

# Charge Density Waves in Transition Metal Dichalcogenides

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उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

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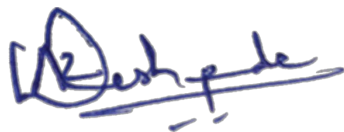




## CERTIFICATE

We certify the work incorporated in the thesis entitled, '**Charge Density Waves in Transition Metal Dichalcogenides**', submitted by **Imrankhan Mulani**, was carried out by the candidate under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.

Date: January 23, 2024



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## DECLARATION

I, **Imrankhan Mulani**, declare that the work presented in the thesis entitled '**Charge Density Waves in Transition Metal Dichalcogenides**' is my own and is original, and where others' ideas have been included, I have adequately cited and referenced the original sources. I solely own the responsibility for the originality of the entire content. This work (in part or in full) has not been submitted to any University or institution for awarding any degree or diploma. I also declare that I have adhered to all academic honesty and integrity principles and have not misrepresented, fabricated, or falsified any idea/data/fact/source in my submission. I understand that violation of the above will cause disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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Imrankhan Mulani

## ABSTRACT

During the early 1930s, Rudolf Peierls delved into the study of basic atomic systems, leading to a significant revelation: the intrinsic instability of one-dimensional atomic chain structures to external perturbation (e.g., applying electric field or reducing temperature) led to a phase transition, introducing a new electronic state. Notably, the elusive nature of perfect one-dimensional systems in the nature underscored the depth of Peierls's conceptual insights. His thorough elaboration of this concept is meticulously documented in his influential 1955 work, "Quantum Theory of Solids,". He presented a model that explains the electronic phase of materials in a one-dimensional chain of atoms (e.g., linear chain compounds).

Peierls' model revolved around a one-dimensional atomic lattice where each site contributed an electron (half-filling), prompting a restructuring when the temperature lowered. The Peierls instability arises from Fermi surface nesting, which leads to an increased Lindhard susceptibility for specific momentum vectors. The system spends energy by distorting the lattice, that is by generating elastic strain. However, the system ultimately lowers energy by reorganizing the Fermi surface and opening a band gap (Metal-insulator transition). This restructuring of the Fermi surface is energetically favorable state despite the initial energy investment in the form of elastic strain or lattice distortion. This interaction between electron density and lattice resulted in the formation of a charge density wave (CDW), resembling a standing wave. Initially explored in relation to superconductivity, CDW phases were later discovered in various materials. However, describing CDW at a microscopic level proved challenging for all cases. Their similarity seemed more apparent at a higher observational level rather than within the microscopic framework. Understanding how CDW form became intricate and specific to each material, lacking precise predictive models for their occurrence in different materials goes beyond the explanatory capacity of Peierls' model.

The current focus of research delves into categorizing materials based on the underlying microscopic mechanisms dictating various charge density waves (CDW). Many newly discovered systems stand apart from the conventional Peierls' model, showcasing deviations. They don't exhibit the expected metal-insulator transition, Fermi surface nesting, or escalating electronic susceptibility during the CDW phase, as Peierls' model suggests. Instead, differing in dimensionality, these systems display robust electron-electron or electron-phonon coupling. Of particular interest

are materials where CDW formation arises from electron-phonon coupling and the presence of excitonic condensation instability. Due to their diverse electronic properties, Transition Metal Dichalcogenides (TMDCs) offer a promising arena for this exploration. Our investigation focuses specifically on two TMDCs: Titanium diselenide ( $1T\text{-TiSe}_2$ ) and Niobium diselenide ( $2H\text{-NbSe}_2$ ), each exemplifying distinct CDW systems. Our objective is to conducting an extensive examination of CDW within these materials. We aim to manipulate CDW using external factors like strain and doping, harnessing the Scanning Tunneling Microscopy (STM) for meticulous exploration. The STM stands out as a vital tool in unraveling the complexities of CDW formation, thanks to its ability to map electron density with an Angstrom-level spatial resolution. This capability allows STM to shed light on the structural and electronic attributes involved in CDW formation.

The semimetal titanium diselenide ( $1T\text{-TiSe}_2$ ) exhibits a propensity to form CDW below a certain temperature, typically around  $T_{CDW} \sim 200K$ . The material's indirect band gap significantly increases the chances of exciton (bound states of electrons and holes) formation. Within the realm of CDW mechanisms, ongoing discussions often revolve around the Jahn-Teller effect and exciton condensation. Exploring the impact of metal atom doping, specifically focusing on Titanium self-doping due to the non-stoichiometric nature of  $\text{TiSe}_2$ , has led to valuable insights into the material's electronic states. Introducing a substantial number of Ti atoms through intercalation creates a localized environment abundant with electrons, thereby influencing the larger-scale CDW arrangement within the material. Remarkably, atomic-scale measurements via STM have unveiled an intriguing trend: the size of CDW domains correlates with the concentration of intercalation. Further examination into the autocorrelation length of these domains and the phase coherence across their boundaries concerning the number of intercalants suggests a potential association between the CDW transition and exciton condensation. This observation hints at the possibility of a mechanism that goes beyond the electron-phonon interactions in this intricate interplay of phenomena within  $1T\text{-TiSe}_2$ .

The study of charge density waves (CDWs) in materials like  $\text{TiSe}_2$  has indeed seen significant attention, especially in understanding their nature and behavior. The CDW phase is often characterized by scalar order parameters like electronic charge density or exciton binding energy. The charge degree of freedom can sometimes couple with directional order, imparting vectorial characteristics to the CDW order parameter. The breaking of symmetry within the directional order can affect this

coupling, consequently giving rise to novel forms of charge ordering. Recent scholarly discussions have been particularly focused on  $\text{TiSe}_2$ , highlighting its chiral nature within the CDW phase. This chiral behavior signifies a state where mirror symmetry is broken, carrying significant implications for the material's physical properties. STM-based investigations have provided substantial evidence supporting orbital ordering. This observed orbital ordering could potentially be linked to the chiral behavior observed in  $1T\text{-TiSe}_2$ . Understanding the connection between orbital ordering and the manifestation of chiral behavior opens avenues for exploring novel physical phenomena and applications in such materials.

In the metallic niobium diselenide ( $2H\text{-NbSe}_2$ ), coexistence of CDW ( $T_{CDW} \sim 33K$ ) and superconductivity ( $T_{SC} \sim 7K$ ) are predominantly governed by strong electron-phonon coupling. By manipulating strain, we meticulously probed CDW ordering in  $2H\text{-NbSe}_2$  through STM imaging, uncovering a new CDW ordering pattern. The study of CDW in  $\text{NbSe}_2$  presents intriguing insights into the influence of local strain on strong electron-phonon coupling. Through precise STM imaging, a novel  $2\sqrt{3}a_0 \times 2\sqrt{3}a_0 R(30^\circ)$  tri-directional ( $3Q$ ) CDW order has been identified in bulk crystals of  $\text{NbSe}_2$ . The simultaneous presence of  $1Q$  and  $3Q$  charge ordering supports the notion that electron-phonon coupling parameters rely on momentum and orbital characteristics. However, the alignment of the  $3Q$  CDW wavevector along the  $\Gamma\text{-K}$  direction challenges existing models, prompting a reevaluation or expansion of current theoretical frameworks. The observed relationship between strain variations and the emergence of both the unidirectional ( $1Q$ )  $4a_0 \times 1a_0$  stripe CDW order and the novel tri-directional ( $3Q$ )  $2\sqrt{3}a_0 \times 2\sqrt{3}a_0 R(30^\circ)$  order suggests a potential quantum phase transition near a critical point. This transition seems to occur as the system approaches a critical threshold, allowing these distinct charge ordering patterns to coexist. These findings highlight the necessity of exploring strain effects within two-dimensional (2D) monolayers of transition metal dichalcogenides (TMDs) and bulk materials. Investigating these phenomena in bulk crystals offers valuable insights into the intricate behavior of CDWs and their relationship with electron-phonon interactions in more realistic material contexts.

This research ambitiously aims to unravel the microscopic mechanisms governing the formation of charge density waves (CDWs) within the expansive field of CDW studies. Through a comprehensive examination of  $\text{TiSe}_2$ , our work has notably advanced the understanding of the exciton condensation phase and its vulnerability to intrinsic defects. This progress has paved the way for creating theoretical mod-

els that elucidate interactions between defects and excitons, offering insights into their practical implications. Additionally, our exploration into the chiral nature of CDWs in  $1T$ -TiSe<sub>2</sub>, linked with orbital ordering, has unveiled new perspectives. Similarly, our investigation of strain-modulated CDWs in NbSe<sub>2</sub> has provocatively challenged established notions primarily rooted in electron-phonon interactions. This has prompted a significant reassessment of the mechanisms governing phase transitions, involving intricate interplays between electron-electron and electron-phonon interactions. This contribution represents a step forward, expanding the landscape of CDW research beyond the confines previously set by the Peierls model.

## PUBLISHED CONTENT AND CONTRIBUTIONS

- [1] **Mulani, Imrankhan**, Walve Vaibhav, Gargee Bhattacharyya, Priya Mahadevan, and Aparna Deshpande. “Unveiling new charge order in  $2H\text{-NbSe}_2$ ”. In: *under preparation* (2023).
- [2] **Mulani, Imrankhan**, Walve Vaibhav, Luminita Harnagea, and Aparna Deshpande. “Nature of chiral charge density waves in  $1T\text{-TiSe}_2$ ”. In: *under preparation* (2023).
- [3] Umashankar Rajput, Akhtar Md F, **Mulani, Imrankhan**, Giriraj Vyas, S Bhowmick, Aparna Deshpande, and Prashant Kumar. “Understanding substrate-supported freestanding borophene at the atomic scale”. In: *Under review* (2022).
- [4] Rejaul Sk, Debayan Mondal, **Mulani, Imrankhan**, Priya Mahadevan, and Aparna Deshpande. “Emergent Negative Differential Resistance with an Undisturbed Topological Surface State”. In: *The Journal of Physical Chemistry C* 126.39 (2022), pp. 16744–16750.
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*"...We are what they grow beyond. That is the true burden of all masters."*

— Yoda

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## Chapter 1

# INTRODUCTION

*"An experiment is a question which science poses to Nature, and a measurement is the recording of Nature's answer."*

— Max Planck

### 1.1 An overview

It's fascinating how the twin revolutions of relativity and quantum mechanics reshaped our understanding of the universe in the 20th century [1]. The paradigm shift [2] from classical mechanics to these theories transformed our perceptions of space, time, matter, and energy. Relativity, encompassing both special and general theories, revolutionized our notions of space-time and gravitational interactions. Meanwhile, quantum mechanics delved into the microscopic realm, providing a framework for understanding atomic and subatomic phenomena and introducing probabilistic behavior and wave-particle duality.

