (b_{-q}^\dagger + b_q) \quad (1.11)$$

The first term is the simple Hamiltonian for electronic states represented by the creation-annihilation operators  $a_k^\dagger$  and  $a_k$ , which have energy  $\epsilon_k = \hbar^2 k^2 / 2m$  (where  $\hbar$  is the reduced Planck's constant and  $m$  is the mass of the electron). The second term describes lattice vibrations, where  $\omega_q$  are normal mode vibrational frequencies, and  $b_q^\dagger$ ,  $b_q$  are creation-annihilation operators for phonon modes characterized by wavevector  $q$ . Finally, the third term describes electron-phonon coupling, including the interactions of electrons in states  $k$  interacting with phonons of wavevector  $q$ .  $g_q$  is the  $q$ -dependent electron-phonon coupling constant which characterizes the strength of the electron-phonon interaction, and is given by:

$$g_q = i \left( \frac{\hbar}{2M\omega_q} \right)^{1/2} |q| V_q \quad (1.12)$$

where  $M$  is the ionic mass and  $V_q$  is the potential of a single ion in the lattice.

Next, we want to determine the phonon dispersion for this 1D electron gas. By solving the equation of motion for the normal mode coordinates of ionic motion (which we will not show here), and allowing  $g$  to be a constant, independent of  $q$ ,<sup>3</sup> we can obtain the following expression for the renormalized phonon frequency:

$$\omega_{ren,q}^2 = \omega_q^2 + \frac{2g^2 \omega_q}{\hbar} \chi(q, T) \quad (1.13)$$

Notice that this expression includes the Lindhard response function  $\chi(q, T)$  (Equation 1.8), which is both  $q$  and  $T$ -dependent.<sup>4</sup> The maximum value of  $\chi(q, T)$  is at  $q = 2k_F$ ,<sup>5</sup> so we evaluate this expression at  $q = 2k_F$  to better understand the temperature dependence of the phonon frequency. We have:

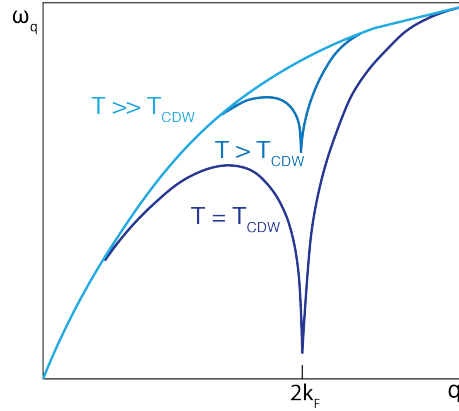
$$\omega_{ren,2k_F}^2 = \omega_{2k_F}^2 - \frac{2g^2 n(\epsilon_F) \omega_{2k_F}}{\hbar} \ln \left( \frac{1.14 \epsilon_0}{k_B T} \right) \quad (1.14)$$

where  $n(\epsilon_F)$  is the density of electronic states at the Fermi level, and  $\epsilon_0$  is a constant. Equation 1.14 allows us to obtain an expression for  $T$  and determine a temperature,  $T_{CDW}$  such that  $\omega_{2k_F} \rightarrow 0$ , leading to a lattice distortion as a result of this “frozen in” phonon.

<sup>3</sup>Gruner does not provide justification for this assumption; presumably, as we are mainly considering phonon behavior near  $k_F$ , it is valid to assume that  $g$  does not vary significantly within a relatively small range of  $q$ .

<sup>4</sup>Recall that  $\chi(q, T)$  includes the  $T$ -dependent Fermi function.

<sup>5</sup>Contrary to our previous encounter with  $\chi(q)$ , where we were dealing with purely electronic effects at  $T=0$ , we are now considering behavior at finite temperature where  $\chi(q)$  no longer diverges at  $q = 2k_F$ .



**Figure 1.5:** Phonon spectra for a 1D metal (Equation 1.14) evaluated for at  $T = T_{\text{CDW}}$ ,  $T > T_{\text{CDW}}$ , and  $T \gg T_{\text{CDW}}$ , showing that  $\omega_q$  approaches 0 at  $q = 2k_F$  for  $T = T_{\text{CDW}}$ .

This type of phonon renormalization was first discussed by Woll and Kohn in 1962,[9] and is referred to as the Kohn Anomaly. Above  $T_{\text{CDW}}$ ,  $\omega_{2k_F}$  will have a finite value. Figure 1.5 shows the phonon spectrum,  $\omega_q$  vs.  $q$ , evaluated at  $T = T_{\text{CDW}}$ ,  $T > T_{\text{CDW}}$ , and  $T \gg T_{\text{CDW}}$ . One can also calculate  $\omega_q$  for electron-phonon coupling in 2D and 3D for  $T = T_{\text{CDW}}$ ; similar to Equation 1.8 (Figure 1.3), less-drastic changes in  $\omega_q$  at  $q = 2k_F$  are observed. In the following sections, we will discuss experimental evidence for CDW transitions in low-dimensional materials.

### 1.3 Examples of charge density wave materials

Experimental evidence for the formation of CDWs exists for a wide variety of materials. This section does not attempt to provide a comprehensive list of these materials, but instead gives an overview of select CDW materials that span an array of structures and behaviors.

From the previous section, it follows that CDW phases are likely to emerge in materials whose conduction of electrons is highly anisotropic, strongly favoring electrons travelling along one crystalline axis which can closely approximate the behavior of 1D metals. Some of the earliest discoveries of CDW materials include those of linear chain compounds, which grow as quasi-one-dimensional crystals that exhibit anisotropic conductivity.[7] One of the simplest examples of a linear chain compound are “Krogmann’s salts,” which contain stacks of the square-planar complex  $\text{Pt}(\text{CN})_4^{2-}$ , and have a typical formula  $\text{K}_2[\text{Pt}(\text{CN})_4\text{X}_{0.3}]$ , where X is usually Br or Cl.[10–13] Modifications to these chains, including changing the overall stoichiometry, replacing the alkali ions, and replacing X with a different atom/molecule, can alter the transport behavior and lead to a CDW ground state, as exemplified by the transport in  $\text{Rb}_{1.75}[\text{Pt}(\text{CN})_4] \cdot 15\text{H}_2\text{O}$  shown in Figure 1.6(a).

Another family of linear chain compounds which are commonly studied for their CDW behavior are the transition metal trichalcogenides  $\text{MCh}_3$ . The earliest electronic transport

measurements on  $MCh_3$  were performed on  $TaS_3$  and  $NbSe_3$ , which revealed CDW transitions, shown in Figure 1.6(b-c). While  $TaS_3$  shows a sharp metal-insulator transition at 210 K that is well-described by a Peierls distortion,[14] the resistance of  $NbSe_3$  shows a steady decrease with temperature, with peaks at two transition temperatures, at  $T_{CDW,1} = 145$  K, and  $T_{CDW,2} = 49$  K.[15] CDWs have since been observed in a variety of other  $MCh_3$  materials. Although these compounds share structural similarities to one another, they can vary in their precise symmetries and bonding, which leads to differences in the nature of their CDW phase transitions. Useful insights can be gained by examining effects of small changes in the material (*i.e.* choice of M, Ch) on the overall electronic behavior.[16, 17]

CDW transitions are also observed in 2D vdW materials. In most 2D CDW transitions, electron-phonon coupling is hypothesized to be the primary driving force behind the CDW distortion due to the complexity of a typical Fermi surface, which limits (but does not wholly prevent) the possibility for Fermi surface nesting.[18] Some of the most well-studied CDW materials are the 2D transition metal dichalcogenides (TMDs), including 1T-TaS<sub>2</sub> which is the subject of study in Chapter 2.

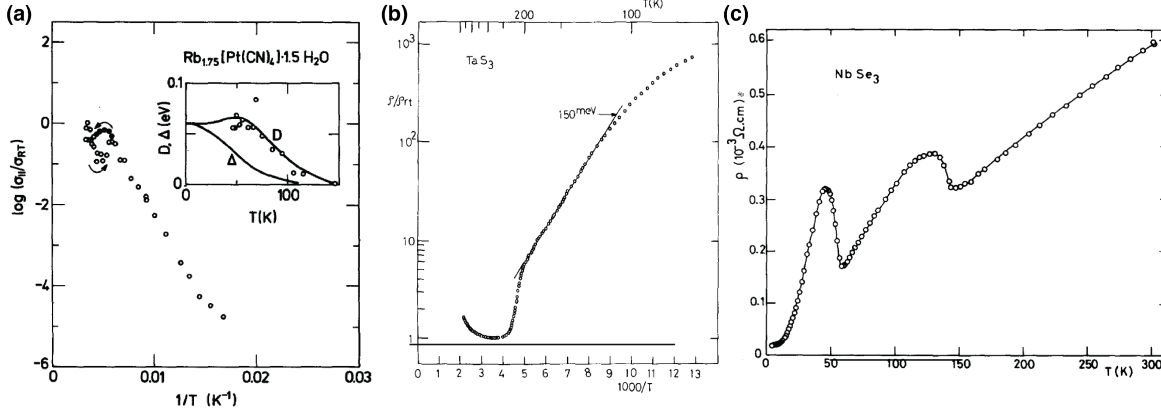
Rare-earth tritellurides ( $RTe_3$ ), which will be discussed in detail in Chapter 3, are 2D CDW materials whose behavior is distinct from the TMDs in that the valence band of  $RTe_3$  is dominated by Te p-orbitals, rather than metal d-orbitals (which is the case for the TMDs); the consequence of this is that the distortion happens mainly in the square net Te layers. Fermi surface nesting is believed to play a significant role in the CDW transition, which consequently occurs along a single axis.[19]

As mentioned earlier, the strong interplay between CDWs and superconductivity is a major motivation for the study of these materials. Some of the most well-known superconducting materials are the cuprates, which are seen as a gateway to high-temperature superconductivity due to strong electron-electron correlations. As the exact mechanisms for unconventional superconductivity in the cuprates remain a topic of intense debate, studies into their rich correlated phase behavior have revealed that some cuprates can host CDW phases, providing insights into the interplay between CDWs and superconductivity.[20–22]

## 1.4 Manipulation and suppression of charge density wave transitions in transition metal dichalcogenides

### Application of pressure and strain

Application of external pressure or strain to a material will alter the nature of electronic interactions with the crystal lattice. Due to the instability of the electron-phonon coupling that drives the CDW transition in some TMDs, CDWs can be enhanced or suppressed when pressure and/or strain is applied. Compressive and tensile strain have been theoretically predicted to suppress and enhance, respectively, the CDW transition in 1T-TaS<sub>2</sub>,[24] and



**Figure 1.6:** Exemplary early transport measurements of inorganic linear chain compounds, showing (a) conductivity vs. temperature in a Pt chain compound  $\text{Rb}_{1.75}[\text{Pt}(\text{CN})_4] \cdot 15\text{H}_2\text{O}$ ; and resistivity vs. temperature in (b)  $\text{TaS}_3$  (c)  $\text{NbSe}_3$ . Reprinted from references [23], [14], and [15] with permissions from Elsevier.

the effects of strain have been shown experimentally to impact the stability of the CDW phase.[25] The application of hydrostatic pressure was shown to suppress the CDW transition in  $1T\text{-TaSe}_2$ , leading to superconductivity at high pressure.[26] Conversely, increased pressure was shown to enhance the CDW transition temperature in  $1T\text{-VS}_2$  from 105 K at ambient pressure to over 300K with applied pressure.[27]

## Electrostatic and electrochemical gating

The ability to control resistivity by low-energy electrical stimuli would make CDWs useful for computing applications. In the CDW TMDs, which are mostly (nearly-)metallic at room temperature, direct electrostatic gating can pose a challenge due to electric field screening effects, but studies have been able to achieve moderate effects of out-of-plane gating on the CDW using thin samples. A number of studies of in-plane electric gating on  $1T\text{-TaS}_2$  have reported to alter the CDW transition behavior, but further studies suggest that this is actually a result of joule heating in the samples.[28] Additionally, electrochemical intercalation of  $\text{Li}^+$  into  $1T\text{-TaS}_2$  has shown to suppress the CDW transition and induce superconductivity.[29]

## Heterostructures and substrate effects

The pressure, strain, charge, and energy transfer that can result from interlayer interactions in heterostructures, or by effects of substrate material, can modify the CDW by similar mechanisms to those discussed above. A study of  $1H\text{-NbSe}_2$  grown by molecular beam epitaxy on different substrates demonstrated that the choice of substrate can profoundly impact the CDW and superconducting transitions of  $1H\text{-NbSe}_2$ . [30] Additionally, two different studies of  $1T\text{-TaS}_2$  interfaced with a non-CDW TMD,  $\text{MoS}_2$ , have been reported: in one study, the

presence of MoS<sub>2</sub> was found to reduce the conductivity of the low-resistance incommensurate CDW state in the 1*T*-TaS<sub>2</sub>/MoS<sub>2</sub> heterostructure. A reduction in the CDW energy gap in 1*T*-TaS<sub>2</sub> was also calculated.[31] Another study found that interfacing 1*T*-TaS<sub>2</sub> with MoS<sub>2</sub> could impact the optical properties of both materials, most significantly in that it led to the appearance of an additional peak in the photoluminescence spectra that is attributed to interlayer charge transfer.[32]

## 1.5 Overview of remaining chapters

The rest of this dissertation proceeds as follows: Chapter 2 contains studies of CDW suppression in 1*T*-TaS<sub>2</sub> through the creation of vdW heterostructures, whereby TaS<sub>2</sub> is interfaced with a semiconducting TMD, 1*H*-WSe<sub>2</sub>. Samples containing standalone and overlapping portions of 1*T*-TaS<sub>2</sub> and 1*H*-WSe<sub>2</sub> are fabricated, and are characterized by electronic transport measurements, Raman spectroscopy, and photoluminescence spectroscopy to study the effects of this interfacial interaction on the CDW transitions in 1*T*-TaS<sub>2</sub> and excitonic transitions in 1*H*-WSe<sub>2</sub>. Open questions which arise from these findings and planned experiments are discussed, as well as possible future related directions to explore.

Chapter 3 contains preliminary work on attempted modification of rare-earth tritelluride materials, particularly HoTe<sub>3</sub>, by electrochemical intercalation. Rare-earth tritelluride crystals are synthesized by flux growth and characterized using basic electronic transport and Raman spectroscopic measurements. In-situ electrochemical measurements are carried out to observe lithium-ion intercalation in HoTe<sub>3</sub> by optical microscopy and Raman spectroscopy. Complications arise due to sample degradation. Future outlooks for this research are discussed.

Together, these demonstrate the investigation of two different methods for the modification of 2D CDW materials, utilizing their 2D nature to impart charge transfer across, and charge doping in, the vdW gap. These studies contribute to a broader understanding of tunable behavior in CDW materials, and the tunability of 2D materials in general.