Physics took divergent paths with one route expanded from quantum mechanics, exploring its application to increasingly complex systems, eventually leading to solid-state physics. This field bridged the microscopic quantum world with macroscopic condensed matter, unlocking deeper scientific understanding and unexpected practical applications. The study of complex systems and condensed matter has evolved into a frontier of physics, intertwining fundamental research with technological advancements [3]. The approach of reductionism, aiming to understand systems by exploring their fundamental constituents, has been central to these developments. From discovering elementary particles through particle accelerators to exploring emergent properties in condensed matter systems, physics has strived to uncover the underlying principles governing our universe.

This journey—from the atomic and subatomic world to the complexities of condensed matter—represents a continuum of exploration, continually challenging our understanding and driving theoretical advancements and practical innovations. Within this continuum lies a profound realization: the structure of matter isn't uniform but rather stratified, forming layers where emergent phenomena manifest at

each level of aggregation. At the heart of this expedition lies the concept of order, generating patterns that elucidate the underlying symmetries within the material world like crystalline structures showing exquisite periodicity. Much akin to the layers in the continuum of matter, phase transitions demonstrate an inherent stratification, each transition unveiling emergent phenomena and instabilities that redefine the material's nature. Exploring these transitions enriches our comprehension of matter and underpins the development of novel materials and technologies, birthing innovations that reshape our world.

### 1.1.1 Order and symmetry in condensed matter systems

In understanding physical systems, equilibrium signifies a state with no net energy or particle influx or efflux. The characterization of different states of matter relies on macroscopic parameters such as internal energy ( $U$ ), temperature ( $T$ ), entropy ( $S$ ), pressure ( $P$ ), and volume ( $V$ ). Statistical mechanics play a crucial role in establishing how these macroscopic parameters link to the microscopic states of a system's constituents. This linkage defines the physical state of matter. A visual representation of this relationship, showcasing the interplay between physical states and macroscopic parameters, takes the form of a phase diagram. In this diagram, equilibrium phases correspond to the free energy minima ( $F = U - TS$ ). The appearance of various states in the phase diagram arises from the interplay between the two terms in the free energy equation: internal energy and entropy. Entropy tends toward disorder, while energy leans toward order, manifesting diverse states within the diagram.

Condensation corresponds to the constraining dynamics of microscopic constituents of a macroscopic system in configuration space (position space) or momentum space. This implies some order or regularity in the configuration or momentum space of the condensed system. The most common order manifests as the positional ordering of atoms, a correlation between the position of atoms. If the correlations tend to infinity, it is a long-range order; if only a few neighbors are correlated, it is short-range. The random distribution of atoms is a perfect disorder. Crystalline solids have long-range order with a spatial periodicity; quasicrystals are also in long-range order with rotational symmetry, but no translational periodicity; glasses and liquids are in short-range order without any periodicity; and gases are perfectly disordered. Another important kind of order is in the momentum space. Order in momentum space, or wave order, is expressed by the occupation of the same momentum states. Order in the system originates through the interaction between

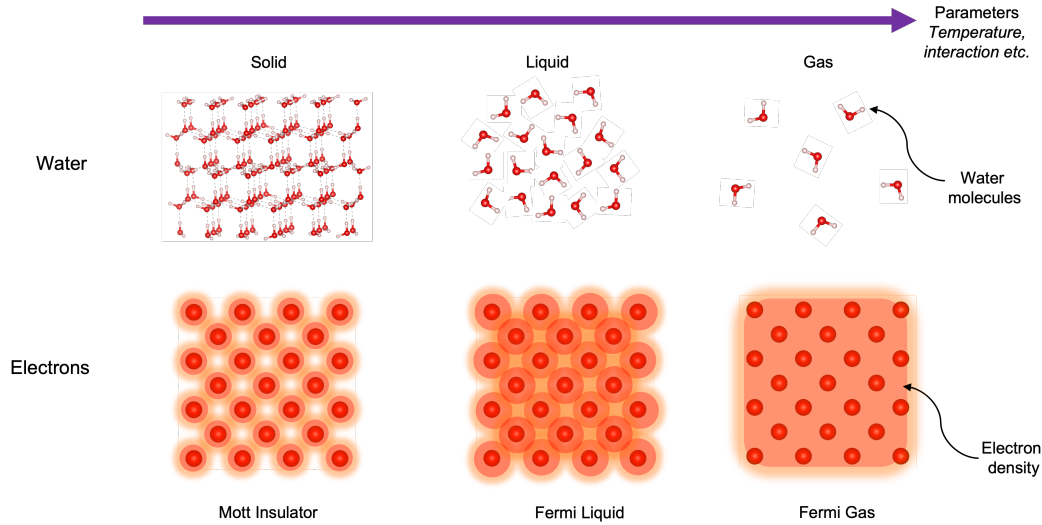


Figure 1.1: Illustration of phases in the many-body system. Different phases correspond to different symmetry of the order parameter

the particles. There is also another type of order in particles with spin. Ordering in spin happens as they align along the same direction; otherwise, randomly oriented spins are disordered. We can conclude that condensed matter means the study of condensation or ordering in phase space divided into position and momentum space.

A phase transition from one order to another is a cooperative phenomenon. The concept of order can be generalized for the correlation between different quantities of the system. The measure of an order can be associated with the system's symmetry. The spatially periodic system possesses translational and rotational symmetry. The mathematically rigorous formulation of the state or phase of the system can be described by the kind of symmetry the system has (its symmetry group). The presence or absence of symmetry in a particular state of matter is unambiguous. A certain symmetry ceases to exist after phase transition. For example, liquid-to-crystalline solid transition, a larger group of continuous rotation, and translational symmetry in liquids reduced or broken to discrete translation and rotations in the periodic crystalline phase (see Figure 1.1). The value of a particular order parameter different from zero can describe an ordered phase after phase transition. This model of phase transition was first proposed by Lev Landau and order parameters are defined phenomenologically in this model [3]. The order parameter is a mathematical entity, an expectation value of a certain macroscopic quantity; it can be a complicated quantity like tensors with many components or a simple number. It is zero above the transition temperature and gets a finite value below the transition.

This order parameter describes qualitative and quantitative aspects of symmetry in the low symmetry phase. The critical temperature  $T_c$  marks the phase transition's temperature. Some examples of symmetry-broken phases are listed in Table 1.1.

Condensed matter systems are many-body interacting systems, and finding their ground and corresponding excited states is difficult. The Landau Fermi liquid theory is a foundational framework in condensed matter physics, particularly in understanding the behavior of interacting electrons. The theory describes a system of interacting electrons in a metal, that exhibit collective behavior despite their mutual interactions. In a Fermi liquid, electrons behave as if they were weakly interacting particles, like free particles, despite the Coulomb repulsion between them. One of the central ideas of the Landau Fermi liquid theory is the concept of quasiparticles. These quasiparticles are not the actual electrons themselves but are collective excitations or quasi-bound states formed by interactions among the electrons. They carry the quantum numbers of electrons but have modified properties due to their interactions with the surrounding medium. This theory provides a framework for understanding various macroscopic properties, such as electrical conductivity, thermal conductivity, specific heat, and magnetic susceptibility. It successfully explains phenomena like the behavior of metals at low temperatures, the Landau damping of collective excitations, and the temperature dependence of the electronic specific heat in metals. Different theories of quasiparticles like phonon (excitation of lattice), magnon (excitation of ordered electronic spins), exciton (electron-hole pair), and others were developed consequently.

| Broken Symmetry  | Phenomena           | Ordered phase            | Elementary excitation |
|------------------|---------------------|--------------------------|-----------------------|
| Translation      | Crystallization     | Crystal solids           | Phonon                |
|                  | Electronic          | Charge                   | Phason                |
|                  | crystallization     | density waves            | Amplitudon            |
|                  | Electronic          | Spin                     | Phason                |
| Time reversal    | crystallization     | density waves            | Amplitudon            |
|                  | Ferromagnetism      | Ferromagnet              | Magnons               |
|                  | Anti-ferromagnetism | Anti - ferromagnet       | Magnons               |
| Gauge invariance | Superconductivity   | Superconductor           | Electrons             |
|                  | Superfluidity       | $^4\text{He}$ superfluid | Phonon<br>Roton       |

Table 1.1: Interesting examples of broken symmetry phenomenon in condensed matter system. Adapted from reference [3].



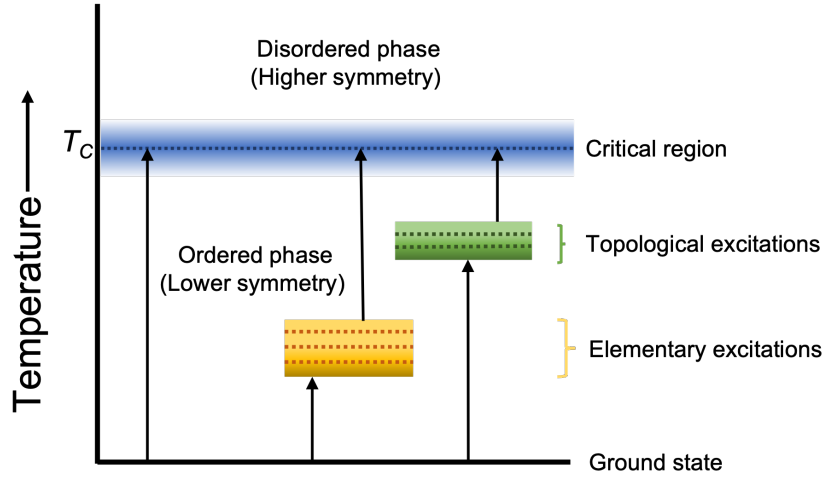


Figure 1.2: Illustration of broken symmetry phase of a system with energy states of excitations in the typical many-body system. Adapted from reference [3].

There are also finite energy excitations in interacting systems known as topological defects and dislocations in crystals and magnetic domains. The existence and behavior of these topological defects highlight the intricate interplay between material structure, properties, and external influences. Elementary excitations and topological defects try to restore the broken symmetry after phase transition. Near critical points where phase transitions occur, certain system properties can be described in terms of quasiparticles. Their behavior and interactions can become dominant, leading to critical phenomena such as diverging correlation lengths or power-law behavior in various physical quantities. Naturally, excitations can play central roles in phase transitions. In specific phase transitions, some excitation goes to lower energy states, breaking the symmetry and leading to a phase transition. In contrast, some defect-mediated phase transitions exemplify the influence of topological excitations. Topological defects like dislocations in crystals or domain walls in magnetic materials also significantly impact phase transitions. In some cases, the formation, motion, or annihilation of these defects can drive phase transitions or significantly affect the characteristics of the transition. The energetics of excitations and phase transition are schematized in Figure 1.2. In certain exotic phases of matter, like topological phases, defects and quasiparticles are inherently linked due to their topological nature. Topological defects in these phases often host quasiparticles with non-trivial properties, such as anyons or Majorana fermions, which play crucial roles in the phase transitions between different topological phases.

To summarise, a small piece of metal presents a complex assembly of free

electrons within a lattice of ions. Typically conceptualized as an electron sea, these electrons in metals are primarily independent, with minimal interactions among themselves or with the ion lattice. Classified as Fermions following Fermi-Dirac statistics, these electrons collectively constitute a non-interacting Fermi gas. However, their behavior varies across different materials, and by manipulating electron interactions, diverse phases of electron gas or Fermi gas can be induced. Adjusting these interactions can gradually shift the Fermi gas towards a Fermi liquid phase. Further enhancement of interactions leads to a transition into a strongly correlated fermionic system. Strong interactions ultimately prompt the electronic system to crystallize (Wigner crystallization) [3]. The enhanced electron-electron or electron-lattice interactions are observed in various phases, such as the charge density wave (CDW) transition. The formation of periodic modulations in the electron density gives rise to the emergence of the CDW phase, characterized by the periodic arrangement of charges within the material. This transition showcases the profound impact of electron interactions on the material's behavior and phase transitions, underscoring the link between electronic phases and phenomena like the CDW transition in condensed matter systems. The CDW state is an interesting example of how the interaction leads to phase transition manifesting as a positional ordering. Therefore, spatial local density probes can be used to trace back the interaction.

This thesis will use a local electron density probe scanning tunneling microscope (STM) to systematically investigate the broken symmetry phenomenon of charge density waves (CDW) arising from electron-electron and electron-lattice interactions in different systems.

## 1.2 Outline of thesis

In the early 1950s, the theoretical groundwork for understanding superconductivity in different materials led to the proposal of charge density waves (CDW) as an intriguing correlated phenomenon [4, 5]. At temperatures below the transition temperature ( $T_{CDW}$ ), the material lattice symmetry spontaneously breaks, resulting in a modulation of electronic charge density characterized by a specific wavevector. Utilizing the Scanning Tunneling Microscope (STM), a remarkable tool that harnesses electron tunneling in quantum mechanics, we can map the electronic density of states with atomic-scale precision.

This thesis investigates CDW in transition metal dichalcogenides, specifically focusing on  $1T$ -TiSe<sub>2</sub> and  $2H$ -NbSe<sub>2</sub>. **Chapter II** provides an overview of TMDC,

covering their physical structure, synthesis methods, and electronic properties. Moving to **Chapter III**, the focus intensifies on CDW. Beginning with the classical Peierls proposal within the context of the electronic structure of solids, this chapter attempts to classify CDW, exploring various proposed schemes and investigating materials across these classes.

**Chapter IV** serves as the core for experimental methodologies, elucidating the theoretical basis of the experimental principles before detailing the physical apparatus. Our study employs low-temperature STM to examine  $1T\text{-TiSe}_2$  and  $2H\text{-NbSe}_2$ . **Chapter V** specifically delves into  $1T\text{-TiSe}_2$ , a non-stoichiometric semimetal forming CDW below  $T_{CDW} \sim 200K$ . The presence of an indirect band gap in  $1T\text{-TiSe}_2$  favors exciton formation, contributing to the suggested mechanisms for CDW formation, such as the Jahn-Teller effect or exciton condensation [6]. Moreover, metal doping, particularly Ti self-doping in  $1T\text{-TiSe}_2$ , unveils insights into local electronic states, large-scale CDW ordering, and its excitonic character, proposing exciton condensation-driven CDW transitions [7].

Studies utilizing X-ray diffraction and transport measurements have revealed chiral CDW [8], while optical experiments have observed the nematic phase in the charge ordering of  $1T\text{-TiSe}_2$  [9]. In **Chapter VI**, our investigation probes the chiral nature of CDW in  $1T\text{-TiSe}_2$  using STM.

Shifting the focus to  $2H\text{-NbSe}_2$ , a metallic material exhibiting both CDW ( $T_{CDW} \sim 33K$ ) and superconductivity ( $T_{SC} \sim 7K$ ), **Chapter VII** details our STM exploration. The electron-phonon coupling mechanism governs the CDW formation in  $2H\text{-NbSe}_2$  [10]. Applying strain allows us to manipulate electron-phonon coupling and electron hopping, revealing CDW ordering in strained  $2H\text{-NbSe}_2$ . In summary, this work advances our comprehension of the excitonic nature of CDW and symmetry-broken electronic phases in  $1T\text{-TiSe}_2$  while also unveiling a novel tri-directional CDW state in strained  $2H\text{-NbSe}_2$ , opening new avenues for tuning electronic orders through strain manipulation.

## Chapter 2

### TRANSITION METAL DICHALCOGENIDES

*"What we observe as material bodies and forces are nothing but shapes and variations in the structure of space."*

— Erwin Schrodinger

#### 2.1 An overview

Transition metal dichalcogenides (TMDCs) belong to a class of materials that exhibit a layered structure composed of a transition metal layer sandwiched between two layers of chalcogen atoms (such as sulfur, selenium, or tellurium). This unique atomic arrangement results in a two-dimensional (2D) nature within each layer while retaining weak van der Waals interactions between the layers. TMDC shows fascinating electronic properties, particularly in its monolayer form, which differs significantly from the bulk material. In the monolayer configuration, they transition from an indirect to a direct bandgap semiconductor, making them attractive for optoelectronic applications. This change in band structure enhances their light-matter interaction capabilities, enabling promising advancements in photodetectors, solar cells, and light-emitting diodes (LEDs). Moreover, TMDC possesses remarkable mechanical flexibility and strength, which is crucial for flexible electronic devices and nanomechanical systems. Their atomically thin structure grants them unique electrical properties, such as high charge carrier mobility, making them potential candidates for next-generation transistors and electronic devices operating at nanoscale dimensions [11].

While TMDCs have long been acknowledged in material applications, research efforts predominantly focused on their bulk properties [12]. The pivotal moment occurred with the groundbreaking discovery of graphene in 2004—a single-atom-thick layer of carbon atoms—achieved by mechanically exfoliating it from bulk crystal using simple means like scotch tape [13]. This seminal experiment, credited to Andre Geim and Konstantin Novoselov, earned them the 2010 Nobel Prize in Physics [14]. Graphene's exceptional mechanical and electronic traits captivated attention, notably its surprising electron mobility at room temperature despite its

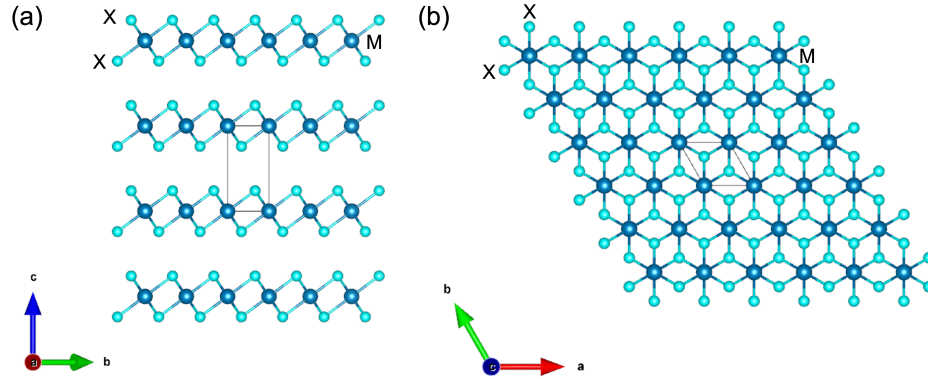


Figure 2.1: Illustration depicting the structure of transition metal dichalcogenides (TMDCs), where transition metal atoms  $M$  (dark blue color) are positioned between two layers of chalcogen atoms  $X$  (light blue color). The layers are bonded through van der Waals interactions. (a) Side view showcasing the layered nature of TMDCs. (b) Top view displaying a hexagonal lattice formed by the arrangement of chalcogen and transition metal atoms

two-dimensional nature [15]. This revelation ignited a quest for analogous two-dimensional materials, thereby shifting the focus towards investigating quasi-2D layered materials and transition metal dichalcogenides (TMDs).

## 2.2 Properties of TMDC

The composition of TMDC comprises  $MX_2$ , where  $M$  represents a transition metal, and  $X$  signifies a chalcogen ( $S$ ,  $Se$ , or  $Te$ ). Van der Waals (vdW) forces facilitate the bonding of layers into a bulk crystal structure. Each layer comprises transition metal and chalcogen atoms, illustrated in Figure 2.1. Within this family of materials, diverse properties emerge from combining different transition metals with chalcogens, resulting in semiconductors (e.g.,  $MoS_2$ ,  $WS_2$ ), semimetals (e.g.,  $WTe_2$ ,  $TiSe_2$ ), metals (e.g.,  $NbS_2$ ,  $VSe_2$ ), and superconductors (e.g.,  $NbSe_2$ ,  $TaS_2$ ) [16]. Interestingly, TMDCs with identical chemical compositions but varying structural polymorphs exhibit distinct electronic characteristics; for instance,  $2H$ - $MoS_2$  demonstrates semiconducting behavior, whereas  $1T$ - $MoS_2$  displays metallic properties [17].

### 2.2.1 Crystal structure

TMDC has numerous structural polymorphs [18]. The main three types are  $1T$ ,  $2H$ , and  $3R$ , which are divided into various subtypes. The letter in the polymorph symbol refers to the symmetry of the unit cells ( $T$  for trigonal,  $H$  for hexagonal,

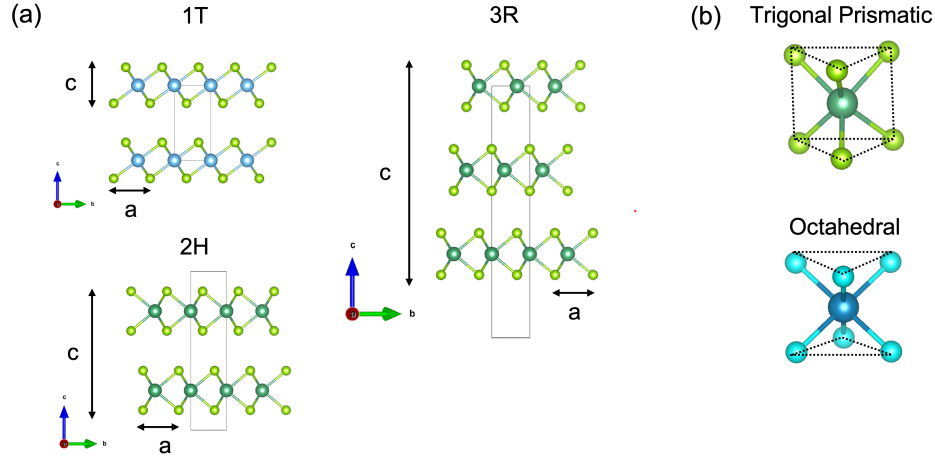


Figure 2.2: Schematic representation of TMDC structural polymorphs. (a) Illustration of different structural configurations:  $1T$  structure featuring a single layer per unit cell with tetragonal symmetry;  $2H$  polymorph comprising two layers per unit cell, exhibiting trigonal prismatic coordination and hexagonal symmetry;  $3R$  with three layers per unit cell and rhombohedral symmetry. (b) Depiction of metal atom coordination within a TMDC unit cell, trigonal prismatic and octahedral arrangements.

and  $R$  for rhombohedral symmetry). The digit before the letter indicates the number of layers within the unit cell (e.g.,  $2H$  structural unit cell has two layers with AB stacking) [19]. Figure 2.2(a) is a schematic of the structure of the most stable polymorphs for many TMDC. The metal coordination in unit cells is different for different polymorphs, such as octahedral in a case of  $1T$  or trigonal prismatic in a case of  $2H$  and  $3R$ , as shown in figure 2.2(b). In the context of metal coordination within the unit cell, the octahedral coordination configuration exhibits an inversion center, indicating symmetry elements that result in identical positions when spatially inverted. Conversely, the prismatic coordination lacks such an inversion center. This symmetry often influences optical, electronic, and vibrational characteristics, impacting phenomena like selection rules in spectroscopy or electronic band structures such as circular dichroism or the appearance of additional electronic states due to the breaking of inversion symmetry.