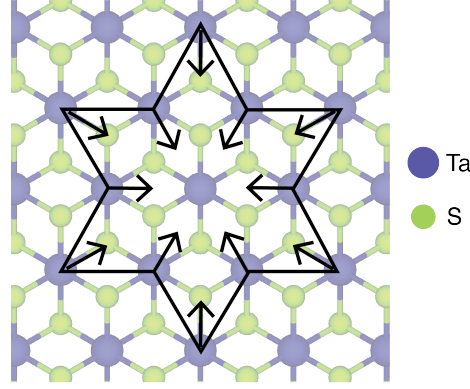
## Chapter 2

# Suppression of charge density waves in tantalum disulfide via interfacial interaction with tungsten diselenide

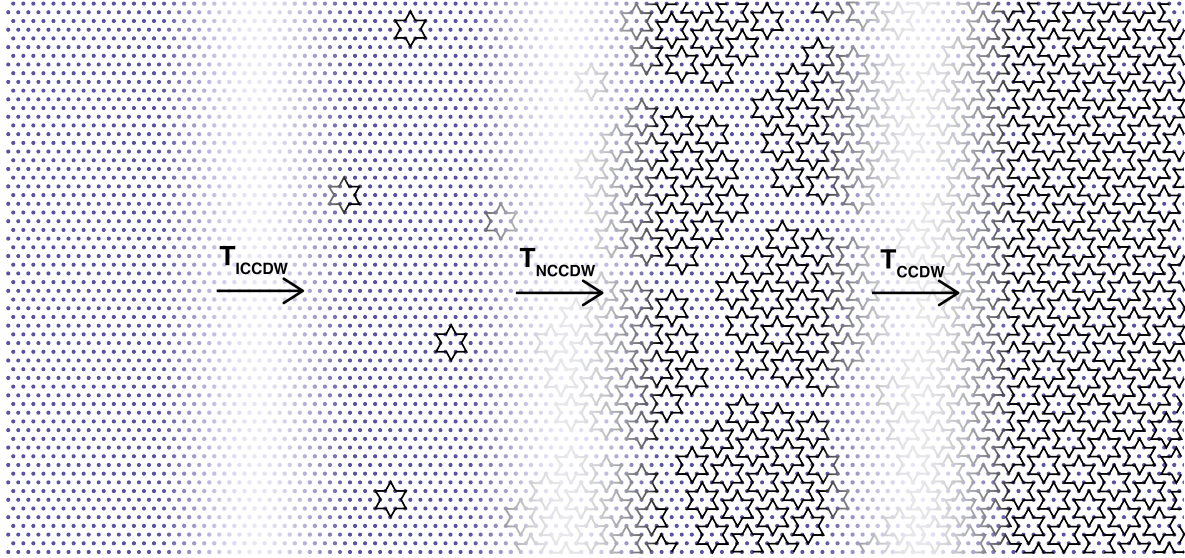
### 2.1 Introduction

Charge density waves (CDWs) are periodic lattice distortions that modulate charge carrier density at the band edge and lead to stark changes in resistivity. CDW states, and their corresponding resistivities, can be tuned using a variety of external stimuli, making CDW systems attractive candidates for next-generation computing applications.[28, 33, 34] Furthermore, CDW phases are known to compete with superconductivity, and thus, a superconducting state can emerge by suppression of a CDW transition.[29, 35] 1T-TaS<sub>2</sub> is a layered van der Waals (vdW) material with a rich CDW phase diagram, exhibiting transitions to incommensurate (IC), nearly-commensurate (NC), and commensurate (C) CDW phases as temperature is decreased below given critical temperatures  $T_{\text{CDW}}$ . During these transitions, “David star” clusters form as groups of 12 Ta atoms contract towards a center Ta, resulting in the formation of a  $\sqrt{13} \times \sqrt{13}$  CDW superlattice. Figure 2.1 depicts the CDW distortion at the atomic level, and Figure 2.2 illustrates the metallic, ICCDW, NCCDW, and CCDW phases and their corresponding temperature-dependent transitions. These phase transitions, especially the NCCDW-CCDW transition, are strongly dependent on crystal thickness: as 1T-TaS<sub>2</sub> approaches the few-layer and single-layer limit, signatures of the NCCDW-CCDW phase transition begin to vanish from charge transport measurements.

In addition to these dimensional effects, CDW behavior in 1T-TaS<sub>2</sub> is highly sensitive to external stimuli such as electrostatic and ionic gating,[29] Se-doping,[36] and externally-applied pressure and strain, which have been used to modulate the CDW transitions and, in some cases, achieve superconductivity. At the 2D interface, interactions including interfacial charge transfer, as well as internal strain, can also lead to modulation of CDW transitions. 2D vdW heterostructures can host moiré superlattices when constituent materials are stacked



**Figure 2.1:** Illustration of CDW distortion in  $1T$ -TaS<sub>2</sub>, showing 12 Ta ions contracting towards a center Ta ion. This distortion results in the formation of a  $\sqrt{13} \times \sqrt{13}$  CDW superlattice.



**Figure 2.2:** Schematic of CDW phase transitions in  $1T$ -TaS<sub>2</sub> showing metallic-ICCDW, ICCDW-NCCDW, and NCCDW-CCDW phase transitions with decreasing temperature. Dots represent Ta ions; S ions are omitted for simplicity.



with a small twist or exhibit a small lattice mismatch, leading to atomic reconstruction to minimize Coulombic repulsion between atoms, which then creates intrinsic strain.[37, 38] A notable example of this is in  $1T$ -TiTe<sub>2</sub>/ $1T$ -TiSe<sub>2</sub> heterostructures, where moiré superlattice formation gives way to substantial enhancement of the CDW in  $1T$ -TiTe<sub>2</sub>. [39]

The possible energetic and structural interactions that can occur between dissimilar vdW layers provide for a rich area of study of these effects in CDW materials. In this work, we create heterostructure samples consisting of multilayer  $1T$ -TaS<sub>2</sub> and monolayer  $1H$ -WSe<sub>2</sub> and investigate the effects of interfacial interactions between  $1T$ -TaS<sub>2</sub> and  $1H$ -WSe<sub>2</sub> on the charge transport of  $1T$ -TaS<sub>2</sub>, phonon modes of  $1T$ -TaS<sub>2</sub>, and excitonic transitions of  $1H$ -WSe<sub>2</sub>.

## 2.2 Electronic transport

### Fabrication of heterostructure devices

To measure the effects of interfacing  $1T$ -TaS<sub>2</sub> with  $1H$ -WSe<sub>2</sub> on electronic transport properties, we fabricate devices using single flakes of TaS<sub>2</sub> that are partially covered by WSe<sub>2</sub> to systematically characterize the interfacial effects of WSe<sub>2</sub>. The device schemes and fabrication methods varied slightly across the different samples, but as we will discuss below, this does not appear to have a significant impact on the observed transport behavior. Two main fabrication schemes are used, one involved prefabricated bottom contacts, wherein hBN/WSe<sub>2</sub>/TaS<sub>2</sub> is stacked directly on top of the contacts; and one involving edge contacts, wherein hBN/WSe<sub>2</sub>/TaS<sub>2</sub> is first stacked, and metal contact is made at the flake edge. A capping layer of hBN is used throughout to protect the TaS<sub>2</sub> and WSe<sub>2</sub> from air exposure which can lead to sample degradation.

### hBN exfoliation

Chips of SiO<sub>2</sub>/Si (with either 90 nm or 285 nm SiO<sub>2</sub>) are cut into approximately 1 cm squares and cleaned for at least 60 minutes in an ozone cleaner at 150 °C. During cleaning, 2-4 hexagonal boron nitride (hBN) crystals (received from T. Taniguchi and K. Watanabe), typically around 0.5-1 mm in diameter, are placed close together onto a piece of Scotch Magic tape, and repeated folding of the tape tessellates the crystals until a sufficiently large portion of the tape is covered by exfoliated hBN. The SiO<sub>2</sub>/Si chips are then removed from the ozone cleaner, and immediately placed onto the tape. Moderate finger pressure is applied intermittently for 10 minutes to press the tape onto each chip and encourage transfer of thin hBN layers from the tape onto the SiO<sub>2</sub> substrate. After this, the tape is peeled swiftly off the chips.

### TaS<sub>2</sub> exfoliation

90 nm SiO<sub>2</sub>/Si chips are ozone cleaned for 30-60 minutes, followed by light O<sub>2</sub> plasma cleaning for 2-3 minutes. Chips are quickly removed from the plasma cleaner and cycled into an Ar glovebox. In the glovebox, chips are placed on a hotplate set to 200 °C for at least 1 hour. Crystals of 1*T*-TaS<sub>2</sub> (HQ Graphene) are stored in the Ar glovebox to prevent degradation. As the chips are heating, a  $\sim 2 \times 2$  mm piece of 1*T*-TaS<sub>2</sub> is placed onto Scotch Magic tape and tessellated. Chips are taken one-by-one off of the hotplate and placed onto the tape. A large amount of finger pressure is applied for 10 minutes, and the tape is swiftly peeled off to (hopefully) yield thin flakes on the SiO<sub>2</sub> substrate.<sup>1</sup>

### WSe<sub>2</sub> exfoliation

285 nm SiO<sub>2</sub>/Si chips are ozone cleaned for 30-60 minutes, followed by light O<sub>2</sub> plasma cleaning for 2-3 minutes. A piece of Gel-Pak 4 polydimethylsiloxane (PDMS) film is cut and stuck onto a glass microscope slide, leaving its protective plastic film on the top surface. Chips are quickly removed from the plasma cleaner and cycled into an Ar glovebox along with PDMS slide. In the glovebox, chips are placed on a hotplate set to 200 °C for at least 1 hour. Crystals of 2*H*-WSe<sub>2</sub> (HQ Graphene) are stored in the Ar glovebox to prevent degradation. The hotplate is turned off, allowing the chips to cool slightly. Meanwhile, a  $\sim 2 \times 2$  mm piece of WSe<sub>2</sub> is placed onto Scotch Magic tape and tessellated. The protective film from the PDMS is removed, and the tape with exfoliated crystals is pressed gently onto the PDMS to transfer flakes. Chips are taken one-by-one off of the hotplate and placed face-down onto the PDMS. Each chip is pressed using a moderate amount of pressure for  $\sim 20$  seconds and then lifted off of the PDMS. The advantage of this PDMS exfoliation method over the method described for TaS<sub>2</sub> is that it tends to yield more (and larger) monolayer flakes. The downsides of this method are that (1) the monolayers will frequently contain wrinkles or tears as a result of the mechanical force required to peel the chips off of the PDMS, and (2) PDMS leaves a residue coating on the top surface of the flake/substrate. The interface between the bottom of the flake and the substrate should not have any residue, so when WSe<sub>2</sub> is picked up and stacked on top of TaS<sub>2</sub>, a clean WSe<sub>2</sub>-TaS<sub>2</sub> interface can still be achieved.

### Stacking of heterostructures

Thin flakes of hBN, monolayers of 1*H*-WSe<sub>2</sub>, and 1*T*-TaS<sub>2</sub> flakes of a desired thickness were identified by optical contrast.[40] WSe<sub>2</sub> and TaS<sub>2</sub> flakes tend to cleave along the lattice planes, so flakes with clearly defined 60° edges were prioritized in order to align (or misalign) the flake during stacking. Due to the risk of sample degradation, TaS<sub>2</sub> flakes were exfoliated less than 48 hours, ideally less than 24 hours, before stacking. For the bottom-contact

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<sup>1</sup>Samra Husremović perfected this exfoliation method and performed the TaS<sub>2</sub> exfoliation for some of the samples studied here.

samples, it was crucial to identify flakes of TaS<sub>2</sub> which contained a sufficiently large region of uniform thickness such that electrical contact would only be made, and current would flow, across a uniform sample of TaS<sub>2</sub>. For the edge contact devices, reactive ion etching was used to remove non-uniform sections of the flake, leaving a uniform channel for transport measurements.

hBN/1H-WSe<sub>2</sub>/1T-TaS<sub>2</sub> stacks were formed via a dry transfer method using a home-built micro-manipulation stage in an Ar glovebox.[41] This method is carried out by carefully melting a polymer “stamp” over a flake to lift it off the SiO<sub>2</sub> substrate. The stamp is prepared as follows: A 5% w/w solution of poly(bisphenol A carbonate) (PC, Sigma Aldrich) in chloroform (Lab Chem) is pipetted onto a glass slide. Another slide is placed on top and pulled away, leaving a thin puddle of the PC solution on both slides. Heating the slides at 115 °C for 1-3 minutes causes the solvent to evaporate, leaving a dry film of PC on the slides. A square of PDMS ( $\sim 4 \times 4$  mm) is cut and placed on a (separate) glass slide. The slides with PC film are removed from the hotplate, and a razor blade is used to slice the film into small rectangles ( $\sim 1 \times 2$  mm). A rectangle of PC is carefully placed on top of the PDMS.<sup>2</sup> The slide containing the stamp is secured face-down in the micro-manipulator, and a chip containing an hBN flake is placed on a temperature controlled stage. While the exact temperature conditions for stacking can vary, typically, to pick up hBN, the stage is heated to 80 °C. The stamp is carefully lowered until the PC just touches the substrate, but not the flake. The stage is slowly heated to 120 °C, causing the PC to melt over the flake. The sample is cooled, causing the PC to contract and lift the flake from the chip. The stamp is then lowered over a chip containing a WSe<sub>2</sub> flake, aligning the hBN over the WSe<sub>2</sub>, and a similar melting/cooling process is used to pick up the WSe<sub>2</sub> with the PC/hBN. Next, the stamp is lowered over the TaS<sub>2</sub> flake, making sure to carefully align the hBN/WSe<sub>2</sub> over the TaS<sub>2</sub>. For the edge contact samples, the stamp is melted over the flake by heating the sample to 160 °C, allowing the PC to fully melt and release from the PDMS onto the chip. For the bottom contact samples, the stamp is melted over the TaS<sub>2</sub> to a relatively high temperature (140-160 °C) and then quickly cooled to pick up the TaS<sub>2</sub>. The chip containing bottom contacts is lightly plasma cleaned for 3 minutes immediately before cycling into the glovebox; the stamp is then melted to 160 °C and released to place the stack on top of the bottom contacts.<sup>3</sup> Following release of the PC stamp, the chip is slowly cooled then taken out of the glovebox and placed in chloroform under ambient atmosphere for 1-2 hours to dissolve the PC film; the chip is then removed from the chloroform, quickly rinsed with isopropanol, and dried with a flow of N<sub>2</sub>.

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<sup>2</sup>This will typically take several tries, as a flat PC stamp, free of bubbles, folds, or dirt, will melt more controllably, with decreased risk of falling off of the stamp.

<sup>3</sup>For most dry-transfer stacking procedures, it is helpful to release the stamp at 180 °C; however, Husremović et al found that heating past a certain temperature can cause the formation of “mirror domains” in 1T-TaS<sub>2</sub> which leads to abnormal behavior.[42] To prevent this, along with other degradation, we aim to minimize sample heating.

### Bottom contact fabrication

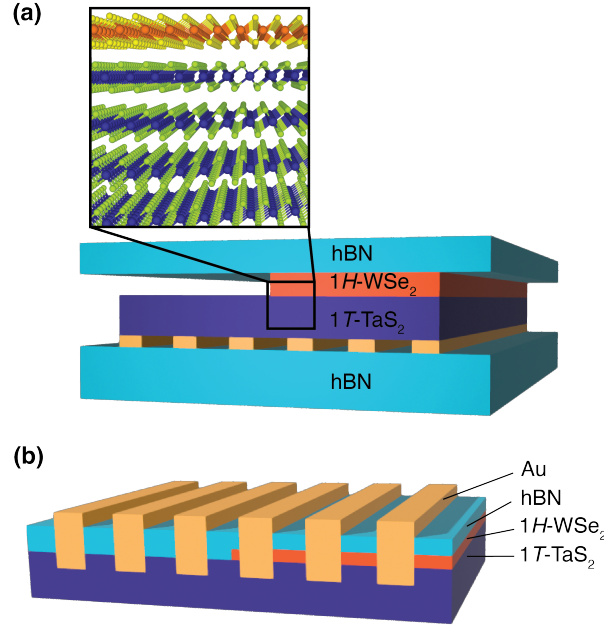
Prefabricated bottom contacts were made as follows: 10-30 nm flakes of hBN with uniform, flat surfaces were identified by optical microscopy and characterized by atomic force microscopy. Electron-beam lithography (Crestec CABL-UH Series Electron Beam Lithography System) was used to define electrical contacts on the hBN. Thermal evaporation (NRC thermal evaporator) or electron-beam evaporation (Electron Beam 10 kW 6-pocket Evaporator) was used to deposit thin films of 0.5 nm/7-10 nm Cr/Pt or Cr/Au. To lift off the excess Cr/Au, the chip was submerged in acetone overnight. The choice of metal did not impact the measurements, however, Pt is preferred as it tends to lift off cleanly, and can be annealed prior to stacking. For the 6- and 8-layer devices, the contacts were first patterned such that the contacts were only in the very center of the hBN flake, with flake edges exposed prior to stacking, creating a fully hBN-encapsulated stack. After stacking, electron-beam lithography was used to pattern connections to the bottom contacts, etching into the stack by reactive ion etching with  $\text{SF}_6/\text{O}_2$ , immediately followed by thermal evaporation of 0.5 nm/100 nm Cr/Au. For the 26 L device, the complete set of contacts (including thin contacts on hBN and thick contacts at the flake edge/contact leads) were evaporated prior to stacking such that no additional etching or evaporation was required. For this sample, the PC film was not dissolved, adding extra protection from air exposure. While the first method is in theory preferable as a means to minimizing air exposure, the second method accomplishes this equally well (if not better) by minimizing further fabrication between stacking and measurement.

### Edge contact fabrication

15- and 18-layer devices were fabricated by creating edge contact to the  $\text{TaS}_2$  flakes, as described in References [41, 43]. Following stacking, electron-beam lithography was used to define contact patterns across the stack. Reactive ion etching by  $\text{CHF}_3/\text{O}_2$  was used to etch into, but not all the way through, the  $\text{TaS}_2$ , which was quickly confirmed by optical microscopy. Immediately following, the chip was placed under vacuum in a thermal evaporator, and Cr/Au (0.5 nm/100 nm) was evaporated. To lift off the excess Cr/Au, the chip was submerged in acetone overnight. Electron-beam lithography was again used to define a suitable device channel to remove non-uniform portions of the flakes, including thinner/thicker  $\text{TaS}_2$ , or thicker  $\text{WSe}_2$ , which were etched away with  $\text{SF}_6/\text{O}_2$ . While this method briefly exposes the edges of the device to air, the Au/ $\text{TaS}_2$  contact region had minimal air exposure.

### Transport signatures of CDW suppression

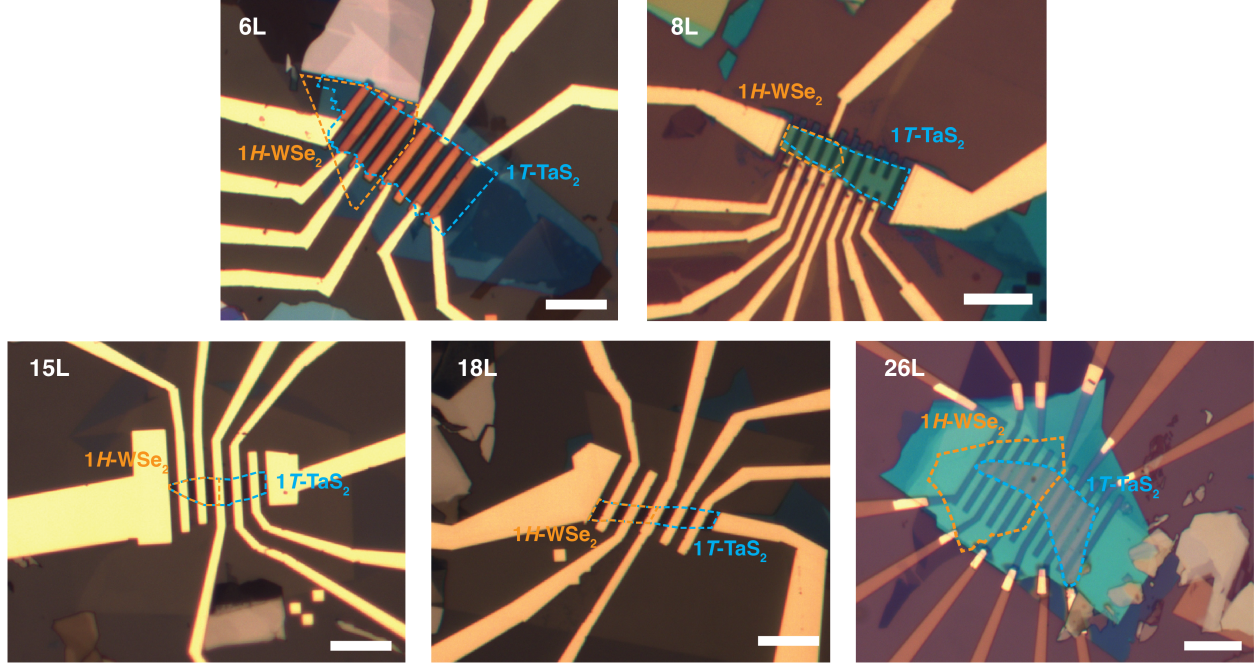
Electronic transport measurements were performed to characterize the effects of interfacial interaction with  $\text{WSe}_2$  on the transport behavior of 1T- $\text{TaS}_2$ . Temperature-dependent longitudinal resistance ( $R_{xx}$ ) was measured in 1H- $\text{WSe}_2$ /1T- $\text{TaS}_2$  heterostructure samples containing 6-, 8-, 15-, 18-, and 26-layer 1T- $\text{TaS}_2$  using conventional lock-in techniques. A



**Figure 2.3:** Schematics of (a) bottom contact and (b) edge contact devices. The magnified view in (a) depicts monolayer WSe<sub>2</sub> stacked on multilayer TaS<sub>2</sub>. The image in (b) is intended as a cutaway view of the edge contact device; the metal contacts will extend downward over the flake edge.

constant alternating current of 0.1-0.5  $\mu\text{A}$  (17.777 Hz) was applied between source and drain contacts, one of which was located on the TaS<sub>2</sub> side and the other located on the TaS<sub>2</sub>/WSe<sub>2</sub> junction side. The 2-probe voltage drop was measured between the source and drain contacts, and 4-probe  $V_{xx}$  was measured between pairs of contacts fully contained on either side of the device using a lock-in amplifier (Stanford Research SR830). All measurements were performed in a Quantum Design Physical Property Measurement System (PPMS). Due to the relatively large bandgap of WSe<sub>2</sub> compared to 1T-TaS<sub>2</sub>, we assume that WSe<sub>2</sub> does not contribute significantly to the measured transport behavior.

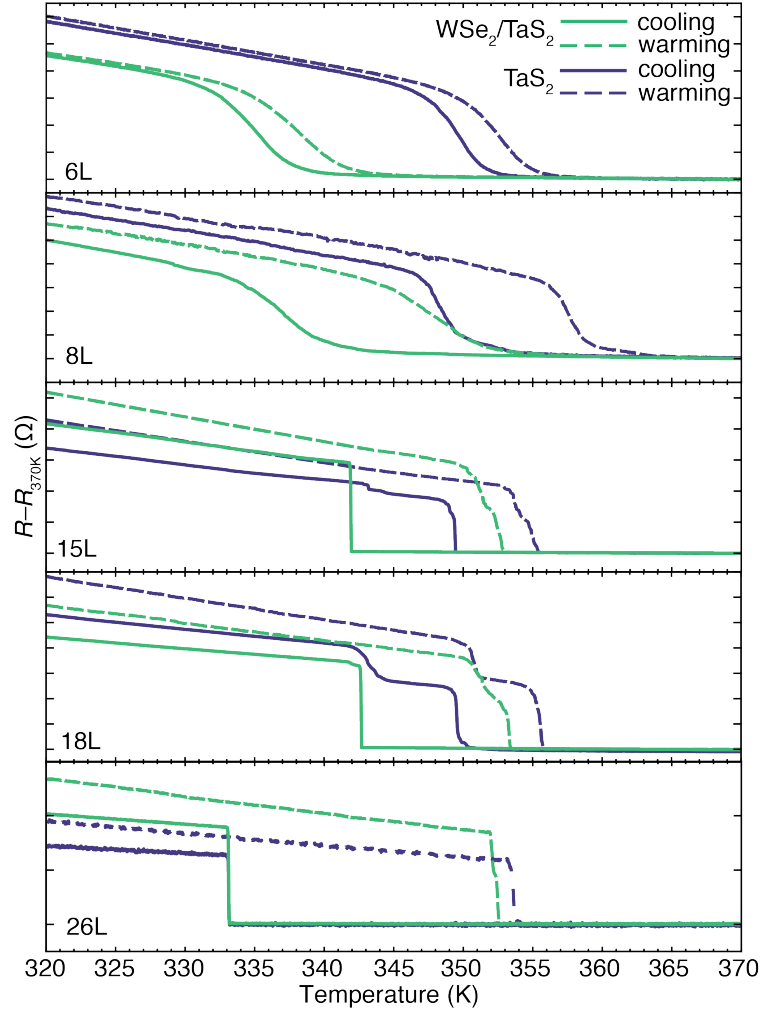
Figure 2.5 shows temperature-dependent transport data between 320-370 K for samples of different TaS<sub>2</sub> thickness, acquired from 370-50-370 K using a 1 K/min cooling/warming rate; this temperature range and relatively low sweep rate should, theoretically, allow the 1T-TaS<sub>2</sub> to fully transition between its ICCDW, NCCDW, and CCDW phases. At 370 K, 1T-TaS<sub>2</sub> is in the nearly metallic ICCDW phase, and relatively little change in resistance is observed within this temperature range. As the sample is cooled, we observe a sharp change in resistance, associated with the ICCDW-NCCDW transition. In all samples, with the exception of the 26-layer sample, the ICCDW-NCCDW transition is measured at lower temperature in WSe<sub>2</sub>/TaS<sub>2</sub> junction than in the standalone TaS<sub>2</sub>, indicating that interaction with WSe<sub>2</sub> suppresses the CDW transition; this effect is illustrated in Figure 2.7. Additional temperature-dependent  $R_{xx}$  measurements were performed on the 6 and 18-layer devices



**Figure 2.4:** Annotated optical micrographs of devices.  $\text{TaS}_2$  thickness (number of layers) is labeled on each image,  $\text{TaS}_2$  and  $\text{WSe}_2$  flakes are outlined in blue and orange, respectively. White scale bar on each image is  $10 \mu\text{m}$ . Note that all heterostructure stacks are capped with hBN, and the 6-, 8-, and 26-layer devices have hBN on the bottom.

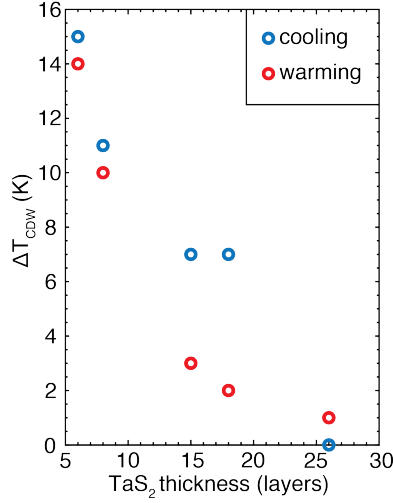
using 0.5, 2, and 5 K/min cooling/heating rates. While the precise transition temperatures and hysteresis widths shifted slightly with different sweep rates, we observe no significant effects of heating/cooling rates on the ICCDW-NCCDW transition in these samples. Figure 2.6 summarizes the difference in  $T_{\text{CDW}}$  on the two regions of the device during both heating and cooling at 1 K/min.  $\Delta T_{\text{CDW}}$  decreases monotonically with increasing  $\text{TaS}_2$  thickness, showing that the effect of interfacial interaction with  $\text{WSe}_2$  can only be detected by electronic transport in  $1T$ - $\text{TaS}_2$  crystals thinner than  $\sim 26$  layers. These shifts in the ICCDW-NCCDW transition are similar to those observed as a result of lithium intercalation and Se doping.[29, 36] DC current-voltage measurements of  $1T$ - $\text{TaS}_2$  grown by chemical vapor deposition (CVD) on  $\text{MoS}_2$ . [31]

Beyond the observed pattern of thickness-dependent CDW suppression by  $\text{WSe}_2$ , subtle differences are present among these transport data, namely variation in hysteresis widths across different-thickness samples and apparent two-step CDW transitions in the 15-layer and 18-layer samples that are not present in the other samples. We first note that, owing to the different device fabrication methods used, each sample likely experiences varying degrees of external (macroscopic) strain from substrate and/or contact morphology, resulting in differential “pinning” of the CDW phases. Pinning, here, refers to the tendency of a given CDW phase to resist undergoing a phase transition; in this case, pinning is caused by applied

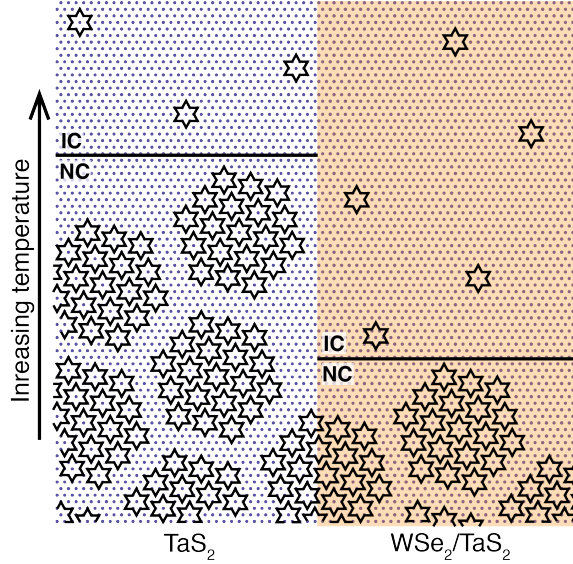


**Figure 2.5:** Longitudinal resistance measured between 320-370 K of  $1H$ - $WSe_2/1T$ - $TaS_2$  devices containing 6-, 8-, 15-, 18-, and 26-layer  $TaS_2$  covered partially by  $WSe_2$ ; data are shown for  $TaS_2$  standalone and  $WSe_2/TaS_2$  heterojunction sides of each device. Solid and dashed lines show data acquired during cooling and warming, respectively. Y-axis tick scale is 100 Ohm for all plots, except for that of the 8L device where the scale is 500 Ohm.





**Figure 2.6:** Difference in  $T_{CDW}$  measured on TaS<sub>2</sub> standalone and WSe<sub>2</sub>/TaS<sub>2</sub> hetero-junction sides of each device vs the number of TaS<sub>2</sub> layers.  $\Delta T_{CDW}$  is shown for both ICCDW-NCCDW (cooling) and NCCDW-ICCDW (warming) transitions.



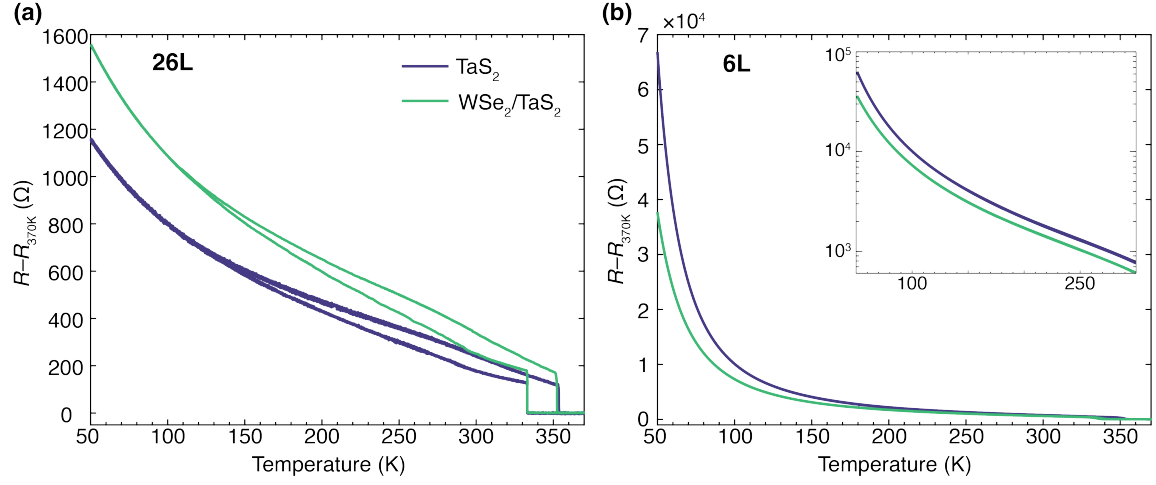
**Figure 2.7:** Schematic illustrating disparate NCCDW-ICCDW transition temperatures in hBN/1H-WSe<sub>2</sub>/1T-TaS<sub>2</sub> devices, where 1T-TaS<sub>2</sub> undergoes a NCCDW-ICCDW at a lower temperature in hBN/1H-WSe<sub>2</sub>/1T-TaS<sub>2</sub> compared to hBN/1T-TaS<sub>2</sub>.



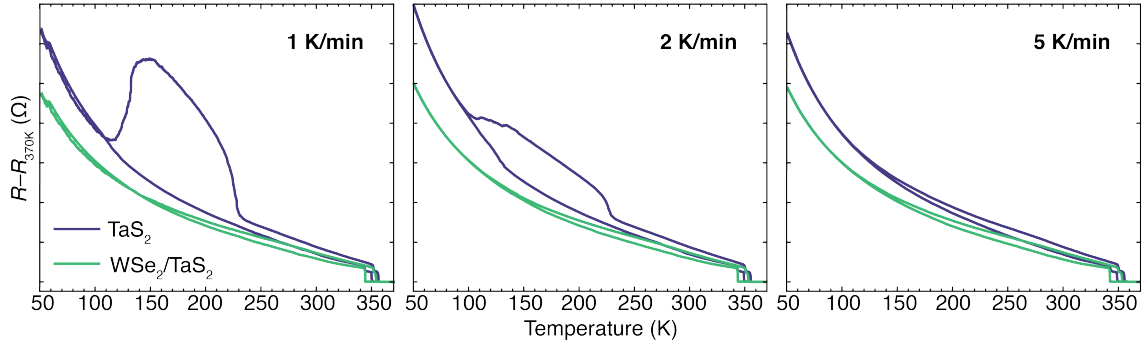
strain, which can raise the energy barrier for the atomic rearrangement that accompanies a CDW phase transition.[44] We posit that pinning phenomena can be implicated in the abnormal transport behavior observed in the 18-layer TaS<sub>2</sub> device (and observed to a lesser degree in the 15-layer device), wherein  $R_{xx}$  measured on the standalone TaS<sub>2</sub> region of the device shows both a larger jump in  $R_{xx}$  occurring at a higher temperature than in the WSe<sub>2</sub>/TaS<sub>2</sub> heterojunction, and a smaller jump occurring at a nearly identical temperature to the heterojunction. As noted above, the 18- and 15-layer TaS<sub>2</sub> devices were fabricated with edge, rather than bottom, contacts, meaning a sample could experience increased strain at the edges of the flake, causing pinning that temporarily persists across both sides of the sample, leading to two-stage CDW transition behavior. Replicate measurements on a similar heterostructure with the bottom contact scheme used in other devices will be carried out in the near future to verify whether this is indeed an effect of device morphology. Although variance in the ICCDW-NCCDW hysteresis width of 1 *T*-TaS<sub>2</sub> from applied strain has been observed,[44] thickness-dependent studies on thin flakes of 1 *T*-TaS<sub>2</sub> also measure non-monotonic variance in ICCDW-NCCDW hysteresis widths.[29, 45] All parts of each device should experience pinning of the same nature throughout, and thus we comment on the relative behavior of the two sides of the device. That the thickest and thinnest samples were fabricated by similar means (compared to the medium-thickness samples) lends support to our conclusion that interfacial interaction with WSe<sub>2</sub> suppresses the ICCDW-NCCDW transition in thin 1 *T*-TaS<sub>2</sub>, and other external variables are unlikely to explain this observation.