The unit cells of TMDC are characterized by lattice vectors of equal magnitude ( $|\mathbf{a}| = |\mathbf{b}|$ ) forming an angle of  $\gamma = 120^\circ$  within the plane, along with a third vector ( $\mathbf{c}$ , where  $|\mathbf{c}| \neq |\mathbf{a}|$ ) perpendicular to the plane defined by  $\mathbf{a}$ - $\mathbf{b}$ , depicted in Figure 2.2(a). According to Kolobov et al. (2016) [19], the Hermann-Mauguin notation assigns the  $2H$  and  $1T$  structures to the symmetry groups  $P6_3/mmc$  (no. 194) and

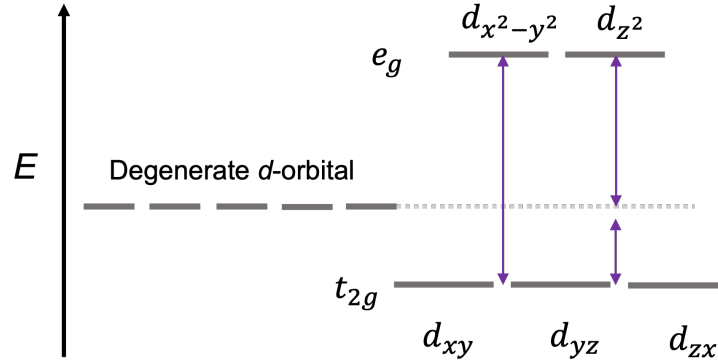


Figure 2.3: Crystal field splitting of  $d$ -orbitals of transition metal. Degeneracy of the  $d$  orbitals lifted as ligands (chalcogen atoms) are brought near the metal ion.

$P\bar{3}m1$  (no. 164), respectively. Typically, the lattice parameters of  $1T$  compounds fall within the range where  $|a| \approx (3 - 4) \text{ \AA}$  and  $|c| \approx (6 - 7) \text{ \AA}$ . In contrast, the  $2H$  polymorphs exhibit approximately double the length along the  $c$ -axis, within the range of  $(12 - 14) \text{ \AA}$ , as illustrated in Figure 2.2.

### 2.2.2 Electronic structure

The coordinate geometry and the extent of filling of inner  $d$  orbitals of metal atoms strongly influence the electronic properties of TMDC. The electronic configuration of transition metals is  $(n - 1)d^x ns^2$  with  $x = 1 \text{ to } 10$  depending on the position in the periodic table. Chalcogen atoms valence shell has electronic configuration  $ns^2 p^4$  ( $ns^2 p_x^1 p_y^1 p_z^2$ ). Crystal field theory helps us grasp how transition metal orbitals, initially identical in energy, split when influenced by the chalcogen atom coordination of a particular symmetry. Initially, the five degenerate  $d$  orbitals maintain their identical energy levels within a consistent charge environment. However, when ligands (like chalcogen atoms) approach metal ions, they cause the degeneracy to break and the energy levels to shift while maintaining an unchanged average energy, as shown in Figure 2.3. The energy of a non-bonding  $d$  band lies between the bonding and anti-bonding bands in the  $2H$  and  $1T$  TMDC. In  $D_{3d}$  symmetric octahedrally coordinated structures, the orbitals split into  $e_g$  (containing orbitals  $d_{z^2}$  and  $d_{x^2-y^2}$ ) and  $t_{2g}$  (with orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ ). For  $D_{3h}$  symmetric trigonal prismatic structure orbitals split into three degenerate groups (i)  $d_{z^2}$  (ii)  $d_{x^2-y^2} + d_{xy}$  (iii)  $d_{xz} + d_{yz}$  as in figure 2.4.

TMDCs acquire their distinctive electronic characteristics from the filling fraction of bands formed due to crystal field splitting. Compared to transition metal

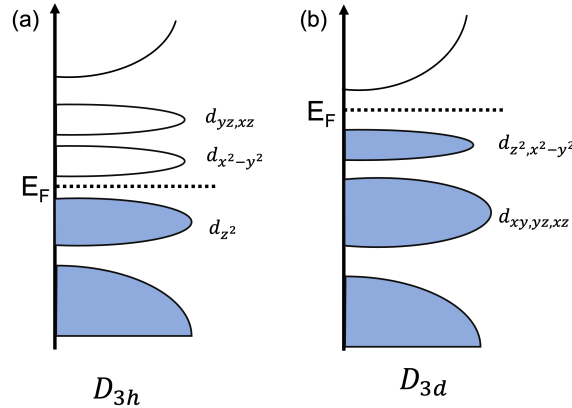


Figure 2.4: Illustrative representation of the density of states (DOS) of TMDC for different coordinate symmetries.  $D_{3d}$  symmetry structure splits the degenerate  $d$ -orbitals into two energy groups while  $D_{3h}$  structure splits into three groups. The properties of TMDC depend upon how these states are filled [19].

atoms, the influence of chalcogen atoms on the electronic structure is minimal. A fully occupied highest orbital in TMDCs results in a semiconducting nature, while partial occupation leads to a metallic behavior [19].

### 2.3 Synthesis of TMDC

Transition metal dichalcogenides (TMDC) are a class of materials that include naturally occurring compounds like molybdenite and synthetically produced variants. Molybdenite, discovered in 1923 by Dickinson [20], is the primary naturally occurring TMDC and consists of molybdenum disulfide ( $\text{MoS}_2$ ). Alongside molybdenite, there are two other notable naturally occurring members: Drysdalite ( $\text{MoSe}_2$ ) and Tungstenite ( $\text{WS}_2$ ) [11]. However, the spectrum of TMDCs expands far beyond these naturally occurring compounds. Researchers have developed various synthesis techniques to fabricate other TMDC, broadening the range of materials available for study and application. These synthesis methods enable the synthesis of TMDC with distinct properties and compositions.

Several methods are employed in synthesizing TMDCs :

#### 2.3.1 Molecular beam epitaxy (MBE)

The molecular beam epitaxy (MBE) is a layer-by-layer atomic growth of material. The MBE methods originated in the 1960s to grow high-purity semiconducting material limited by the quality of the vacuum[21]. With advances in vacuum pumps and *in situ* growth monitoring techniques, the utility of MBE for the growth of



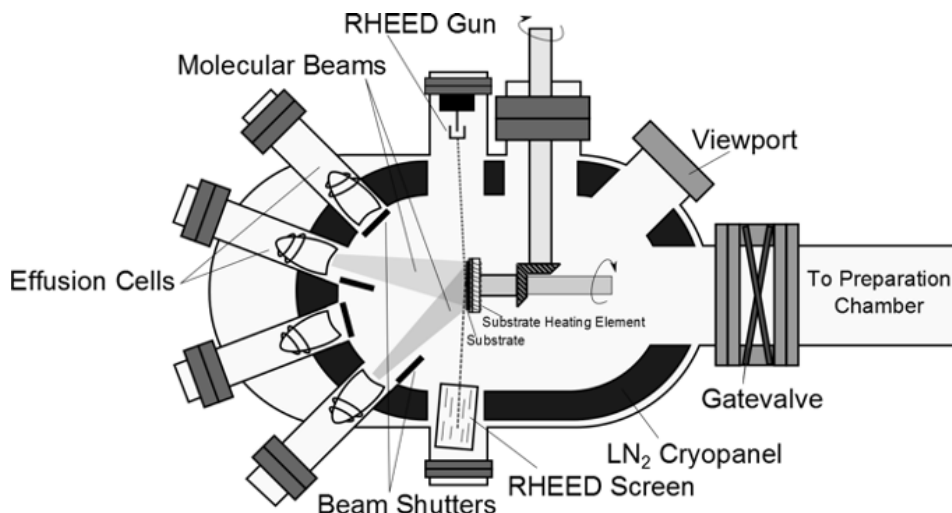


Figure 2.5: Illustration of a simple chamber for molecular beam epitaxy (MBE). Effusion cells are a source of atomic or molecular beams. Created by Nikhil P. at Wikipedia (Licence: CC BY-SA 3.0)

pristine materials increases many-fold. The first scalable method utilized to synthesize TMDC [22]. An ultra-high vacuum chamber has several precursor sources to form a molecular beam. To avoid collision between the molecules/atoms in the generated beam, the opening of the effusion cell needs to be smaller than the mean free path of the evaporate. A substrate on which crystal films grow is preheated with molecular beam depositing reactants in a controlled manner. A low energy electron beam diffraction setup monitors the crystallinity and thickness during growth *in situ* (Figure 2.5). Epitaxial growth of the TMDC occurs on the substrate irrespective of the lattice matching between TMDC and substrate [23]. A huge mismatch between lattices induces defects and polycrystallinity.

### 2.3.2 Chemical vapor transport (CVT)

In 1852 R. Bunsen observed the vapor transport process forming hematite in the presence of hydrogen chloride in a volcanic eruption of Vesuvius called it "pneumatolysis" [24]. He tried to imitate the process in a laboratory. People tried growing different crystals using Bunsen's method [25]. The paradigm-shifting moment arrived in 1956 when H. Shafer published a paper reporting the growth of iron(III) oxide in the presence of HCl in a closed system kept under a temperature gradient [26]. The term 'chemical vapor transport' was first used in this paper, and formulas for predicting transport rate were presented. Numerous solid-state compounds have been synthesized since then using this technique. The most practical methods for

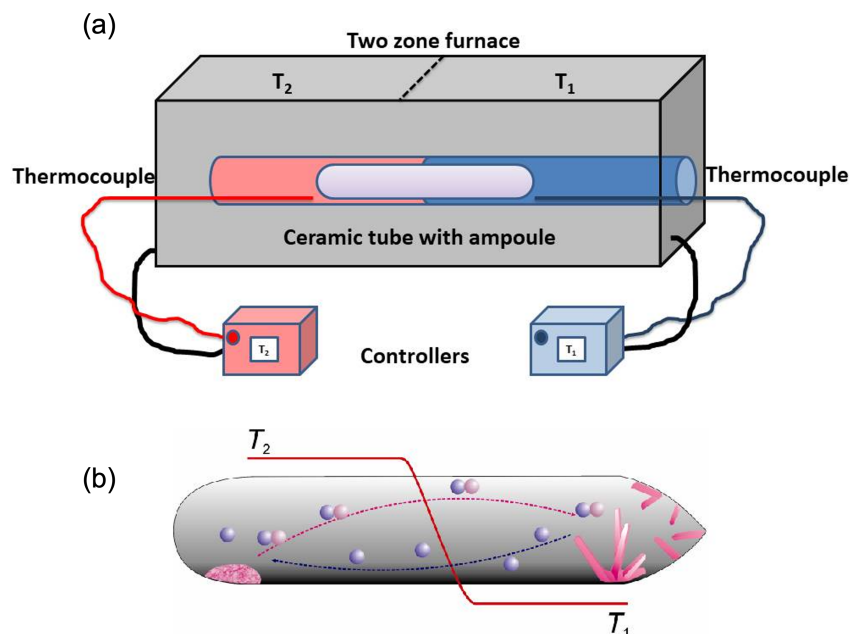


Figure 2.6: (a) Closed system with ampoule kept in a temperature gradient. A conventional two-zone furnace is used for this process. (b) The temperature gradient is set inside the ampoule from  $T_2$  to  $T_1$  between the two ends. Reactants are volatilizing at  $T_2$  and crystallizing at lower temperature  $T_1$  at the other end.

synthesizing large single-crystal TMDC are chemical vapor transport (CVT) and its variants like chemical and physical vapor deposition. In CVT, the solid precursor material is converted into the gaseous molecular form using a transport agent and deposited as a single crystal or thick film [27]. Usually, the growth temperature of crystals is lower than the melting temperature of their source materials. Almost all TMDC single crystals and thick films can be grown with this method. Tuning the growth temperatures can also induce crystal defects [7]. CVT can also be used for the purification of nonvolatile solids. Figure 2.6 depicts the simple principle of CVT.

### 2.3.3 Physical vapor deposition (PVD)

The first physical vapor deposition was carried out by Faraday in 1957 by evaporation of wire in an electric arc [29]. With improvements in vacuum technology, the first arc vaporization was demonstrated in the 1930s. This technique was used to prepare paper capacitors by depositing metals on paper. Physical vapor deposition (PVD) is developed as a surface modification method, making desirable surface changes. In this method, the material is vaporized in gaseous form from its

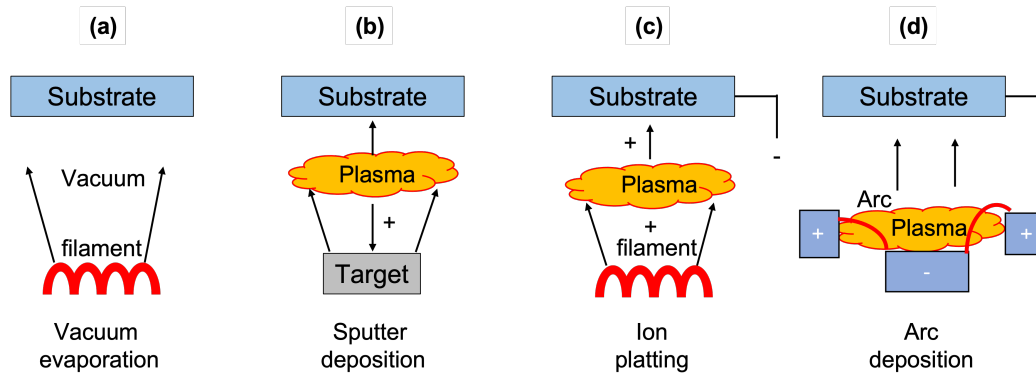


Figure 2.7: (a) Material can be deposited by thermal vaporization in the vacuum. (b) Sputtering is a vaporization process where atoms are ejected from a solid surface by gaseous ions accelerating from plasma but not by substrate heating. (c) A substrate is continuously or periodically bombarded by energetic ions generated by creating plasma, a form of PVD known as ion plating, and (d) Arc vapor deposition uses a high current to vaporize an electrode and deposit the vaporized material on a substrate in a vacuum. Figure is adapted from [28]

source through a vacuum, plasma, or electrolyte environment and deposited on the substrate. Here the driving force of deposition is physical contact between evaporate and the substrate. [28]. The different types of physical vapor deposition techniques are shown in Figure 2.7.

### 2.3.4 Chemical vapor deposition (CVD)

In the 1880s Sawyer patented the process of chemical vapor deposition to coat carbon or metals on the filaments of light bulbs to increase their lifetime [30]. Advances in the technique in the early 1970s led to the discovery of methods to deposit hard materials like titanium carbide, nitride, diamond, etc., using this technique [31]. Nowadays, CVD is used to grow high-quality semiconducting thin films for technological applications. Naturally, CVD became the most cost-effective and easiest method for growing TMDC thin films. This is a chemical reaction-based deposition. The reaction precursors are sealed or fed into a chamber; the reaction occurs in a gaseous phase, on the substrate, or both [32]. The product of the reaction forms on the surface of the substrate, or intermediate products cause chemical reactions with the substrate surface. This method is useful for thin layers and small sample sizes. The first method used to synthesize TMDC in the 1990s was metal-organic CVD (MOCVD) using precursors in the gas phase [33]. The arrangement of the apparatus and the principle of CVD is described in Figure 2.8.

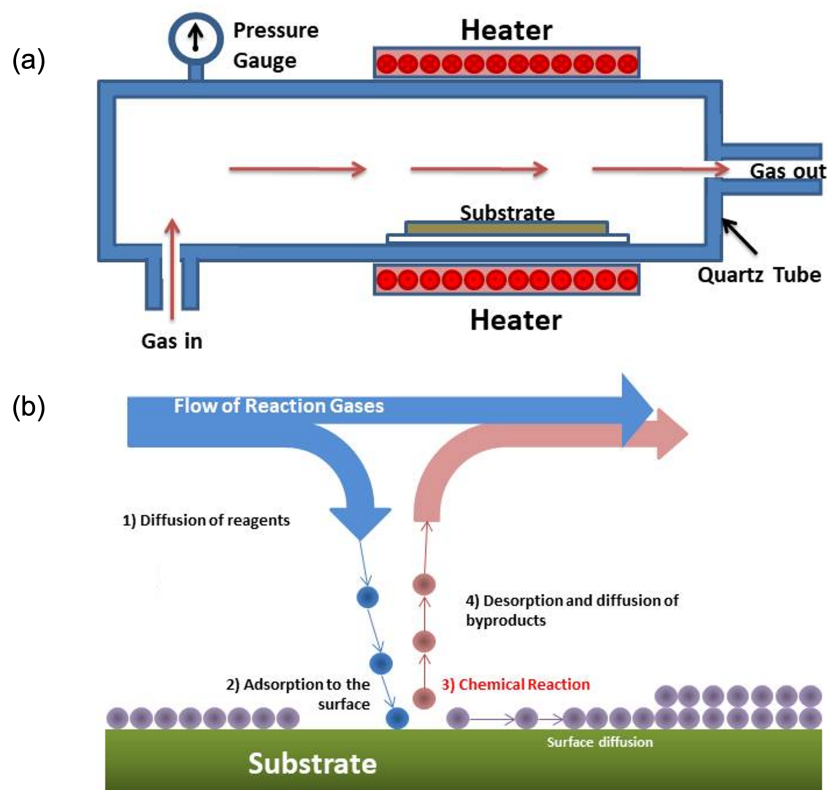


Figure 2.8: (a) A typical chemical vapor deposition (CVD) reactor (b) Principle of CVD.

These synthesis methods, among others, play a pivotal role in expanding the library of TMDC materials, enabling researchers to explore their diverse properties and potential applications across various fields, including electronics, photonics, and catalysis.

## 2.4 Electronic properties

The wide spectrum of electronic properties found in TMDC stems from their diverse chemical compositions, layered structures, and various structural polymorphisms. These materials exhibit a gamut of characteristics, ranging from insulating and semiconducting behaviors to metallic and correlated phases such as superconductors, Mott insulators, and even topological phases [11, 19]. Some interesting TMDC materials are categorized according to their electronic states in table 2.1. The layered configuration prevalent in most TMDC allows for thickness tunability, enabling exploration down to monolayer limits. When reduced from bulk crystals to monolayers, notable shifts occur in their electronic behavior—such as in molyb-

| Electronic Property            | Material                                                 |
|--------------------------------|----------------------------------------------------------|
| Metallic                       | NbS <sub>2</sub> , NbSe <sub>2</sub> , NbTe <sub>2</sub> |
|                                | TaS <sub>2</sub> , TaSe <sub>2</sub> , TaTe <sub>2</sub> |
|                                | VS <sub>2</sub> , VSe <sub>2</sub>                       |
| Semimetallic                   | TiSe <sub>2</sub> , WTe <sub>2</sub>                     |
| Semiconducting                 | MoS <sub>2</sub> , MoSe <sub>2</sub> , MoTe <sub>2</sub> |
|                                | WS <sub>2</sub> , WSe <sub>2</sub>                       |
|                                | ReS <sub>2</sub> , ReSe <sub>2</sub> , ReTe <sub>2</sub> |
| Superconducting                | NbSe <sub>2</sub> (in $2H$ phase)                        |
|                                | TaS <sub>2</sub> , TaSe <sub>2</sub> (in $2H$ phase)     |
|                                | TiSe <sub>2</sub> (after Cu doping)                      |
| Charge density waves<br>states | NbS <sub>2</sub> , NbSe <sub>2</sub>                     |
|                                | TaS <sub>2</sub> , TaSe <sub>2</sub>                     |
|                                | TiSe <sub>2</sub>                                        |
|                                | VS <sub>2</sub> , VSe <sub>2</sub>                       |
| Topological phases             | MoSe <sub>2</sub> , MoTe <sub>2</sub> ( $1T'$ )          |
|                                | WTe <sub>2</sub> ( $1T'$ )                               |

Table 2.1: List of electronic properties of some interesting TMDC [19].

denum disulfide (MoS<sub>2</sub>), transitioning from an indirect bulk band gap in the  $2H$  polymorph to a direct band gap semiconductor [34].

This reduction in thickness influences electron and phonon behavior due to quantum confinement, impacting the density of states occupation and altering the coupling of different interacting degrees of freedom. MoS<sub>2</sub> serves as an example where electronic properties progressively shift from three-dimensional to two-dimensional limits. The exceptional diversity and tunability inherent in TMDC render them highly promising for varied applications in electronics [35]. This breadth of properties within TMDC has notably broadened the scope for constructing nanoscale devices, known as van der Waals heterostructures. These structures leverage the unique properties of individual 2D materials by stacking them in precise configurations akin to assembling building blocks [36]. This approach facilitates the tailored generation of desired properties, further expanding the potential applications of TMDC-based devices.

In addition to the diverse electronic properties found in TMDC, our focus here zeroes in on the intriguing charge density wave states within this class of materials. The manifestations of CDW in TMDC exhibit a wide range of diversity directly linked to the material's chemical composition and structural polymorphism. The forthcoming chapter will delve into different models and variations of CDW. Within

this study, our focus centers on two CDW materials:  $1T$ -TiSe<sub>2</sub> (characterized by excitonic condensation-driven CDW) and  $2H$ -NbSe<sub>2</sub> (dominated by strong electron-phonon coupling-driven CDW). Our investigation revolves around understanding the tunability and dependency of CDW phases concerning physical parameters such as strain and temperature, as well as chemical parameters like intercalation and orbital ordering.