While changes in the ICCDW-NCCDW transitions of 1 *T*-TaS<sub>2</sub> and WSe<sub>2</sub>/TaS<sub>2</sub> are readily apparent, the effects of interfacial interaction on the lower temperature NCCDW-CCDW transition cannot be observed in these measurements, owing to the fact that this transition is known to become suppressed in transport measurements of thinner samples of 1 *T*-TaS<sub>2</sub>. [29, 43, 45] Similar to these previously-reported transport measurements of 1 *T*-TaS<sub>2</sub>, these samples do not exhibit a sharp transition to the CCDW phase, instead showing a smooth, rapid, increase as the sample is cooled. Figure 2.8 shows transport behavior over the 50-370 K range for the 6-layer (thinnest) and 26-layer (thickest) devices. Although a sharp transition is not observed, hysteretic behavior  $R_{xx}$  below the  $T_{\text{NCCDW}}$  behavior becomes more prominent in the thicker samples. Additionally, an abrupt transition to the CCDW phase was observed around 130 K in the 18-layer TaS<sub>2</sub> device upon warming from 50K; this  $R_{xx}$  vs temperature profile has been observed previously in transport measurements of moderately-thin TaS<sub>2</sub>. [29, 45] Similar to previous reports, we could suppress this transition by increasing the temperature sweep rate from 1 K/min to 5 K/min, as shown in Figure 2.9. Notably, these sharper transitions to the CCDW phase were only measured on the standalone TaS<sub>2</sub> portions of the device and were absent in the WSe<sub>2</sub>/TaS<sub>2</sub> heterojunction; however, we cannot definitively comment on the role of WSe<sub>2</sub> in suppressing this transition, as it was also not measured uniformly throughout the standalone TaS<sub>2</sub> portion of the device.

Overall, the transport measurements carried out here show that interaction with WSe<sub>2</sub> has a significant impact on  $T_{\text{CDW}}$  for the ICCDW-NCCDW (and NCCDW-ICCDW) transition in thin 1 *T*-TaS<sub>2</sub>, up to approximately 26 layers. While temperature-dependent transport



**Figure 2.8:** Plots of longitudinal resistance vs temperature between 50-370 K, showing warming and cooling scans measured on both sides of (a) 26-layer and (b) 6-layer device. Inset in (b) shows data between 50-300 K plotted with a logarithmic scale on the y-axis.



**Figure 2.9:** Temperature sweep rate comparison of 18-layer device, showing  $R$  vs  $T$  for  $T = 50 - 370$  K at sweep rates of 1 K/min, 2 K/min, and 5 K/min.

measurements are an excellent way to accurately measure  $T_{\text{CDW}}$ , they do not provide detailed insight into the mechanisms governing this behavior. In the following sections, we discuss spectroscopic methods carried out in order to further characterize the electronic and structural consequences of interlayer interaction between  $1H$ - $\text{WSe}_2$  and  $1T$ - $\text{TaS}_2$ .

## 2.3 Optical studies

### Raman spectroscopy

Raman spectroscopy (Horiba Multiline LabRam Evolution) was conducted using 633 nm continuous wave laser with an ultra-low frequency filter. Spectra were typically collected with 50–80  $\mu\text{W}$  power and an 1800 gr/mm grating, with 20 second acquisition times and 2-4 accumulations; spectra which are directly compared were acquired with identical parameters. For temperature dependent measurements, samples were secured in an optical cryostat (Cryo Industries of Amercia), which was evacuated to  $\sim 10^{-6}$  torr and cooled with liquid nitrogen. The samples were placed with thermally conductive vacuum grease onto a copper puck, which is temperature controlled using resistive heating (LakeShore Cryotronics Model 325). Due to fluctuations in the system, temperatures reported throughout are accurate to  $\pm 5$  K. The laser beam was focused on the sample into a spot size of approximately 1  $\mu\text{m}$ , although some defocusing is expected in temperature-controlled measurements due to the optical cryostat window. Heterostructure stacks for spectroscopic measurements were fabricated by similar methods to those of the transport samples, excluding the electrical contacts. All samples for optical studies were fabricated on a 90 nm  $\text{SiO}_2/\text{Si}$  substrate, which helps enhance the otherwise weak signal obtained from  $\text{TaS}_2$ . Exposure to the laser beam can heat the sample and cause damage, especially in stacks that are capped, rather than fully-encapsulated, with hBN when spectra are acquired in ambient conditions; the 3-layer sample studied here was fully encapsulated by hBN while the 6-layer sample was not.

Figure 2.11 compares room temperature Raman spectra of an hBN encapsulated stack of  $\text{WSe}_2/\text{TaS}_2$  with monolayer  $\text{WSe}_2$  and 3-layer  $\text{TaS}_2$ . Spectra on each region were acquired with the same excitation power and acquisition parameters, allowing for comparison of peak intensities as well as frequencies. We begin by comparing the  $\text{WSe}_2$  and heterojunction spectra. In the  $\text{WSe}_2$  spectrum, the  $E_{2g}^1$  and  $A_{1g}$  vibrational modes, which are well characterized for the family of  $2H$  TMDs, are observed as closely spaced peaks around 257 and 261  $\text{cm}^{-1}$ , and arise from in-plane and out-of-plane motion, respectively, of the chalcogen ions relative to the metal ions. Due to the excitation wavelength used here, additional peaks are observed in the spectrum which arise from resonant excitations of  $\text{WSe}_2$ . [46] No significant shifts in peak frequencies are observed between the  $\text{WSe}_2$  and  $\text{WSe}_2/\text{TaS}_2$  spectra. The peaks from the  $E_{2g}$  and  $A_{1g}$  modes decrease in intensity in the heterojunction spectrum, while there are no apparent reductions in peak intensities from the resonant modes. The decreased sharpness of the  $E_{2g}$  and  $A_{1g}$  peaks is likely caused by convolution with a peak at a similar frequency in the  $\text{TaS}_2$  spectrum.

The Raman spectrum of  $1T$ - $\text{TaS}_2$  shows a series of low-intensity modes above 200  $\text{cm}^{-1}$ , and higher-intensity modes below 150  $\text{cm}^{-1}$ . The low-intensity peaks between 200–400  $\text{cm}^{-1}$  are comprised of several closely-spaced modes; peaks measured near 228 and 241  $\text{cm}^{-1}$  have been calculated to arise from in-plane  $E_g$  vibrations of the S relative to the Ta; the peak near 380  $\text{cm}^{-1}$  is attributed to  $A_{1g}$  modes arising from out-of-plane vibrations S. The peak at 300  $\text{cm}^{-1}$  likely contains overlapping  $E_g$  and  $A_{1g}$  modes. [47, 48] Along with their

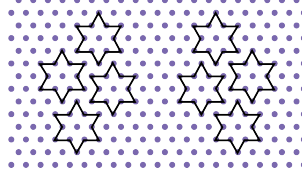
low intensity, higher frequency peaks all overlap in frequency with modes of  $\text{WSe}_2$ ; as such, these modes do not bear further discussion in the comparison between  $\text{TaS}_2$  and  $\text{TaS}_2/\text{WSe}_2$  heterojunction spectra. We next turn our attention to the set of low frequency modes of  $1T\text{-TaS}_2$ , observed below  $100\text{ cm}^{-1}$ . Comparing the  $\text{TaS}_2$  and heterojunction spectra, a drastic decrease in peak intensity is observed in the low-frequency modes. Previous studies calculate that the phonon modes around  $50\text{-}100\text{ cm}^{-1}$  are associated with the band-folded Brillouin zone of the CDW phase. These are in-plane  $E_g$  and out-of-plane  $A_g$  vibrational modes wherein Ta ions vibrate relative to one another.[47, 49]

Figure 2.12 shows Raman spectra of  $\text{WSe}_2/\text{TaS}_2$  stacks with 3, 6, and 50 layer  $\text{TaS}_2$  and monolayer  $\text{WSe}_2$ , acquired at 100 and 300 K, comparing spectra acquired on standalone  $\text{TaS}_2$  and  $\text{WSe}_2/\text{TaS}_2$  heterojunction regions of each stack. At all temperatures, the intensities of CDW vibrational modes are greatly reduced in thin (3-layer and 6-layer)  $\text{TaS}_2$  when covered with  $\text{WSe}_2$ . This effect disappears completely in the 50-layer sample (labeled as “bulk” in Figure 2.12); the  $\text{TaS}_2$  and  $\text{WSe}_2/\text{TaS}_2$  spectra are nearly identical). At both temperatures, the peak intensities for the 6-layer and 3-layer sample are decreased by approximately 30 percent and 60 percent, respectively, in the heterojunction compared to the  $\text{TaS}_2$ . In the 3-layer sample only, peaks appear to broaden in the heterojunction, and appear to red-shift by a few  $\text{cm}^{-1}$ . We can quantify these behaviors in more detail at 100 K, when the  $\text{TaS}_2$  has further transitioned into its distorted CDW phase. This transition leads to sharper peaks with increased intensity. For both the 3-layer  $\text{TaS}_2$  and  $\text{WSe}_2/\text{TaS}_2$  spectra at 100 K, the spectral region between  $40\text{-}110\text{ cm}^{-1}$  was fit to a sum of Lorentzian oscillators. Peak centers and associated uncertainties were determined by fitting the region of the spectrum to a sum of Lorentzian oscillators, which are summarized in Table 2.1. Clear red-shifting by  $2\text{-}3\text{ cm}^{-1}$  of the modes at  $99$  and  $83\text{ cm}^{-1}$  is observed, the mode at  $69\text{ cm}^{-1}$  remains unchanged, and the mode at  $59\text{ cm}^{-1}$  becomes slightly blue-shifted by  $1\text{ cm}^{-1}$ .

| $\text{TaS}_2$   | $\text{WSe}_2/\text{TaS}_2$ |
|------------------|-----------------------------|
| $58.7 \pm 0.2$   | $60.0 \pm 0.8$              |
| $69.3 \pm 0.1$   | $69.3 \pm 1.0$              |
| $82.75 \pm 0.03$ | $80.0 \pm 0.1$              |
| $99.0 \pm 0.1$   | $96.5 \pm 0.3$              |

**Table 2.1:** Vibrational frequencies (in  $\text{cm}^{-1}$ ), obtained by Lorentzian fits, of CDW vibrational modes in  $1T\text{-TaS}_2$  and  $1H\text{-WSe}_2/1T\text{-TaS}_2$  measured at 100 K between  $40\text{-}110\text{ cm}^{-1}$ .

The decrease in intensity of low-frequency  $\text{TaS}_2$  vibrational modes observed in the thin samples of  $\text{WSe}_2/\text{TaS}_2$  likely results from an increase in disorder. The formation of the CDW superlattice can be thought of as a transition to a highly ordered structure; even moderate suppression of the CDW transition by  $\text{WSe}_2$  would subsequently increase the degree of discommensuration, and therefore the disorder, in the sample, lowering the Raman scattering cross section for vibrational modes of the CDW superlattice. Peak broadening



**Figure 2.10:** Illustration of chiral domains in 1T-TaS<sub>2</sub>.

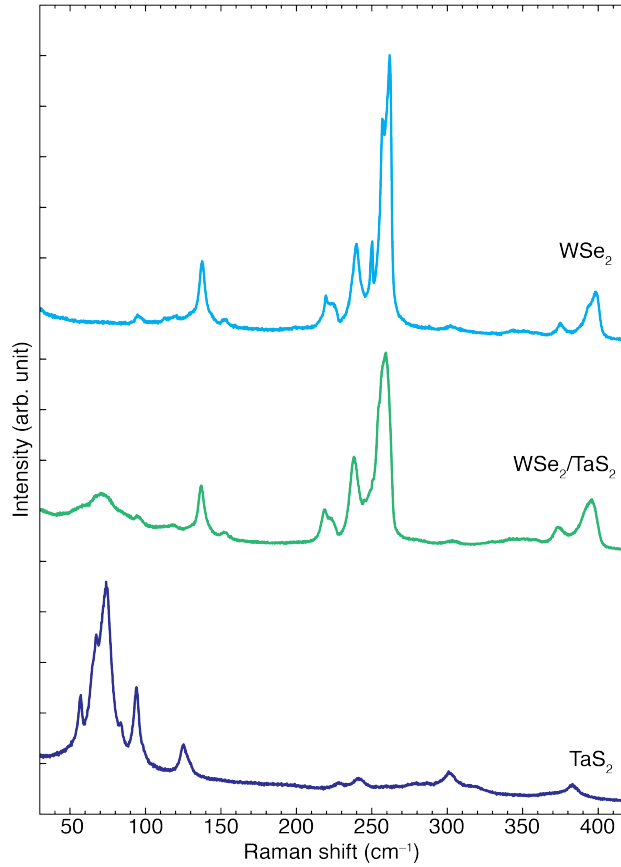
can also be attributed to disorder due to dissipation of the vibrational energy from the CDW superlattice to the surrounding discommensurate regions.

Lattice vibrational frequencies can be sensitive to strain and charge doping. The measured differences in frequencies of corresponding modes, as summarized in Table 2.1, can likely be attributed to some combination of charge transfer interaction and lattice strain between the TaS<sub>2</sub> and WSe<sub>2</sub>, but the exact nature of this behavior is unclear based on the measured spectra. Shifting of vibrational frequencies as a result of charge doping has been well-studied in graphene and has also been observed in TMDs.[50] In the semiconducting 2H TMDs WSe<sub>2</sub> and MoS<sub>2</sub>, the A<sub>1g</sub> mode is thought to be strongly sensitive to charge transfer, while the E<sub>g</sub> mode is thought to be sensitive to strain; however, these principles may not accurately apply to the CDW vibrational modes of TaS<sub>2</sub>. Calculations predict that strain will lead to softening of the CDW superlattice E<sub>g</sub> and A<sub>g</sub> modes in monolayer 1T-TaS<sub>2</sub>; however, the degree of softening is not consistent throughout either set of modes,[47] suggesting that strain could impact some modes of the same symmetry more than others.

Although the 6-layer spectra in Figure 2.12 show decreased peak intensities, they do not show clear shifting of the measured frequencies seen in the 3-layer sample. Subsequent Raman measurements were carried out on the 6-layer sample using circularly polarized light. The vibrational modes of 1T-TaS<sub>2</sub> are sensitive to chiral excitation sources due to the chiral nature of the CDW superlattice.[49] This chirality arises from the two possible  $\pm 13.9^\circ$  rotations of the superlattice relative to the undistorted TaS<sub>2</sub> lattice. This can be understood by examining the illustration in Figure 2.10. The star clusters can tile in two energetically equivalent, but distinct, superlattices which are mirror images of one another. The chiral lattice will exhibit a different response to circular contrarotation excitation/detection configurations,  $\sigma^+\sigma^-$  and  $\sigma^-\sigma^+$ , where the sample is excited with circularly polarized light in one rotation, and circularly polarized light of the opposite rotation is detected.

Figure 2.13(a) shows spectra taken in two different contrarotation excitation/detection schemes. Unlike the spectra acquired with conventional linearly polarized light in Figures 2.11 and 2.12, where E<sub>g</sub> and A<sub>g</sub> modes overlap in the low-frequency region of the spectrum, measuring in the contrarotating scheme suppresses A<sub>g</sub> modes allowing for clear observation of the E<sub>g</sub> modes.[49] Considerable peak shifting is observed, as summarized in Figure 2.13(b), and the highest frequency peak appears to split into two peaks on the heterojunction.