While the burgeoning realm of 2D materials has sparked significant enthusiasm in TMDC, comprehension of their bulk properties remains imperative before delving into investigations at the 2D level. The evolution of experimental tools and methodologies represents a substantial advancement from the techniques employed in the 1960s to scrutinize these materials. The advent of novel tools and perspectives substantiates the rationale for revisiting this domain in Physics.

## Chapter 3

# CHARGE DENSITY WAVES

*"Not only is the Universe stranger than we think, it  
is stranger than we can think."*

— Werner Heisenberg

### 3.1 An overview

A charge density wave (CDW) refers to a phenomenon in condensed matter physics where the electrons within a material organize themselves into a periodic spatial modulation of their density. Most of the bulk and surface properties of the material depend on the electron density distribution [37]. In a CDW, the distribution of electrons becomes spatially modulated, creating areas of higher and lower electron density within the material. This phenomenon typically arises due to interactions between electrons, often influenced by the underlying lattice structure of the material. The periodic modulation can occur due to various factors, such as electron-electron interactions, electron-lattice interactions, or a combination of both [38]. When a material enters a CDW state, it undergoes a transition from its normal phase to a state where the electron density becomes periodically ordered. This ordering can lead to intriguing properties and behaviors in the material, affecting its electrical conductivity, magnetism, and other physical properties. CDWs are significant in understanding the behavior of various materials, particularly in fields like solid-state physics and the study of advanced materials, as they can substantially impact a material's properties and functionality.

All conductors are lattices of closely packed ions embedded in a sea of delocalized or free electrons. An electron carries a charge ( $-e$ ) and a spin ( $\hbar/2$ , 'intrinsic' angular momentum). The interaction between lattice, electronic charge, and spin degree of freedom manifests in the emergence of various physical states like superconductivity and magnetism. To understand CDW, we first need to understand the quantum structure of solids. A simplified quantum structure of electrons in metals is presented first. Rudolf Peierls theorized the model of CDW in 1955 for a one-dimensional (1D) linear chain of atoms [4]. Peierls postulated that in a one-dimensional metal, electron-lattice interactions lead to instability in the system

as the temperature decreases. This instability caused by electron-lattice interactions leads to changes in the Fermi surface properties accompanied by softening of phonon modes (quantized lattice vibrations). The "softening" of phonon modes refers to a phenomenon where the energy associated with certain vibrational modes decreases, causing a reduction in the corresponding frequencies. It impacts thermal conductivity, mechanical properties, phase transitions, and the overall stability of materials. Here, electron-phonon interactions affect the phonon spectrum, causing softening in specific vibrational modes. These ideas can be extended to materials with 2D and 3D structures. We begin with a simple model and then discuss more complex models of CDW.

### 3.2 Electrons in solids

Arnold Sommerfeld devised a model after the discovery of quantum mechanics that could describe properties of solids [39]. The Sommerfeld model was a significant advancement in understanding the behavior of electrons in solids, particularly in metals. This model expanded upon the free electron model put forward by Paul Drude, introducing quantum mechanics to describe electrons in a crystalline lattice. Sommerfeld incorporated the principles of quantum theory into the existing classical free electron model, considering electrons as a Fermi gas within the solid. The energy of electrons in a solid is quantized as a number of states per unit volume. Although a one-centimeter cube of a solid contains approximately  $10^{22}$  number of free electrons. This many-body (particle) problem can be simplified into many one-body problems by assuming no interactions amongst electrons. Electrons move freely inside the available volume of material without being affected by the presence of other electrons. This behavior is somewhat analogous to how particles behave in an ideal gas. The first step in understanding solids is starting with the assumption of a single electron confined to a finite volume in solids and deriving the electronic dispersion using the Schrodinger equation. The time-independent Schrodinger equation for a single non-relativistic particle of mass  $m$ , in a three-dimensional potential,  $V(\mathbf{r})$  with energy  $E$  is given by,

$$-\frac{\hbar^2 \nabla^2}{2m} \psi(\mathbf{r}) + V(\mathbf{r}) \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (3.1)$$

where  $\nabla^2$  is the Laplacian, and  $\psi(\mathbf{r})$  is the particle wavefunction. For a free electron (i.e  $V(\mathbf{r}) = 0$ ) of mass  $m_e$  equation 3.1 becomes



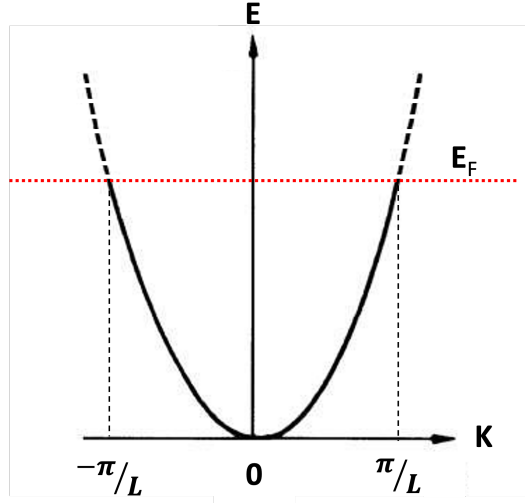


Figure 3.1: A parabolic band structure of simple one-dimensional solid. Fermi level,  $E_F$ , is the energy of the highest occupied state.

$$-\frac{\hbar^2 \nabla^2}{2m_e} \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (3.2)$$

If the electrons are confined to a cube of side  $L$  having a volume  $L^3$ , and wavefunction satisfies the periodic boundary condition  $\psi(\mathbf{r}) = \psi(x, y, z) = \psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L)$ , equation 3.2 is then solved by plane wave *ansatz*  $\psi(\mathbf{r}) \propto e^{i(\mathbf{k} \cdot \mathbf{r})}$  where  $\mathbf{k} = (k_x, k_y, k_z)$ . Periodic boundary condition leads to  $e^{ik \cdot x} = e^{ik \cdot (x+L)}$  implies  $k_x = \frac{2\pi n_x}{L}$ ,  $n_x$  is an integer. We can write the normalized wavefunction as

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{L^3}} e^{i(\mathbf{k} \cdot \mathbf{r})} \quad (3.3)$$

The components of three-dimensional wavevector  $\mathbf{k} = (k_x, k_y, k_z) = (\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L})$  and  $n_x, n_y$  and  $n_z$  are integers. The energy of particle 3.2 is then

$$E = \frac{\hbar^2 \mathbf{k}^2}{2m_e} = \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2 + k_z^2), \quad (3.4)$$

The energy of an electron is quantized and depends on the three-dimensional wavevector  $\mathbf{k}$ . We can obtain the linear momentum of electrons from the elec-

tronic dispersion by operating momentum operator,  $\mathbf{p} = -i\hbar\nabla$  on the electron wavefunction,

$$\mathbf{p} \psi(\mathbf{r}) = -i\hbar\nabla \psi(\mathbf{r}) = \hbar\mathbf{k} \psi(\mathbf{r}) \quad (3.5)$$

$$\mathbf{p} = \hbar\mathbf{k} \quad (3.6)$$

Equation 3.6 is known as the de Broglie relation. The relationship derived in equation 3.4 for a single electron can be extended to  $N$  independent electrons. The superposition of energy states of all electrons results in "bands" of energy with allowed momentum states. The dependence of the energy on the momentum is known as electronic dispersion. To simplify the model further, we assume a one-dimensional solid with  $N$  free electrons confined on a line segment of length  $L$  along the  $x$ -axis. Dispersion relation for electrons one-dimensional solids with momentum  $K$  then become  $E = \hbar^2 K^2 / 2m_e$  and  $K = 2\pi n / L$  where  $n$  is an integer taking values  $(\pm 1, \pm 2, \dots)$ . As illustrated in Figure 3.1, a single band forms in a one-dimensional model. Electrons in solids can then be described by a set of quantum mechanical properties (quantum numbers) like energy state (related to linear momentum  $K$ , which depends on integer  $n$ ), angular momentum, and the internal degree of freedom spin (has  $\pm \hbar/2$ ). The exclusion principle, proposed by Wolfgang Pauli in 1925, is a fundamental concept in quantum mechanics; it states that no two identical particles with half-integer spin, such as electrons within a quantum system, can occupy the same quantum state simultaneously. According to this principle, two electrons per state can fill the band, reaching  $N/2$  states. The energy of the highest occupied state is known as "Fermi energy." This model assumes the temperature of the system set to  $T = 0$ .

Electrons in the solids are indistinguishable fermions (spin angular momentum  $1/2$  (in the units of  $\hbar$ ) particles). At finite temperatures, the statistical distribution of electrons in different energy states is described by Fermi-Dirac statistics. The probability of electrons occupying a state with energy  $E$  is given by the Fermi-Dirac (FD) distribution at temperature  $T$  as

$$f(E, T) = \frac{1}{e^{(E - \mu / k_B T)} + 1} \quad (3.7)$$

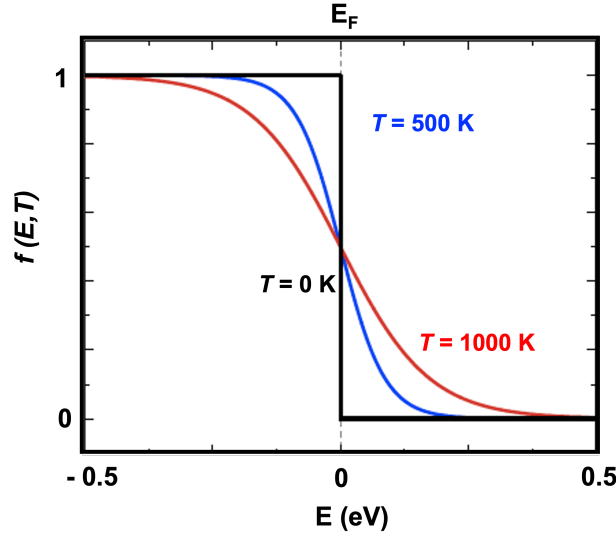


Figure 3.2: Fermi-Dirac distribution  $f(E, T)$  and its broadening at various temperatures.

, where  $k_B$  is the Boltzmann constant, and  $\mu$ , is the chemical potential (related to the number of particles in the system). At  $T = 0$ ,  $\mu = E_F$  where  $E_F$  is a Fermi energy. The FD distribution is a step function at  $T = 0$  where for occupied states with energy  $E < \mu$ ,  $f(E) = 1$  and for an unoccupied state  $E > \mu$  have  $f(E) = 0$  as shown in Figure 3.2. Thermal broadening at finite temperature leads to smearing of FD distribution by  $\Delta E \propto k_B T$  around  $\mu$ . Electrons with energy in the  $\Delta E$  range around the Fermi energy can contribute to electronic dynamics in solids. The notation  $E_F$  - defined at zero temperature is called Fermi energy but is frequently used in the literature even for finite temperatures.