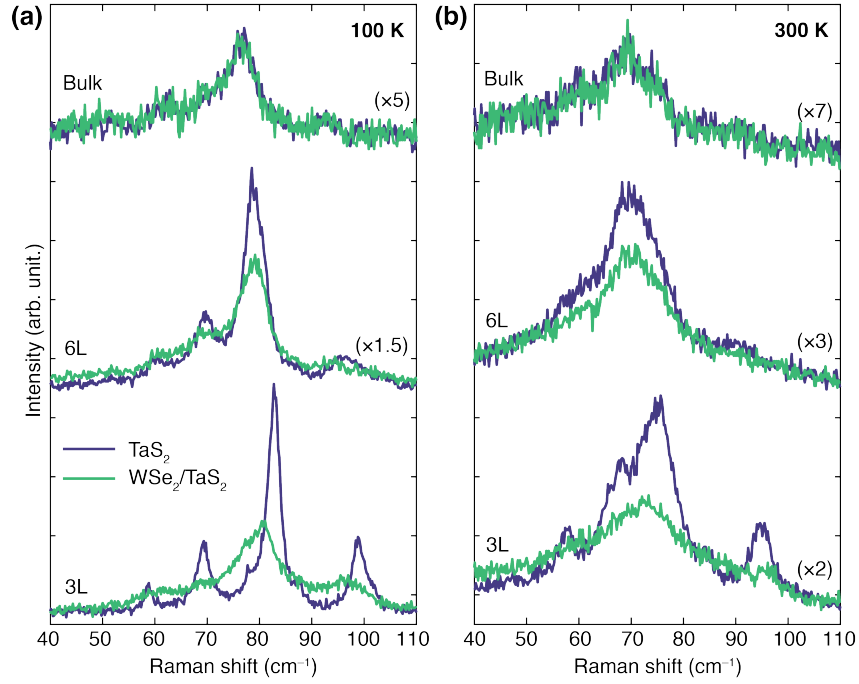
Finally, we consider the results of Raman measurements in the context of our electronic transport measurements. In transport studies, the impact of the WSe<sub>2</sub>/TaS<sub>2</sub> only produced a measurable effect on the transition temperatures between the ICCDW-NCCDW phases;



**Figure 2.11:** Raman spectra of  $\text{WSe}_2$ ,  $\text{TaS}_2$ , and  $\text{WSe}_2/\text{TaS}_2$  regions of a  $\text{hBN}/\text{WSe}_2/\text{TaS}_2/\text{hBN}$  heterostructure sample containing 3-layer  $\text{TaS}_2$ , taken under ambient conditions.

the transport behavior of the  $\text{TaS}_2$  and the  $\text{WSe}_2/\text{TaS}_2$  heterojunction was equivalent the region was fully transitioned into the NCCDW phase. Raman experiments were carried out below  $T_{\text{CDW}}$  for the ICCDW-NCCDW transition, so in these measurements we are observing effects of the  $\text{WSe}_2$  while  $\text{TaS}_2$  is in the NCCDW/CCDW phase. Though Raman spectra demonstrate a measurable impact of the  $\text{WSe}_2$  interface on the CDW vibrational modes of  $\text{TaS}_2$ , it is clear that the extent of these impacts is not significant enough to impart dissimilar electronic transport behavior within the NCCDW phase.<sup>4</sup> While the results of Raman studies provide clues into the nature of the interactions occurring at the  $\text{WSe}_2/\text{TaS}_2$  interface, a definitive picture of this interaction is still unclear.

<sup>4</sup>Comparison of the Raman and transport measurements is further complicated by the fact transport measurements on 3-layer devices could not detect the ICCDW-NCCDW transition, and electrical contact to the 3-layer  $\text{TaS}_2$  was generally unreliable.

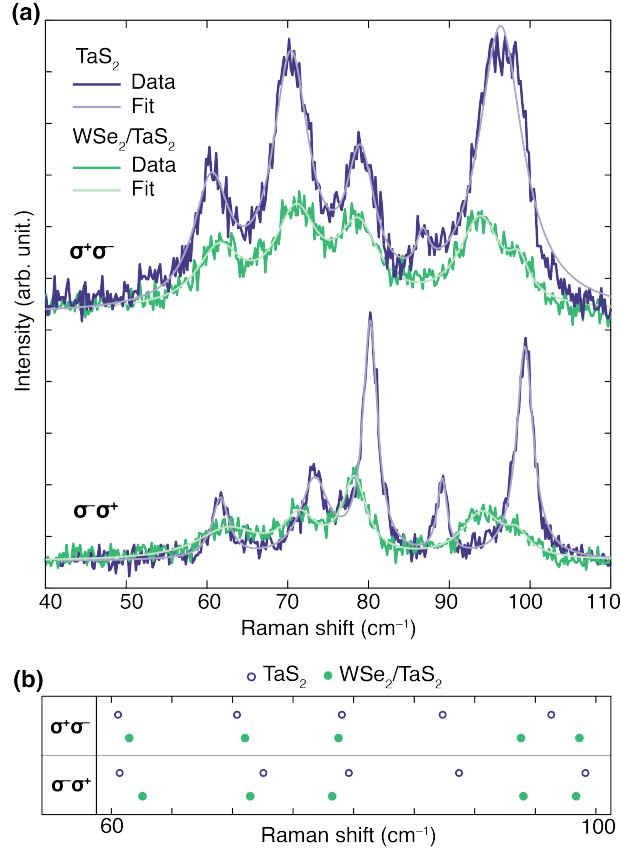


**Figure 2.12:** Comparison of Raman spectra at (a) 100 K and (b) 300 K for heterostructures with different TaS<sub>2</sub> thickness. Some plots are scaled for clarity, with scale factors indicated above each scaled plot.

## Photoluminescence spectroscopy

Variable temperature photoluminescence (PL) experiments were performed on the same 3- and 6-layer TaS<sub>2</sub> heterostructure samples used in the Raman studies in order to better understand the effects of interaction with TaS<sub>2</sub> on excitonic transitions in WSe<sub>2</sub>, with the intent of gaining further insight into the possible charge/energy transfer between layers. PL measurements for the 3-layer sample were carried out in a similar manner to the temperature-dependent Raman, but with a 600 gr/mm grating, and 2 second acquisition with 2 accumulations. In hopes of gaining insight into behavior well below the predicted  $T_{\text{CDW}}$ , PL experiments between 10-300 K were performed on 6-layer TaS<sub>2</sub> samples at the Lawrence Berkeley National Laboratory Molecular Foundry in the Imaging and Manipulation of Nanostructures facility with the assistance of Medha Dandu, a postdoctoral scholar in the research group of Archana Raja. Temperature was controlled using a He-cooled optical cryostat (Montana Cryostation s200), and a 532 nm continuous wave Coherent Sapphire laser attenuated to 750 nW of excitation power was used.

Figure 2.14 shows normalized PL spectra acquired on the hBN/WSe<sub>2</sub>/TaS<sub>2</sub>/hBN heterostructure containing 3-layer TaS<sub>2</sub>, taken on both the standalone WSe<sub>2</sub> region and the WSe<sub>2</sub>/TaS<sub>2</sub> region. Note that due to its very small bandgap (less than 0.5 eV) no significant PL signal is observed on the standalone TaS<sub>2</sub> region of the stack. A large peak resulting from

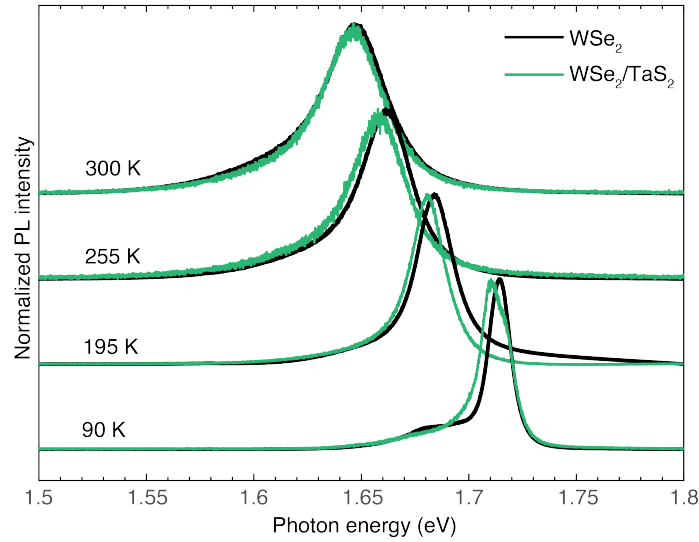


**Figure 2.13:** Circularly polarized Raman of 6-layer heterostructure sample. (a) Raman spectra of TaS<sub>2</sub> and WSe<sub>2</sub>/TaS<sub>2</sub> taken with opposite contrarotation configurations. Lorentzian fits are plotted in lighter colors on top of the raw data. (b) Plots of peak frequencies obtained from fits for both regions of the sample in both contrarotation configurations.

the A-exciton of WSe<sub>2</sub> is observed, which shifts to higher energy with decreasing temperature, consistent with previously reported data.[51, 52] The overlaid PL spectra, taken on WSe<sub>2</sub>/TaS<sub>2</sub>, are all red-shifted by approximately 3 meV (no pattern of increased or decreased shifting is observed with temperature change). Peak shifting is typically indicative of changes in the dielectric screening environment, which shifts the exciton binding energy due to charge transfer. Pronounced red-shifts in the WSe<sub>2</sub> exciton binding energy have been measured in WSe<sub>2</sub>/graphite and WSe<sub>2</sub>/graphene compared to WSe<sub>2</sub>/hBN, with exciton peaks shifting up to 100 meV.[32, 53] While the peak shifting in WSe<sub>2</sub>/TaS<sub>2</sub> does not occur on such a pronounced scale, this behavior still suggests that a charge transfer interaction similar to that of WSe<sub>2</sub>/graphene could occur in this system.

Figure 2.15 shows PL spectra acquired between 10-300 K for the 6-layer sample, plotted with accurate intensity scales. Significant PL quenching is observed in the WSe<sub>2</sub>/TaS<sub>2</sub>, which has been observed in several previous studies of semiconductor PL with a metallic substrate;



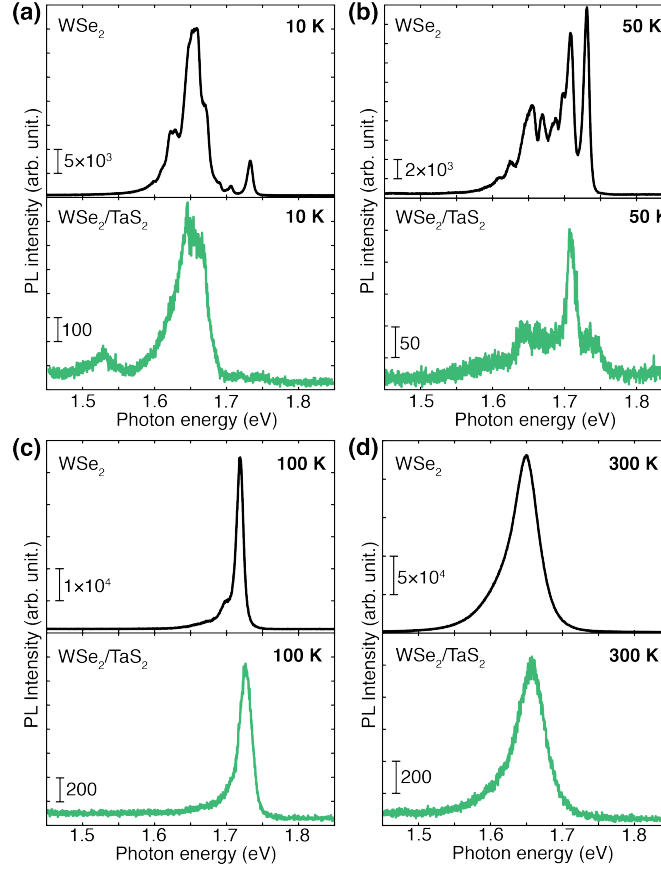


**Figure 2.14:** Normalized PL spectra of  $\text{WSe}_2$  (black) and  $\text{WSe}_2/\text{TaS}_2$  (green) taken at 300, 255, 195, and 90 K.

this implies that charge transfer of the excited electrons in  $\text{WSe}_2$  to the (nearly-)metallic  $\text{TaS}_2$ . The highest energy peak is again assigned to emission from the neutral A exciton of  $\text{WSe}_2$ , and the neighboring peak which appears  $\sim 0.5$  eV below the the A peak is assigned to emission from the trion.[54] The same red-shifting of these peaks is observed with decreasing temperature as in Figure 2.14. At lower temperatures, a series of lower-energy peaks emerge due to emission from bi-excitons. Relative to their respective A exciton peaks, the signal measured from trions and biexcitons is stronger in the  $\text{WSe}_2/\text{TaS}_2$  heterojunction than in the standalone  $\text{WSe}_2$ . In all spectra, the main exciton peak is blue-shifted by approximately 10 meV; note that this is contradictory to the results of the other PL study. While hBN and  $\text{SiO}_2$  are both insulators, they can impart slightly different screening behavior, especially due to the roughness and disorder of  $\text{SiO}_2$  substrates.[55]

At 10K, a lower energy peak is observed in heterojunction that is not present in  $\text{WSe}_2$  spectra (and is also not present in standalone  $\text{TaS}_2$  and background scans). While in some heterostructures, PL from interlayer (or moiré) excitons can appear at low temperature, typically at a lower energy in the spectrum, this is not a likely explanation here, as the bandgap of 1T- $\text{TaS}_2$  in its CCDW phase is still very small ( $< 0.5$  eV, compared to 1.7 eV in monolayer  $\text{WSe}_2$ ), and it is therefore unlikely that this system can host an interlayer exciton. Rather, it is more likely that this peak can be attributed to renormalization of the band structure due to interaction with the  $\text{TaS}_2$ ; however, confirmation via band structure calculations (forthcoming) will be required to verify this.

Due to the presumed complications from substrate effects on the PL data, an alternative method to gain insight into the exciton transitions in  $\text{WSe}_2/\text{TaS}_2$  is reflection contrast (RC) spectroscopy. In RC, a white light source is used to excite the sample, and the reflectance is



**Figure 2.15:** Photoluminescence spectra of hBN/ $\text{WSe}_2$  (upper plots, black) and hBN/ $\text{WSe}_2/\text{TaS}_2$  (lower plots, green) acquired at (a) 10 K, (b) 50 K, (c) 100K, and (d) 300 K. Note that all plots have different y-axis scales, which are specified on each plot.

measured, which will show features arising from excitation of the intrinsic electronic states of a material (contrary to features in PL spectra which arise from the recombination of electron-hole pairs following excitation). Changes in the locations and broadness of these spectral features can be a more direct indication of charge transfer and/or changes in the bandgap.[53, 55] Reflectance spectra were also acquired on the 6-layer heterostructure sample, but data analysis is still underway to determine whether any conclusive results can be obtained from these data. Band structure calculations and angle-resolved photoemission spectroscopy measurements are also in progress to help gain a better quantitative picture of the energetic consequences of interaction between  $1H\text{-WSe}_2$  and  $1T\text{-TaS}_2$ .<sup>5</sup>

<sup>5</sup>Medha Dandu assisted with the reflection contrast data acquisition and analysis, Lilia Xie and Samra Husremović acquired ARPES data, and Katherine Inzani (University of Nottingham) will perform band structure calculations.

## 2.4 Future directions

Beyond computational studies and replicate devices measurements which are currently underway, the results presented above motivate further study into CDW behavior in TMD heterostructures. A natural progression of this work would be to replicate experiments using different 2D vdW materials, especially with the semiconducting group VI TMDs MoS<sub>2</sub>, MoSe<sub>2</sub>, and WS<sub>2</sub>, all of which vary slightly from WSe<sub>2</sub> in lattice constant and in band gap. This would provide further insights into the possibly-competing roles of lattice strain and charge transfer at the interface. Another exciting possibility for further control of the CDW transition would be to exploit electrostatic gating as an additional tuning knob within these structures. Because 1T-TaS<sub>2</sub> is, depending on the phase, a metal or narrow-gap semiconductor, electrostatic gating is difficult due to charge screening. However, the ability to work with very thin samples could allow for direct gating of the TaS<sub>2</sub>. Moreover, it is theoretically possible to selectively gate the semiconducting WSe<sub>2</sub> by fabricating a top gate; electron- or hole-doping the WSe<sub>2</sub> could lead to changes in the nature of charge transfer interaction with TaS<sub>2</sub>. In this instance, gating the WSe<sub>2</sub> could possibly act as a switch for the CDW transition in the TaS<sub>2</sub> beneath the WSe<sub>2</sub>.