The Sommerfeld model significantly improved the understanding of various phenomena observed in metals, such as electrical conductivity and heat capacity, by providing a quantum mechanical framework for describing electron behavior in solids. While it had its limitations, notably not accounting for interactions between electrons and lattice vibrations (phonons). This model laid the groundwork for later, more comprehensive models describing the behavior of electrons in solids.

The concept of a Fermi surface separating occupied and unoccupied states at  $T = 0$  arises from the abovementioned concepts. In the Sommerfeld model, for an independent electron in a volume  $L^3$ , states of fixed energy lie on the sphere in momentum state space. The Fermi surface (the highest occupied states) has a spherical boundary and energy  $E_F$  for this model. Fermi-Dirac statistics in equa-

tion 3.7 dictates that only electron states existing on the sphere (within thermal broadening  $\Delta E \approx k_B T$ ) contribute to dynamics. Comprehending the properties of materials and their responses to external influences relies significantly on understanding the characteristics of the Fermi surface and its dynamics. Real materials exhibit intricate Fermi surfaces, especially considering the complexities arising from electron-electron and electron-lattice interactions. Understanding these intricacies is pivotal for grasping electronic behaviors within solids. The upcoming sections delve into electron behaviors within different spatial dimensions, exploring phenomena like Charge Density Waves (CDW) that emerge beyond the limitations of the simple free electron gas model.

In metals, electrons tend to be evenly distributed, while ions arrange themselves in a perfectly periodic lattice. Within metals, electrons behave akin to a free electron gas. However, as temperatures decrease, certain metals exhibit a periodic variation in their charge density (free electron density). This occurs due to instability in the Fermi surface [4, 38], leading to what's known as a charge density wave (CDW). In response, the ionic lattice rearranges itself, seeking a new equilibrium state. The transitions into CDW phases vary significantly from one material to another.

Creating a generalized, quantitatively predictive model for the origin of CDW across different systems proved challenging. While various mechanisms explaining the formation of CDW have been proposed, achieving a comprehensive, predictive model applicable to diverse systems remains impractical. We'll discuss three types of CDW based on their formation mechanism and the manifestation of certain properties, as outlined in table 3.1, and further explore the details in subsequent sections.

### 3.3 Type I CDW

Consider a 1D case of a linear chain of atoms with lattice constant  $a$  as shown in figure 3.3. This 1D atomic chain, with each site contributing one electron, has electronic dispersion according to equation 3.4 derived in the previous section at temperature  $T = 0$ . For a linear chain of  $N$  atoms,  $L = N \cdot a$  and  $n$  varies from  $\pm 1, \dots, \pm N/2$ . So that the magnitude of the wavevector  $k = 2\pi n/L$  varies from  $-\pi/a$  to  $+\pi/a$ . With each site contributing one electron, the total  $N$  electrons now occupied  $N/2$  states. The highest occupied state then corresponds to  $n = \pm N/4$  and  $k = \pm \pi/2a$ . We define a Fermi wave vector  $k_F = \pm \pi/2a$ . The only allowed zero

energy transition is from Fermi points  $k_F$  to  $-k_F$ , connected by a vector  $\mathbf{q}_0 = 2k_F$ . Peierls showed that this system is unstable when perturbed and undergoes a transition to a new ground state with the periodicity of lattice changes to  $2a$  accompanied by a gap opening near the Brillouin Zone boundary at  $k = \pi/2a$  generating the electronic wave disturbance of wavevector  $\mathbf{q}$  [4, 5]. We discuss the Peierls' model in detail in the following subsection.

| Type I                       | Type II                  | Type III                           |
|------------------------------|--------------------------|------------------------------------|
| Kohn anomaly                 | Kohn anomaly             | no Kohn anomaly                    |
| FSN                          | no FSN                   | no FSN                             |
| EPC                          | strong EPC               | electronic correlations            |
| M-I transition               | no M-I transition        | M-I transition                     |
| (always present)             |                          | (occasionally)                     |
| e.g., Linear chain compounds | e.g., $2H\text{-NbSe}_2$ | e.g., Cuprates, $1T\text{-TiSe}_2$ |

Table 3.1: Classification of CDW according to the mechanism of formation. Abbreviations: **FSN**: Fermi- Surface Nesting, **EPC**: Electron-phonon coupling, **M-I**: Metal-Insulator transition. [40, 41]

### 3.3.1 Peierls' model

Peierls was the first to propose the formation of a phenomenon called Charge Density Wave (CDW) in a one-dimensional (1D) system consisting of an atomic chain. This theoretical framework was articulated using the mean-field theory approximation, a method often used in condensed matter physics to simplify complex interactions within a material.

The description of this system is given by a Hamiltonian that characterizes the coupling between electrons and the lattice. In this case, the Hamiltonian assumes the form of free electrons without mutual interactions, employing an adiabatic approximation. This means that the behavior of the electrons is approximated as if they are responding gradually to changes in the lattice configuration rather than instantaneously. This simplification allows for a more manageable analysis of the electron-lattice interactions within the context of the proposed CDW formation in the 1D atomic chain system, as outlined by Gruner [5].

$$H = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} + \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{q}} g_{\mathbf{q}} a_{\mathbf{k}+\mathbf{q}}^{\dagger} a_{\mathbf{k}} (b_{-\mathbf{q}}^{\dagger} + b_{\mathbf{q}}) \quad (3.8)$$

where  $\epsilon_{\mathbf{k}}$  is the energy of electronic state with momentum state  $\mathbf{k}$ ,  $a_{\mathbf{k}}^{\dagger}$  and  $a_{\mathbf{k}}$  are the creation and annihilation operator for an electron in state  $\mathbf{k}$ ,  $\omega_{\mathbf{q}}$  is the frequency

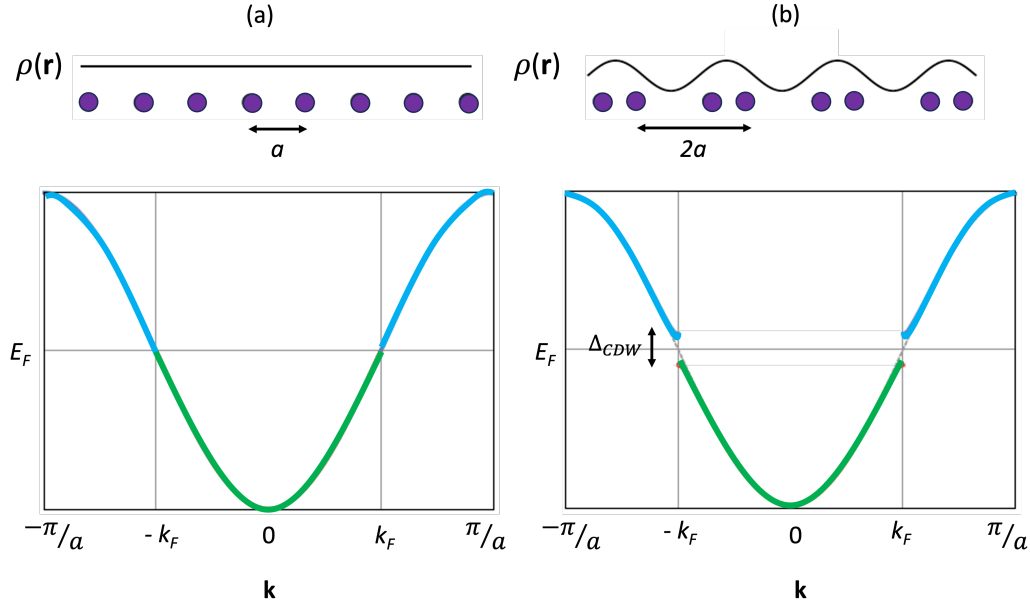


Figure 3.3: Peierls distortion. (a) The 1D atomic chain with spacing,  $a$ , and electron density,  $\rho(\mathbf{r})$ . A green line marks the Fermi level,  $E_F$ . (b) A Peierls distortion leads to forming a standing wave in the electron density with wavelength,  $\lambda_0$ , called a charge density wave (CDW) state. A gap,  $\Delta_{CDW}$ , opens in the electronic dispersion around  $E_F$ , lowering the total energy. Adapted from [40]

of phonon mode,  $b_{\mathbf{q}}^\dagger$  and  $b_{\mathbf{q}}$  are the creation and annihilation operators for phonon in momentum state  $\mathbf{q}$ ,  $N$  is the number density and  $g_{\mathbf{q}}$  is electron-phonon coupling parameter. The system ground state is a filled Fermi level,  $E_F$ , and its Fermi wavevector,  $k_F$ . The 1D lattice with separation,  $a$ , has the uniform charge density,  $\rho(\mathbf{r})$ . A periodic lattice distortion (PLD) occurred due to coupling between electrons and lattice (electron-phonon interactions). Electron-phonon interactions alter the phonon spectrum within materials, leading to softening of certain vibrational modes. The system undergoes a phase transition at a critical temperature known as the Peierls transition temperature. The system spontaneously distorts its periodic lattice structure, creating a periodic arrangement of alternating high and low electron density regions. This distortion lowers the overall energy of the system by allowing electrons to better accommodate within the lattice potential. This transition results in the opening of an energy gap at the Fermi level shown in Figure 3.3 [4]. Opening the gap at a Fermi level causes changes in conductivity, resulting in insulating behavior where the system, initially conducting at higher temperatures, becomes insulating at lower temperatures. The lattice constant doubled to  $2a$  for a half-filled band. This

induces a charge density modulation of a period  $\lambda_0 = \pi/k_F$ . Displacement of lattice ion of mass  $M$  in the momentum state  $\mathbf{q}$  is  $u_{\mathbf{q}}$ , generates a potential

$$v_{\mathbf{q}} = g_{\mathbf{q}} u_{\mathbf{q}} \sqrt{\frac{2M\omega_{\mathbf{q}}}{\hbar}} \quad (3.9)$$

Lindhard's response function is a fundamental entity that describes the response of a many-electron system to an external perturbation, particularly in the context of electronic excitations in a solid. Lindhard's formulation considers the effects of the surrounding environment and the collective behavior of electrons in determining the system's response to the external perturbation. In the free electron gas model, the Lindhard's response function  $\chi_0(\mathbf{q})$  denotes the stability of electronic gas to an external perturbation. PLD generates lattice strain, and the associated change in the lattice energy is denoted by  $\delta E_{lat}$ . Also, perturbation in lattice ions affects the electronic gas via potential  $v_{\mathbf{q}}$  causing energy change  $\delta E_{el}$  of an electron system

$$\delta E_{lat} = \frac{1}{2} M \omega_{\mathbf{q}}^2 u_{\mathbf{q}}^2 \quad (3.10)$$

$$\delta E_{el} = -|v_{\mathbf{q}}|^2 \chi_0(\mathbf{q}) \quad (3.11)$$

The new configuration of the electron-lattice system is stable if the overall energy for a certain phonon mode of momentum  $\mathbf{q}_0$  is lowered as  $\delta E_{lat} + \delta E_{el} < 0$ . Using equation 3.9, 3.10 and 3.11, energy condition can be restated in terms of microscopic parameters as

$$\frac{1}{2} M \omega_{\mathbf{q}}^2 u_{\mathbf{q}}^2 - |v_{\mathbf{q}}|^2 \chi_0(\mathbf{q}) < 0 \quad (3.12)$$

$$\frac{1}{2} M \omega_{\mathbf{q}}^2 u_{\mathbf{q}}^2 - 2 \frac{g_{\mathbf{q}}^2 u_{\mathbf{q}}^2 M \omega_{\mathbf{q}}}{\hbar} \chi_0(\mathbf{q}) < 0 \quad (3.13)$$

$$\frac{4g_{\mathbf{q}}^2}{\hbar \omega_{\mathbf{q}}} > \frac{1}{\chi_0(\mathbf{q})} \quad (3.14)$$

A large value of Lindhard susceptibility typically indicates a strong response of a material's electron system to an external perturbation. For CDW transition to occur large electron-phonon coupling  $g_{\mathbf{q}}$  is then needed for high electronic susceptibility  $\chi_0(\mathbf{q})$  at the wavevector  $\mathbf{q} = \mathbf{q}_0$  [6].