## 2.5 Conclusions

Using electronic transport, Raman, PL, and RC spectroscopy, we characterize the effects of the interfacial interactions between 1T-TaS<sub>2</sub> and 1H-WSe<sub>2</sub> on the CDW transitions of 1T-TaS<sub>2</sub>. Electronic transport and Raman spectroscopy show that the CDW becomes suppressed in sufficiently thin samples of TaS<sub>2</sub> interfaced with WSe<sub>2</sub>. Energetic shifts, intensity decrease, and peak broadening observed in Raman and PL are indicative of charge transfer between the two materials. The exact nature of this charge transfer is not apparent in these measurements, and further insight is needed to better understand the charge transfer process in the WSe<sub>2</sub>/TaS<sub>2</sub> heterostructure. Overall, these results contribute to a further understanding of methods for CDW suppression in 2D materials, and demonstrate the creation of 2D heterostructures as a means to finely tune the behavior of constituent vdW materials.

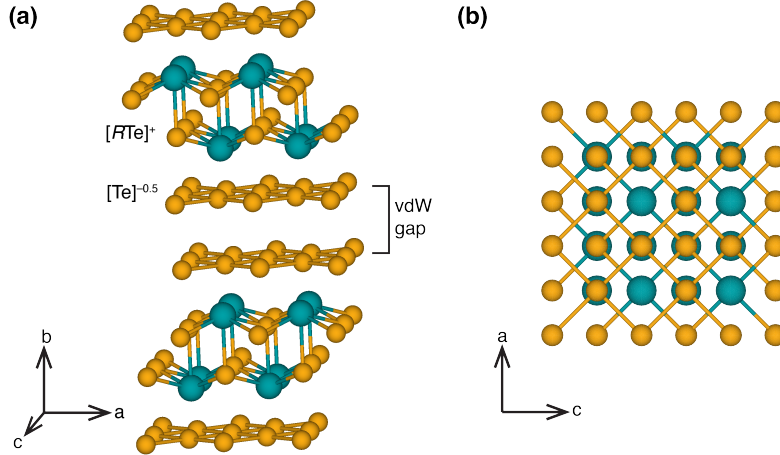
## Chapter 3

# Toward electrochemical modification of charge density waves in rare-earth tritellurides

### 3.1 Introduction

Rare-earth tritellurides ( $R\text{Te}_3$ ) are a family of layered vdW materials consisting of corrugated RTe layers between two square net layers of Te, and the vdW gap of these materials is located between consecutive Te layers (Figure 3.1). Below a given temperature  $T_{\text{CDW1}}$ , the approximately square planar symmetry of the Te net is broken by the formation of a unidirectional CDW transition along the crystalline c-axis.[56–58] For the heavier members of the  $R$  family, a second unidirectional CDW transition at  $T_{\text{CDW2}}$  causes the lattice to distort along the a-axis, perpendicular to the axis of the first transition. These electronic instabilities are concentrated in the Te square net whose in-plane  $p_x$  and  $p_z$  orbitals form wide bands which cross the Fermi level.[59, 60] There exist parallel sections of the Fermi surface, which can be connected by a the CDW wavevector  $\vec{q}_{\text{CDW}} \approx (5/7) \times (2\pi/c)$ , causing Fermi surface nesting and the formation of an incommensurate CDW phase. During this phase transition, the Fermi surface only becomes partially gapped.[19] The consequence of this partial gapping is that, unlike in a variety of other CDW materials which exhibit sharp changes in resistance accompanying CDW transitions, the CDW transitions in  $R\text{Te}_3$  tend to appear as broad peaks in the resistance during cooling, and the material remains in a metallic state.[61, 62] While this makes  $R\text{Te}_3$  less attractive for real-world applications,  $R\text{Te}_3$  still provides for a rich area of study into the underlying physics of CDW formation: Along with the relative simplicity of its uniaxial square net distortions, the  $R\text{Te}_3$  family has highly tunable CDW behavior.

Across the period, as the atomic number of  $R$  increases, several trends are observed, which are summarized in Figure 3.2.  $T_{\text{CDW1}}$ , which is  $> 500$  K for  $\text{LaTe}_3$ , decreases to 240 K for  $\text{TmTe}_3$ . [19, 63] The opposite trend is observed for  $T_{\text{CDW2}}$ :  $\text{TbTe}_3$ , the lightest to



**Figure 3.1:** Crystal structure of  $RTe_3$ , (a) with  $RTe$  block, Te square net layer, and vdW gap labelled, (b) along  $b$ -axis.

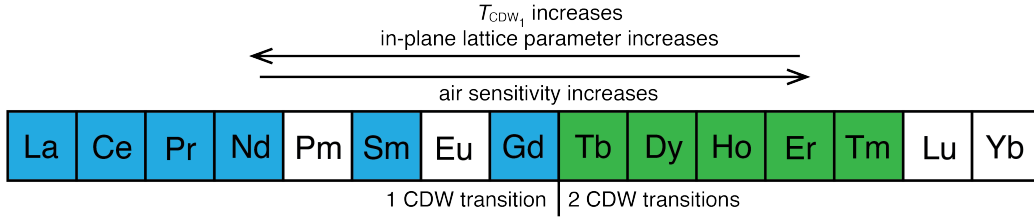
exhibit a second CDW transition, has the lowest  $T_{CDW2}$ . As  $R$  becomes heavier, the in-plane lattice parameter of  $RTe_3$  also decreases. Changing the identity of  $R$  (and therefore the lattice parameter) can be considered as tuning the chemical pressure of the material, with increased pressure lowering (*i.e.* suppressing) the CDW transition.[56, 64]

The manipulation of the CDW transition has similarly been carried out using the application of physical pressure, whereby the electron density increases with contracting unit cell volume, leading to a shift in CDW transition temperatures, along with complete suppression of the CDW in favor of superconductivity at sufficient pressure.[65, 66] While chemical and physical pressure are the most prominent methods that have been used to manipulate CDWs in  $RTe_3$ , [19] other methods including light and topotactic intercalation of Pd have also been demonstrated experimentally to alter the CDW phases in  $RTe_3$ . [67, 68] While chemical and electrochemical intercalation have been utilized to reversibly and controllably dope a variety of vdW materials (including the CDW material  $1T-TaS_2$ , leading to superconductivity), [29, 69–71] these methods have not previously been explored to modify  $RTe_3$ .

Here, we explore electron-doping of  $HoTe_3$  via electrochemical intercalation of  $Li^+$  as a means to modify its CDW transitions. Synthesis and basic characterization of pristine  $GdTe_3$  and  $HoTe_3$  are carried out, as well as in-situ electrochemical studies to optically observe the intercalation of  $HoTe_3$ .

## 3.2 Synthesis of $RTe_3$

$GdTe_3$  and  $HoTe_3$  were synthesized via a Te self-flux technique following previously reported methods.[72] Gd or Ho and Te were weighed into a quartz ampoule in a 97:3 ratio. The ampoule was then evacuated and sealed. The ampoule was placed upright in a furnace and heated from room temperature to 900 °C over 12 hours and cooled to 550 °C at 2 °C/hour.



**Figure 3.2:** Periodic trends in  $R$ . Elements for which a CDW transition has been measured experimentally for  $R\text{Te}_3$  are shaded in blue for  $R\text{Te}_3$  with one CDW transition and green for  $R\text{Te}_3$  with two CDW transitions.  $T_{\text{CDW}1}$  and lattice constant increase for lighter  $R$ . Air sensitivity increases for heavier  $R$ . (Paritally adapted from Reference [19].)

Following heating, the ampoule was quickly removed from the furnace, inverted, and placed into a centrifuge to decant the crystals from the excess Te flux. The ampoule was broken open in an Ar glovebox and gold-colored rectangular crystals were separated from excess flux with tweezers.<sup>1</sup>

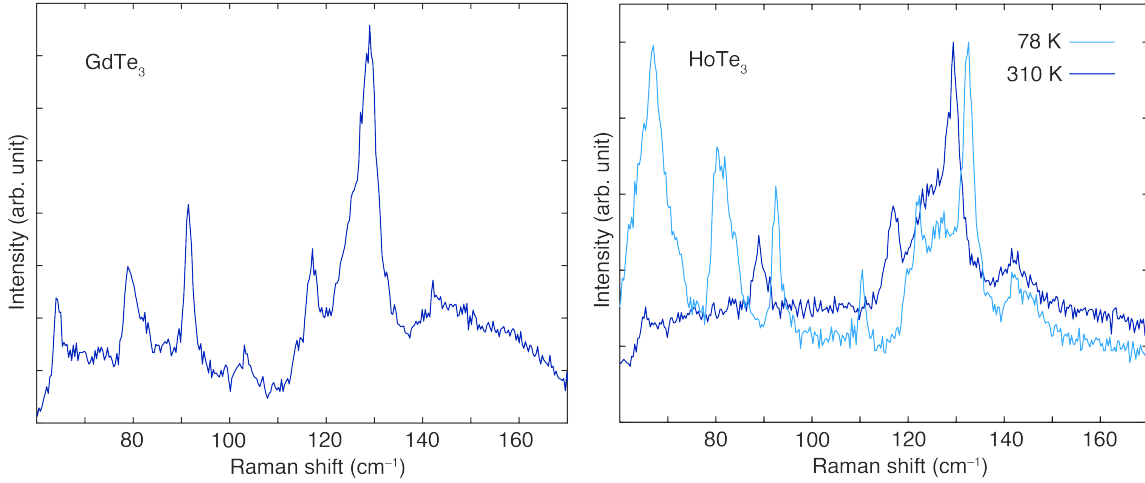
Powder x-ray diffraction patterns were taken using single crystals to verify the structure. (00l) reflections of  $\text{GdTe}_3$  match well with previously reported diffraction patterns.[72] Due to sample degradation, accurate diffraction data could not be obtained for  $\text{HoTe}_3$ .

### Raman spectroscopy of exfoliated $\text{GdTe}_3$ and $\text{HoTe}_3$

To further characterize the flux-grown crystals, we obtained Raman spectra, shown in Figure 3.3. In an Ar glovebox, crystals were exfoliated onto 90 nm  $\text{SiO}_2/\text{Si}$  chips. A chip containing exfoliated  $\text{GdTe}_3$  was taken out of the box, and a Raman spectrum was acquired using a 532 nm laser in ambient conditions ( $\sim 295$  K). A chip with exfoliated  $\text{HoTe}_3$  was secured in an optical cryostat (described in Chapter 2), cooled to 78 K, and heated to 310 K to acquire temperature-dependent spectra above and below the CDW transition temperature. Note that due to different experimental conditions, the appearances of the spectra will vary slightly. In particular, the low frequency edge of the spectrum could be cut off in the  $\text{GdTe}_3$  spectrum, but not in the  $\text{HoTe}_3$  spectrum due to the use of an ultra-low frequency filter.

$T_{\text{CDW}1}$  for  $\text{GdTe}_3$  is 385 K, so it is in its CDW phase at room temperature.[63, 72] Due to its relative stability in air, the Raman spectrum of  $\text{GdTe}_3$  has been well-characterized experimentally, although there are some inconsistencies in exact peak assignments among current literature.[62, 73, 74] A combination of calculated and experimental data attribute the major vibrational modes observed in the  $\text{GdTe}_3$  spectrum in Figure 3.3 to  $A_{1g}$  out-of-plane modes, although these peaks are likely to overlap with  $B_g$  modes which are predicted to appear at similar frequencies in the CDW phase and likely enhance the intensities of the lower-frequency peaks. The peak observed near  $90 \text{ cm}^{-1}$  is not predicted for the undistorted (non-CDW) structure; it is attributed to overlapping modes of A and B symmetries in the

<sup>1</sup>Synthesis was performed with assistance from Lilia Xie.



**Figure 3.3:** Raman spectra (normalized) of  $\text{GdTe}_3$  at room temperature (left) and  $\text{HoTe}_3$  (right) at 310 K (dark blue) and 78 K (light blue). Spectrum of  $\text{GdTe}_3$  was taken with 532 nm excitation in ambient conditions while spectrum of  $\text{HoTe}_3$  was taken in an optical cryostat with a 633 nm laser using an ultra-low frequency filter.

CDW structure.[62] The spectrum of  $\text{HoTe}_3$  in its CDW phase (78 K) closely matches that of  $\text{GdTe}_3$ ; with the exception of the CDW-associated peak just above  $90 \text{ cm}^{-1}$  (which is a slightly higher in frequency than its analogue in the  $\text{GdTe}_3$  spectrum), the peaks overlap almost perfectly with the the  $\text{GdTe}_3$  spectrum. Peaks near 65 and  $80 \text{ cm}^{-1}$  in the spectrum at 78 K are greatly diminished in intensity in the spectrum at 310 K. Interestingly, the peak at  $80 \text{ cm}^{-1}$ , which is predicted to persist in the undistorted structure, seems to vanish almost entirely, while the peak at  $90 \text{ cm}^{-1}$  remains. Other peaks at higher frequency are still present, but are red-shifted which is likely a combined effect of thermally induced phonon softening as well as the predicted lattice distortions.

Despite the better stability of  $\text{GdTe}_3$ , we chose to focus our transport and electrochemical studies on  $\text{HoTe}_3$  due to its lower  $T_{\text{CDW}}$ . In order to properly observe the CDW transition in transport measurements, the high  $T_{\text{CDW}}$  of  $\text{GdTe}_3$  would require heating to a point that could lead to equipment damage. Another consideration is that, while we generally conduct electrochemical intercalation above room temperature to ensure better ion mobility, controlled and quantitative electrochemistry experiments necessitate the ability to quickly cool the sample below room temperature to slow the intercalation reaction. With the high  $T_{\text{CDW}}$  for  $\text{GdTe}_3$ , it would be difficult to observe the effect of electrochemical intercalation on the CDW transition temperature.

### 3.3 Electronic transport in HoTe<sub>3</sub>

#### Device fabrication

##### Exfoliation of HoTe<sub>3</sub>

SiO<sub>2</sub>/Si chips (90 nm SiO<sub>2</sub>) were cleaned by sonicating in 1:1 acetone/isopropanol for 10 minutes, followed by drying with N<sub>2</sub>. In an Ar glovebox, chips were placed on a hotplate set to 150 °C for 30 minutes, after which the temperature was lowered to 100 °C. Flux-grown crystals (stored in the glovebox) were exfoliated with Scotch Magic tape, and then the Scotch tape was pressed onto a piece of Ultron Systems Silicone-Free blue tape (medium-tack). Chips were taken off of the 100 °C hotplate, pressed lightly onto the blue tape, and then peeled off after 30 seconds of light pressing. Some chips were taken out of the glovebox, and atomic force microscopy was used to correlate flake thickness with optical contrast. Flakes to be used for devices were kept in the glovebox.

##### Contact fabrication

Electron-beam lithography was used to define contact patterns on SiO<sub>2</sub>/Si chips (285 nm SiO<sub>2</sub>). Cr/Au (1 nm/9 nm) contacts were thermally evaporated, followed by overnight liftoff in acetone. Lithography/evaporation of Cr/Au (2 nm/ 100 nm) was then repeated to create connection areas for wirebonding.

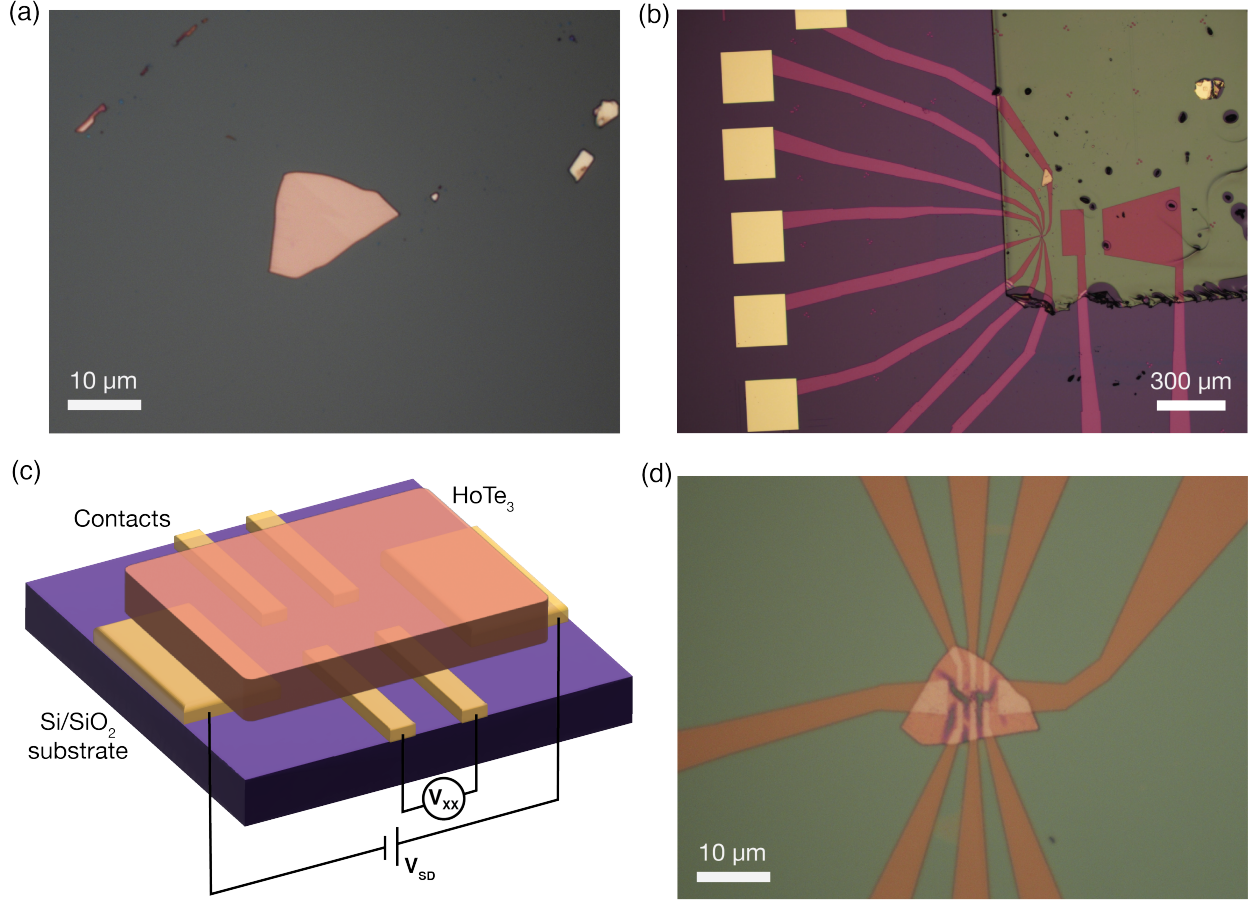
##### Stacking onto bottom contacts

A dry transfer method, as described in Chapter 2, was used to pick up a ~40 nm-thick flake of HoTe<sub>3</sub> (Figure 3.4(a)) exfoliated less than 2 hours before stacking. Bottom contacts were O<sub>2</sub> plasma cleaned for 5 minutes immediately prior to stacking. The PC stamp with HoTe<sub>3</sub> was released onto the contacts, and throughout the final fabrication steps, and the PC film was left on the device for extra protection from air exposure. Figure 3.4(b) shows an optical micrograph of the device at 2x magnification, with contacts and PC film visible, Figure 3.4(d) shows a 100x optical micrograph of the flake stacked on the contacts, and Figure 3.4(c) shows a diagram of the device.

#### Temperature-dependent resistivity

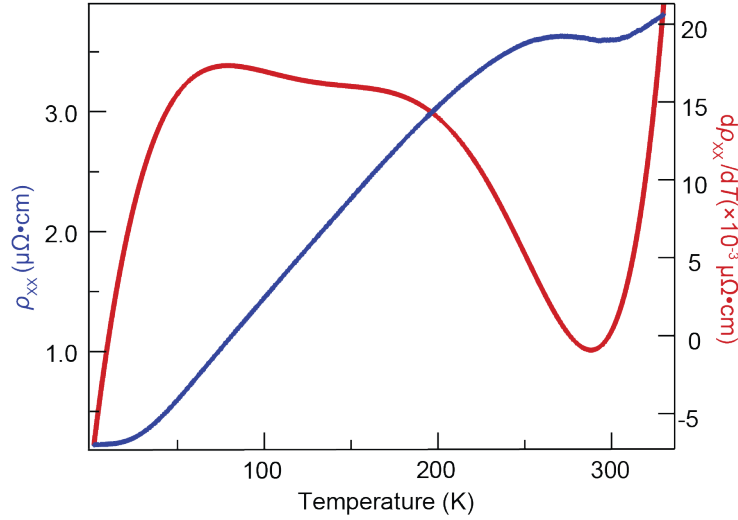
Electronic transport measurements were performed to characterize the temperature-dependent resistivity of HoTe<sub>3</sub> using conventional lock-in techniques. A constant alternating current of 20  $\mu$ A (17.777 Hz) was applied between source and drain contacts, and the 4-probe voltage drop  $V_{xx}$  was measured using a lock-in amplifier (Stanford Research SR830). All measurements were performed in a Quantum Design Physical Property Measurement System (PPMS). Cross-sectional area and distance between contacts were closely estimated to determine the longitudinal resistivity of the sample,  $\rho_{xx}$ .





**Figure 3.4:** (a) Optical micrograph of exfoliated  $\text{HoTe}_3$  flake. (b) Optical micrograph of device, showing contacts and PC film. (c) Simplified diagram of  $\text{HoTe}_3$  device on bottom contacts, showing application of source-drain voltage and measurement of 4-probe longitudinal resistance. (d) Optical micrograph of  $\text{HoTe}_3$  stacked onto bottom contacts covered by PC film.

The  $\rho$  vs. temperature profile during cooling from 330 to 1.8 K at a rate of 1 K/min is shown in Figure 3.5, along with the first derivative  $d\rho/dT$ . Due to the broad and less-pronounced nature of the CDW transition, it is common to use  $d\rho/dT$  to determine  $T_{\text{CDW}}$ . [64] One peak appears near 290 K, which agrees with previous measurements of  $T_{\text{CDW}1}$  for  $\text{HoTe}_3$ . A second peak, which is not readily visible in  $\rho$  vs.  $T$ , but appears as a small, broad peak in  $d\rho/dT$  vs.  $T$ , also agrees with previous measurements of  $T_{\text{CDW}2}$  for  $\text{HoTe}_3$ . [64] Although there exists very little published transport data of exfoliated  $R\text{Te}_3$ , [72, 75] our data, along with the magnitude of  $\rho$ , closely match those of a measurement on exfoliated  $\text{GdTe}_3$ . [72] Beyond the fact that the material is still in a metallic state below the  $T_{\text{CDW}}$ , an additional reason for the weak CDW transition features in transport data is that the transport behavior in  $R\text{Te}_3$ , as with many other CDW materials, is highly anisotropic. However, unlike in



**Figure 3.5:** Plots of resistivity vs. temperature (blue, left axis) and first derivative of resistivity vs. temperature during (red, right axis) of  $\text{HoTe}_3$  during 1 K/min cooling.

other CDW materials, the effects of the CDW will be most pronounced in measurements taken perpendicular to the axis of CDW distortion, where the measured resistivity will be higher.[75, 76] In the case of this device, we are measuring along an undefined direction in the a-c plane, and we do not expect to see major features at the CDW transitions.

### 3.4 In-situ electrochemical studies

#### Observation of intercalation by optical microscopy

Previous studies have observed dramatic color changes in exfoliated graphite flakes during electrochemical intercalation of  $\text{Li}^+$ , allowing for close investigation into the thermodynamics and kinetics of the intercalation process.[70, 77] In order to gain a qualitative understanding of the intercalation of  $\text{HoTe}_3$ , we constructed on-chip electrochemical cells to observe flakes throughout the intercalation reaction.

#### Sample preparation

Thin strips of aluminum foil were taped across  $\text{SiO}_2/\text{Si}$  chips (285 nm) to create exposed stripes. Thermal evaporation was used to deposit Cr/Au (2 nm/100 nm) in the exposed areas to create Au electrodes. An Au-striped chip was then secured with kapton tape to a glass microscope slide, along with two pieces of Au-coated Si. The edges of two Au electrodes were wirebonded to the larger Si/Au pieces. In an Ar glovebox, flux-grown  $\text{HoTe}_3$  crystals were exfoliated as described above on Scotch Magic tape and transferred onto low-tack Ultron blue tape. The blue tape was pressed lightly onto the Au-striped chip so as not to peel off

the Au or disturb the wirebonds (Figure 3.6(a)). Optical microscopy was used to confirm the presence of large flakes on an Au electrode. Next, a  $\text{Li}^+$  polymer electrolyte<sup>2</sup> was dropcast onto the chip, such that it covered two electrodes. Rapid evaporation of the solvent leaves behind a transparent electrolyte film. Figure 3.6(b) shows a photograph of the experimental setup: in an Ar glovebox, the glass slide containing the sample is secured to a temperature-controlled stage (heated to 338 K to promote ion mobility) below a microscope objective. The Au/Si leads are connected to a Tektronix Keithley 2400 SourceMeter to control the potential between the two electrodes.

### Experimental procedure and results

We define the Au electrode with  $\text{HoTe}_3$  flakes of interest as the working electrode (WE) and the other as the counter electrode (CE). During the experiment, the CE potential ( $V_{CE}$ ) was swept to a positive potential to drive intercalation of  $\text{Li}^+$  into the  $\text{HoTe}_3$  at the WE. This experiment was performed several times with slightly different  $V_{CE}$  sweep procedures, and optical micrographs collected during the most thorough of these experiments are shown in Figure 3.6(c-e). This experiment was performed over several  $V_{CE}$  sweep cycles as follows:

1. Figure 3.6(c) shows the flake prior to sweeping  $V_{CE}$ .  $V_{CE}$  was increased from 0 V to 3.0 V at a rate of 0.2 V/min (increased V by 0.1 V every 30 s). At 3.0 V, some color change (indicative of intercalation) in the flake was observed as the formation of dark patches in several spots on the flake, and  $V_{CE}$  was held for 10 minutes until the color changing slowed, still appearing as dark patches throughout the flake. After 10 minutes,  $V_{CE}$  was swept back to 0 V at a rate of 0.1 V/10 s, and held at 0 V for 3 minutes. During the  $V_{CE}$  downsweep, the flake recovered to its original appearance, indicating that the changes are reversible. Similar  $V_{CE}$  sweep rates were used throughout the following steps, and will not be specified for simplicity.
2.  $V_{CE}$  was slowly increased from 0 V to 3.4 V, when color changes were again observed on the flake, beyond what was seen in the first cycle.  $V_{CE}$  was held for 30 minutes until the color changing slowed, with the size and intensity of dark patches growing throughout the flake, along with some visible wrinkles/cracks in the flake which are likely to occur due to interlayer expansion to accomodate  $\text{Li}^+$  in the vdW gap.  $V_{CE}$  was swept back to 0 V, and while the dark patches went away, wrinkles in the flake appeared irreversible, resembling the first image in Figure 3.6(d).
3.  $V_{CE}$  was again increased, and color changes started to occur at 3.3 V. First, similar darkening in patches throughout the flake was observed, followed by steady change to

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<sup>2</sup>The electrolyte was prepared by Jonathon Nessralla as follows: In an Ar glovebox, 3.7 mL of anhydrous acetonitrile (Fisher Scientific), dried with molecular sieves (Alfa Aesar), was added to 0.3 g of polyethylene oxide (PEO; Alfa Aesar) and 50 mg of lithium bis(trifluoromethylsulfonyl)imide ( $\text{LiTFSi}$ ; Alfa Aesar) and stirred overnight to dissolve.

a darker color moving in from the flake edges, as shown in Figure 3.6(d). Other than the first optical micrograph, which was taken immediately at 3.3 V, the others show the flake over a period of 10-20 minutes after  $V_{CE}$  reached 3.3 V.

4. After being held at 3.3 V for 40 minutes, seeing no further visible changes,  $V_{CE}$  was slowly increased to 4.0 V, when additional color changes started to take place. Figure 3.6(e) shows the appearance of vibrant colors on the flake, which stopped changing after 20 minutes.  $V_{CE}$  was decreased to 0 V, then to -3 V, in an attempt to reverse the changes to the flake appearance. During the downsweep, at 1 V, the flake began to return to its darkened appearance, and then to its original light pink color, but with several dark patches and many pronounced wrinkles. Further lowering of  $V_{CE}$  to a negative potential did not change the flake appearance further.
5. Finally,  $V_{CE}$  was increased to 4.5 V. Throughout the sweep, similar color changes were observed. While waiting at 4.5 V the flake appearance transitioned from that of 3.6(e) to similar but much brighter colors.  $V_{CE}$  was swept back to 0 V, after which the flake darkened but did not recover to its appearance at the end of the previous step.

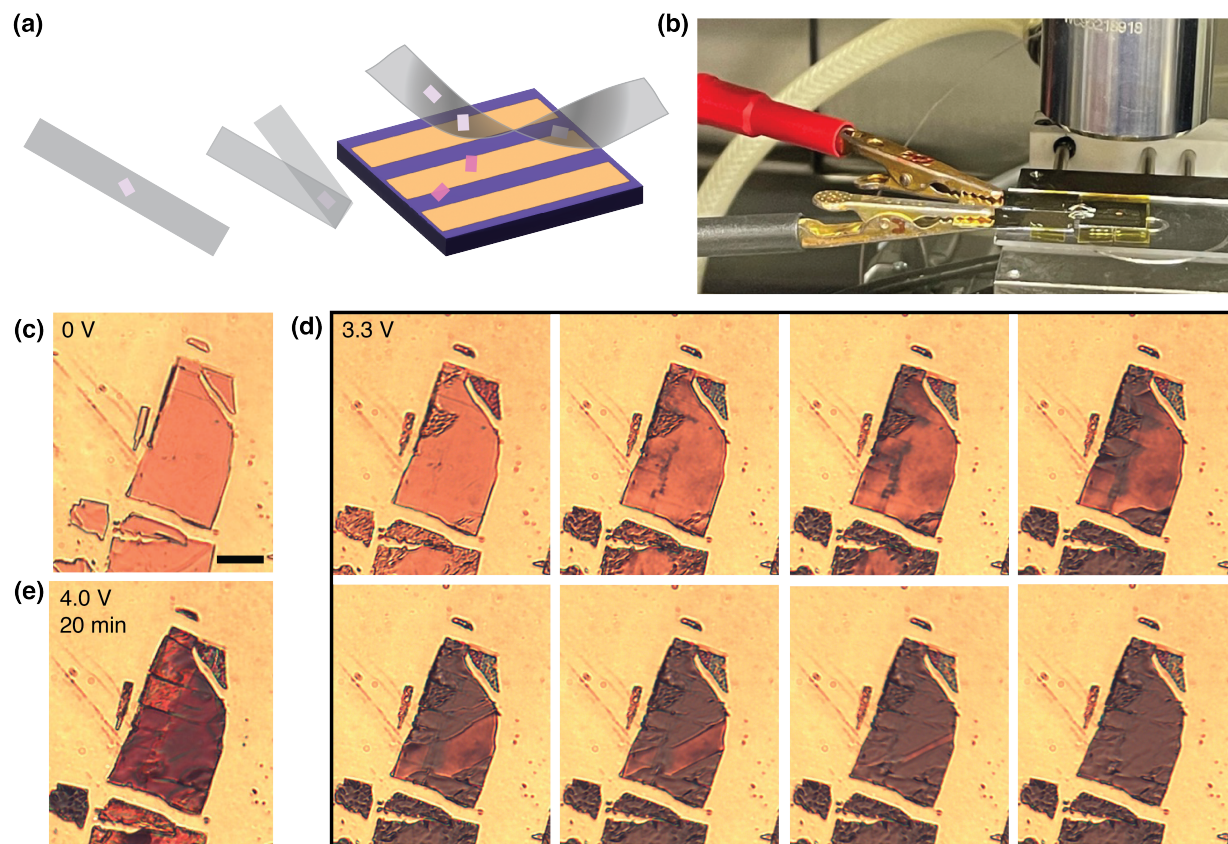
Multiple other experiments were performed in a similar manner, observing similar patterns in the changes to flake appearance. This method is a useful way to characterize the intercalation behavior of  $\text{HoTe}_3$  because of the relative simplicity of sample preparation and because of the high optical contrast of the flake (and its various color-changing stages) on the Au background. The findings of these experiments suggest that intercalation in  $\text{HoTe}_3$  can occur in several phases, which are only partially reversible.

## Electrochemical intercalation of $\text{HoTe}_3$ with simultaneous optical and transport measurements

To better characterize the behavior of  $\text{HoTe}_3$  as it undergoes optical changes during intercalation, we performed a similar experiment to those described above, this time including a 2-probe DC resistance measurement across the  $\text{HoTe}_3$  flake throughout.

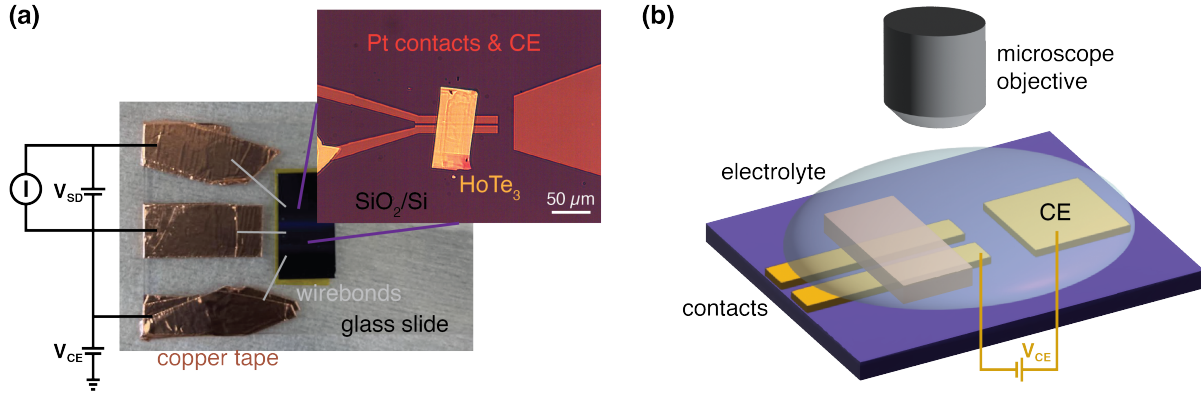
### Sample preparation

Electron-beam lithography followed by electron-beam evaporation of Cr/Pt (1 nm/10 nm) was used to pattern two contacts and a large CE onto a 285 nm  $\text{SiO}_2/\text{Si}$  substrate, similar to previous methods for fabrication of on-chip electrochemical cells.[69, 70] The chip was secured to a glass slide, and both contacts and the CE were wirebonded to pieces of copper tape, which were stuck to the edges of the glass slide. To obtain a  $\text{HoTe}_3$  flake for measurement, a piece of Gel-Pak 4 PDMS was first stuck to a glass slide and cut into small squares with a razor blade. In an Ar glovebox,  $\text{HoTe}_3$  was exfoliated onto Scotch Magic tape and the tape was pressed onto the PDMS squares to transfer flakes. The PDMS squares were searched by optical microscopy until a suitable  $\text{HoTe}_3$  flake was located. The square containing this



**Figure 3.6:** Electrochemical intercalation of HoTe<sub>3</sub> on Au electrode. (a) Illustration of exfoliation of HoTe<sub>3</sub> onto a SiO<sub>2</sub>/Si chip with Au electrodes. (b) Photograph of experimental setup: A chip with Au electrodes is secured to a glass slide along with two pieces of Au-coated Si, and the Au electrodes are wirebonded to the larger Au/Si pieces. HoTe<sub>3</sub> is exfoliated onto the chip, the slide is secured to a heated stage beneath a microscope objective, and alligator clips which attach to the voltage source are secured to the two Au/Si pieces. A drop of Li<sup>+</sup> polymer electrolyte is placed onto a chip such that it is touching two electrodes and covering flakes of HoTe<sub>3</sub>. (c) Optical micrograph of HoTe<sub>3</sub> flake on Au at the beginning of the experiment, at 0 V. (d) Optical micrographs taken during second voltage sweep cycle while voltage is held at the observed intercalation onset potential 3.3 V, showing movement of the intercalation front through the flake. (e) Flake after 20 minutes at 4.0 V with bright colors appearing.





**Figure 3.7:** Experimental setup for electrochemical intercalation of  $\text{HoTe}_3$  with simultaneous optical and transport measurements. (a) Photograph of device on slide, with expanded view showing an optical micrograph of  $\text{HoTe}_3$  flake on contacts without electrolyte. Annotations show different sample components as well as a diagram for the application of a CE potential  $V_{CE}$ , as well as a DC current measurement with a constant source-drain potential ( $V_{SD}$ ) applied. (b) Schematic of on-chip electrochemical cell beneath a microscope objective.  $V_{CE}$  is applied to drive  $\text{Li}^+$  intercalation into the  $\text{HoTe}_3$ .

flake was carefully picked up with tweezers and placed onto another piece of PDMS on a glass slide, forming a stamp for flake transfer. The PDMS stamp containing the flake was secured into a micromanipulator and carefully lowered over the two Pt contacts. The stamp was lifted and the flake was left on the contacts, and a  $\text{Li}^+$  polymer electrolyte droplet was carefully cast onto the sample such that it covered both the flake and the CE. The experimental setup is summarized in Figure 3.7. Two Keithley SourceMeters are used in this measurement: one connected to the CE to apply  $V_{CE}$ , and the other to both contacts to apply a constant DC voltage (10 mV initially; increased to 50 mV later in experiment) and simultaneously measure the current between the two contacts. Instead of manually adjusting  $V_{CE}$  throughout, which was done in the previous experiments, software is used to control the sweep of  $V_{CE}$  and to measure the SD current.

### Experimental procedure and results

Observation of flake appearance and corresponding  $V_{CE}$  sweep was carried out according to the results discussed in the previous section, and some experimental details will be omitted here to focus on the main findings of this study, which are summarized in Figure 3.8.  $V_{CE}$  was swept (1 mV/s) to 2.0 V. After waiting at 2.0 V for 20 minutes with minimal visual change,  $V_{CE}$  was swept to 4.0 V and allowed to equilibrate for 1 hour. Figure 3.9(a) shows transport data  $R$  vs.  $V_{CE}$  throughout the sweep from 0-4 V. Sharp jumps are seen at 2.0 and 4.0 V because  $R$  changed as  $V_{CE}$  was held. We expect  $\text{Li}^+$  intercalation to increase the carrier density of the material due to electron-doping, so a drop in  $R$ , seen here from 1-2.5

V could be indicative of intercalation. Although the visual changes throughout this sweep, shown in Figure 3.9(b), are not as dramatic as the ones we focused on in the previous study (or for the rest of this experiment), some color change is apparent at the bottom of the flake, and there are visible changes at the right edge of the flake. This suggests that intercalation may occur very early on in the potential sweep, even before it is very obvious visually.

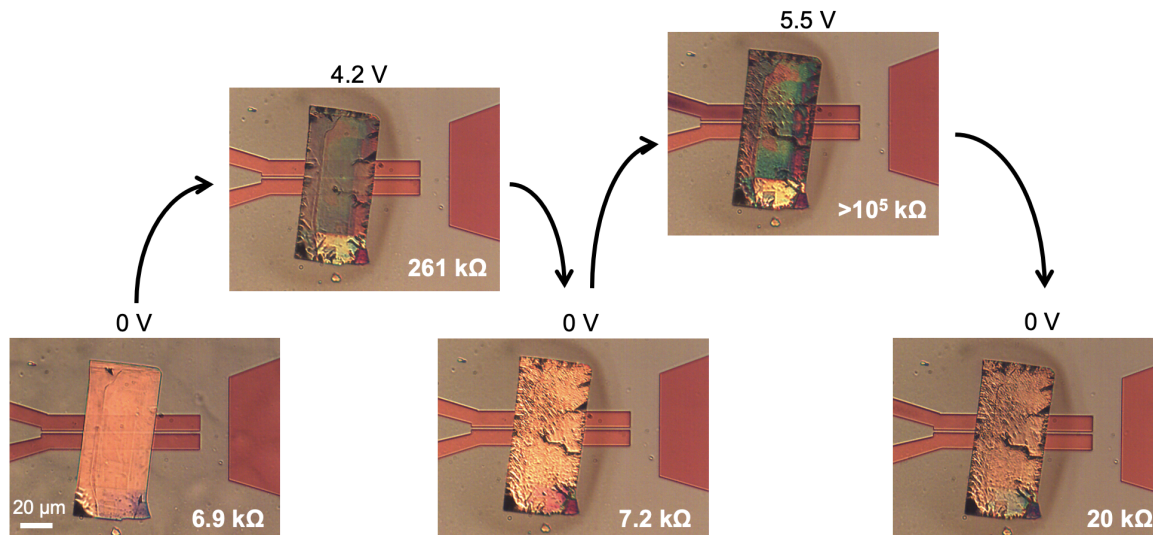
After holding at 4.0 V,  $V_{CE}$  was swept to 4.2 V and held. At 4.2 V, the flake underwent a series of visible changes similar to those previously observed in the intercalated  $\text{HoTe}_3$  on Au: during the first 10 minutes at 4.2 V, small patches throughout the flake appeared to darken, followed by uniform dark regions growing in from the sides of the flake, which we again attribute to the movement of an intercalation front through flake. The intercalation front appears to nucleate at the small features on the right edge of flakes that are visible in Figure 3.9(b). After 10 minutes, the darkened flake gradually began to appear more colorful, as shown in the second image from the left in Figure 3.8.  $R$  increased only gradually throughout the first 20 minutes at 4.2 V, then began to rapidly increase, and after 40 minutes was measured to be around 260 k $\Omega$ . The rapid change in  $R$  coincided with the gradual change in flake appearance, as different colors started to appear. After 40 minutes,  $V_{CE}$  was swept back to 0 V. During the downsweep,  $R$  dropped very suddenly when  $V_{CE}$  reached 3.3 V. At 0 V, while the flake color somewhat recovered to its original appearance, many cracks and wrinkles were visible. However, in terms of magnitude,  $R$ , which was 7.2 k $\Omega$  at 0 V, is relatively close to its original value of 6.9 k $\Omega$  at 0 V.

$V_{CE}$  was cycled once again, this time from 0 V to 5.5 V. Similar to previous observations, the colors intensified past what was seen at 4.2 V. During this transition,  $R$  increased rapidly, reaching  $> 10^5$  k $\Omega$  (the current was too low at this point to detect in our measurement system).  $V_{CE}$  was then swept back to 0 V, where  $R$  was again measurable, but over twice its value at the beginning of the experiment, indicating that the changes undergone at 5.5 V are somewhat irreversible.

## Discussion

We summarize the findings and of the optical measurements as follows:

1. With small increase in  $V_{CE}$ , minor visible changes can be seen. They are accompanied early on by a decrease in  $R$ , and are visibly reversible.
2. Past a threshold potential, the flake will reach “dark phase 1” wherein small patches throughout the flake change color. These changes are mostly reversible visually.
3. When held at the threshold potential, a more uniformly dark front will move in starting from the sides of the flake, which we will call “dark phase 2”. Visually, some changes will be irreversible.
4. After full converting to dark phase 2, the flake will gradually transition to “colorful phase 1” where the flake appears multicolored. This is accompanied by a dramatic,  $\sim 30$ -fold increase in  $R$ . Visually, some changes will be irreversible.

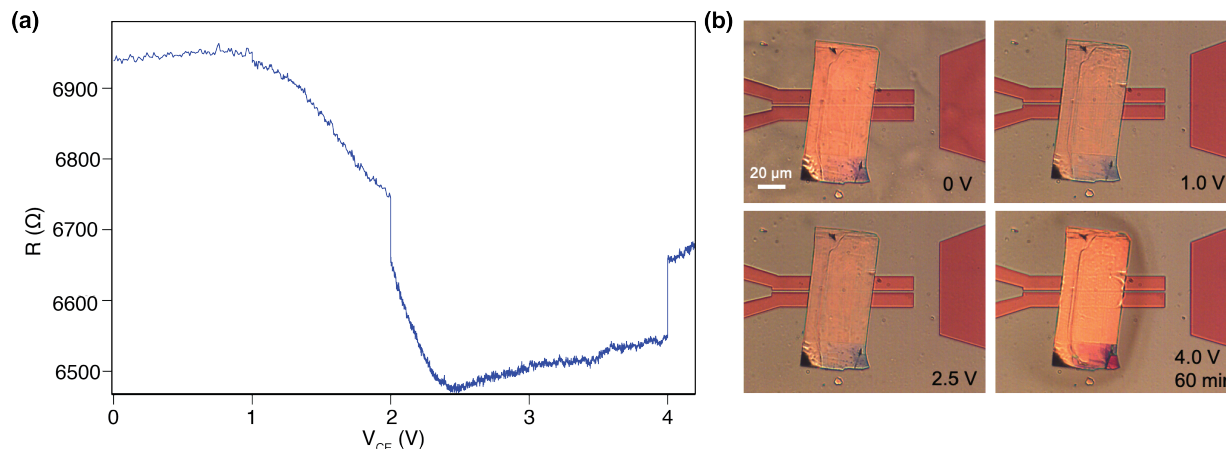


**Figure 3.8:** Optical micrographs taken at different counter electrode potentials (labeled above the images), including 2-probe resistance (labeled in the bottom right corners of the images).

5. Past the threshold potential, the colors of the flake will brighten in “colorful phase 2”.  $R$  increases to a value indicating that the sample has become completely insulating. Changes are only partially irreversible visually, and the material will not return to its original  $R$ .

These findings suggest that the intercalation reaction of interest for electrochemically doping  $\text{HoTe}_3$  may occur at very low  $V_{CE}$  and will not show the same type of visual intercalation front as in graphite.[77] It is possible that further intercalation, visible as the transformation into dark phase 2, will cause some sort of decomposition of the sample, and that the colorful phases will cause the sample to further decompose. A possible mechanism for decomposition is the formation of Li-polytellurides, which variable-length chains of Te bound to Li.[78] These are known to form in a variety of chalcogen-containing compounds upon reaction with an alkali ion. However, the degree of reversibility, especially in  $R$  suggests that some type of reversible metal-insulator transition (likely unrelated to the CDW distortion) could occur. Further experiments to structurally investigate  $\text{Li}^+$  intercalation into  $\text{HoTe}_3$  in-situ are needed, but the instability of  $\text{HoTe}_3$ , which seems to worsen with in the presence of  $\text{Li}^+$ , makes this difficult to accomplish.





**Figure 3.9:** (a) In-situ resistance measurement during Li intercalation of  $\text{HoTe}_3$ . (b) Optical micrographs taken throughout intercalation, corresponding to the resistance measurement in (a).

### Attempts to measure Raman spectra and electronic transport in-situ

Numerous failed attempts were made to fabricate  $\text{HoTe}_3$  devices for in-situ transport studies during electrochemical intercalation. Even though we successfully carried out transport in  $\text{HoTe}_3$  stacked on bottom contacts previously, the presence of electrolyte consistently prevented us from making electrical contact to the  $\text{HoTe}_3$ . Additionally, we attempted to carry out in-situ Raman measurements using a similar experimental setup to measurements conducted on Au electrodes. A glass coverslip was fastened on top of the sample with GE varnish in order to prevent air exposure. Spectra were acquired as  $V_{CE}$  increased; although pronounced changes in the spectra occurred, even those taken at 0 V do not resemble the spectra shown in Figure 3.3; instead, two broad peaks appear at higher frequencies (near 120 and 140  $\text{cm}^{-1}$ ), which are attributed in other studies to decomposed samples, with vibrational modes similar to elemental Te.[73] It is unclear whether this decomposition was a result of improper protection from air exposure, or if it is caused by the electrolyte, but in either case, this shows that  $\text{HoTe}_3$  is likely not suitable for most in-situ electrochemical studies that would provide detailed structural information.

## 3.5 Outlook and future directions

While air sensitivity and the difficulty of observing CDW transitions in transport measurements may limit the feasibility of transport studies on exfoliated  $R\text{Te}_3$ , there are still some possible directions to explore. A material that bears structural similarities to the  $R\text{Te}_3$  family is  $\text{CuTe}$ , which contains layers of Cu sandwiched by Te square nets, and undergoes a very

similar CDW transition to those observed in the  $R\text{Te}_3$  family near 335 K.[79–81] Using a self-flux method, we synthesized crystals of  $\text{CuTe}$ , followed by characterization by powder x-ray diffraction and Raman spectroscopy which matched well with those reported in literature.[79] The advantage of  $\text{CuTe}$  over  $R\text{Te}_3$  is that it is air-stable and would likely be more robust to in-situ electrochemical measurements.<sup>3</sup>  $\text{CuTe}$  could therefore be a promising future area of study for those interested in modifying a quasi-1D CDW material electrochemically.

## 3.6 Conclusions

This chapter presented an overview of  $R\text{Te}_3$  materials and their CDW properties.  $\text{GdTe}_3$  and  $\text{HoTe}_3$  crystals were synthesized by a Te self-flux method and characterized by Raman spectroscopy. Transport measurements confirmed the presence of two CDW transitions in  $\text{HoTe}_3$  at temperatures similar to those observed in previous studies. In-situ studies of electrochemical intercalation observed by optical microscopy (and simultaneous transport measurements) were carried out, revealing several possible phases of intercalation and unexpected changes in resistance upon intercalation. While detailed experiments were limited by sample stability, we demonstrate, to our knowledge, the first study of electrochemical intercalation in  $R\text{Te}_3$ .

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<sup>3</sup>It also has a fun name.

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