1D solid with a half-filled energy band (each lattice site with one electron); the CDW/PLD transition occurs with strong electron-phonon coupling ( $g_{\mathbf{q}}$ ) and small lattice strain energy ( $\omega_{\mathbf{q}}$ ). At a finite temperature, If we assume band dispersion  $\epsilon_{\mathbf{k}} = -E_F \cos(ka)$ , with Fermi energy  $E_F$  and wavevector  $\mathbf{k}_F = \pm\pi/2a$ , the susceptibility diverges at  $\mathbf{q}_0 = 2\mathbf{k}_F$  with decreasing temperature  $T$  as

$$\chi_0(2\mathbf{k}_F, T) = \frac{1}{2}N(0) \ln \left( \frac{2.28E_F}{k_B T} \right) \quad (3.15)$$

The divergence of  $\chi_0(\mathbf{q})$  at  $\mathbf{q}_0 = 2\mathbf{k}_F$  causes instability in the system. The anomaly arises due to the interaction of conduction electrons near the Fermi surface with certain phonon modes. This interaction significantly reduces the energy required to excite these phonons at specific wavevectors, causing the dip or softening observed in the phonon dispersion. Kohn, in 1959, pointed out that lattice motion with wavevector  $2\mathbf{k}_F$  gets screened effectively because of electronic excitations [42]. This Kohn anomaly manifests as a dip or a softening in the phonon frequencies at a particular wavevector (near the boundary of the Brillouin zone) in the phonon dispersion curve. The renormalization (in this context suggests that the initially observed properties might require adjustments or corrections due to the interactions) of phonon mode close to  $2\mathbf{k}_F$  to lower energy (phonon softening) happens because of interaction with the electron system with the divergence of  $\chi_0(\mathbf{q})$  at  $\mathbf{q}_0 = 2\mathbf{k}_F$ . Renormalized phonon frequency  $\tilde{\omega}_{\mathbf{q}}$  can be written in terms of normal mode phonon frequency  $\omega_{\mathbf{q}}^2$  at wavevector  $\mathbf{q}$  as

$$\tilde{\omega}_{\mathbf{q}}^2 = \omega_{\mathbf{q}}^2 \left( 1 - \frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} \chi_0(\mathbf{q}) \right) \quad (3.16)$$

The Kohn anomaly depends on the temperature strongly. The softening of the phonon mode of wavevector  $\mathbf{q}_0$  at  $T_0$  indicates a phase transition to CDW with lattice distortion with wavelength  $\lambda_0 = 2\pi/|\mathbf{q}_0|$ .

The classical Peierls Model of CDW formation thus includes the divergence of Lindhard response function, Kohn anomaly (phonon node softening) in the phonon, and metal-to-insulator transition with periodic lattice distortion and Fermi surface nesting (FSN, discussed in the next section). This model predicts type I CDW behavior in quasi-1D systems, e.g., linear chain compounds like TTF-TCNQ (tetrathiofulvalene-7,7,8,8-tetracyanoquinodimethane). Peierls' model is of limited



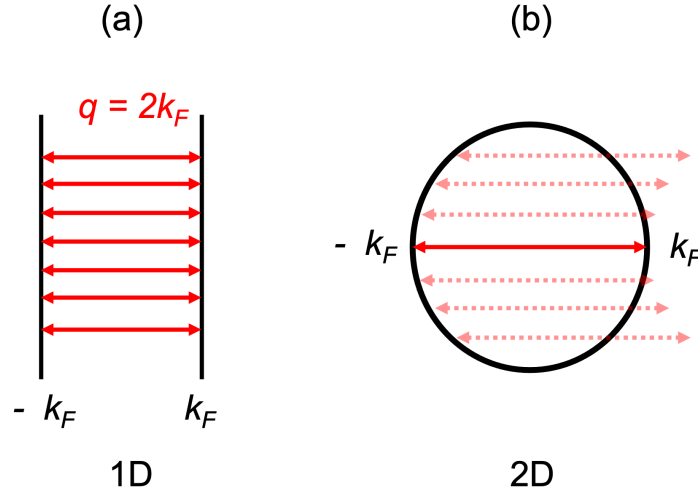


Figure 3.4: (a) A Fermi surface nesting in a one-dimensional system has an open surface of two parallel planes separated by  $\pm k_F$ . The wavevector of length  $\mathbf{q} = 2k_F$  connects the entire Fermi surface. (b) The cylindrical Fermi surface in a 2-dimensional system has no nesting because of its shape; only a small region of the Fermi surface is linked by  $\mathbf{q}$  vectors. Adapted from [43].

value in explaining the CDW in real materials with complex interacting electronic systems.

### 3.3.2 Fermi surface nesting (FSN)

The Fermi surface represents the boundary in momentum space that separates filled and empty electronic states at absolute zero temperature. When portions of this surface match each other due to their particular shapes and orientations, it is termed "nesting." Fermi surface nesting (FSN) is a phenomenon of perfect alignment of specific regions or portions of the Fermi surface when subjected to a slight shift in their momentum or wavevector. The study of Fermi surface shape and its influence on the stability of the ground state is essential in understanding CDW formation. For an ideal 1D case, two parallel sheets form an open Fermi surface connecting  $\pm k_F$  as depicted in Figure 3.4. A single wavevector,  $\mathbf{q}$ , can span the whole Fermi surface, connecting points on the sheets. Single  $\mathbf{q}$  vector connects many points on the parallel segments of the Fermi surface, causing nesting. Seemingly parallel segments of the Fermi surface may not necessarily be nested. The FSN occurs in systems with specific symmetries in their crystal structures or electronic band structures and also depends on temperature. FSN creates constructive interference between electronic states and increases susceptibility to various instabilities or phase

transitions. In a 1D lattice, unlike higher-dimensional systems, the Fermi surface is reduced to discrete points in momentum space due to the restricted movement of electrons along a single direction. Nesting in the Peierls model results from points connected by vector  $\mathbf{q} = 2\mathbf{k}_F$ .

In two-dimensional (2D) and three-dimensional (3D) materials, Fermi surface nesting plays a crucial role in understanding electronic properties. Fermi surface becomes more complex, forming closed surfaces or multiple connected sheets in momentum space. Nesting in materials involves similar principles but with a more intricate geometry. Portions of the Fermi surface may align to enhance scattering and facilitate the formation of various electronic states. Determining the response of the electronic structure to external perturbation using a Lindhard electronic susceptibility function [44] is an excellent way to assess the importance of FSN. To do this in a generalized way, we begin with a system with interacting electrons with charge density  $\rho(\mathbf{r})$  in an external electric field varying with frequency  $\omega$  of potential  $\Phi_{ext}(\mathbf{r}, \omega)$  and calculate the susceptibility function. This external potential induces an electrostatic potential  $\Phi_{ind}(\mathbf{r}, \omega)$  in response. Their sum gives the total potential experienced by the system.

$$\Phi_{tot}(\mathbf{r}, \omega) = \Phi_{ext}(\mathbf{r}, \omega) + \Phi_{ind}(\mathbf{r}, \omega) \quad (3.17)$$

Induced change in the charge density  $\rho(\mathbf{r})$  in presence of external potential is given by

$$\rho_{ind}(\mathbf{r}, \omega) = e^2 \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', \omega) \Phi_{tot}(\mathbf{r}', \omega) \quad (3.18)$$

The response of the electrons  $\chi(\mathbf{r}, \mathbf{r}', \omega)$  contains correlations between charge densities at position  $\mathbf{r}$  and  $\mathbf{r}'$ . The Random Phase Approximation (RPA) is a widely used theoretical framework in many-body physics, in the study of interacting particles within a material. It relies on perturbation theory, treating interactions between particles as a perturbation to an otherwise solvable non-interacting system. It's employed to describe the collective behavior of particles or excitations in a system. Using RPA [40, 45], the function can be expressed in momentum space as  $\chi(\mathbf{q}, \mathbf{q}', \omega)$ . By considering the conservation of momentum in a system of non-interacting electrons, one can indeed simplify the problem by eliminating one of the momentum variables. It is possible to obtain the Lindhard susceptibility function for free electrons by eliminating one of the momentum variables using conservation

of momentum  $\mathbf{k} + \mathbf{q} = \mathbf{k}'$ . The symbol  $\chi_0(\mathbf{q}, \omega)$  often denotes the "non-interacting" or "bare" susceptibility function. The bare susceptibility function for free electrons is given by

$$\chi_0(\mathbf{q}, \omega) = \frac{2}{\hbar} \int_{BZ} d\mathbf{k} f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) \left[ \frac{1}{\omega + (E_{\mathbf{k}} - E_{\mathbf{k}'}) + i\eta} - \frac{1}{\omega - (E_{\mathbf{k}} - E_{\mathbf{k}'}) + i\eta} \right]$$

where  $f$  is the Fermi Dirac (FD) distribution function at energies  $E_{\mathbf{k}}$  and  $E_{\mathbf{k}'}$  for unperturbed,  $\mathbf{k}$  and perturbed,  $\mathbf{k}'$  respectively [46]. The bare susceptibility is a complex function with real and imaginary parts given by  $\chi_0(\mathbf{q}, \omega) = \text{Re } \chi_0(\mathbf{q}, \omega) + i \text{Im } \chi_0(\mathbf{q}, \omega)$ .

$$\text{Im } \chi_0(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{BZ} d\mathbf{k} (f_{\mathbf{k}} - f_{\mathbf{k}'}) \delta(\omega + E_{\mathbf{k}} - E_{\mathbf{k}'}) \quad (3.19)$$

$$\text{Re } \chi_0(\mathbf{q}, \omega) = \frac{2}{(2\pi)^2} \int_{BZ} d\mathbf{k} \frac{f_{\mathbf{k}} - f_{\mathbf{k}'}}{\omega + E_{\mathbf{k}} - E_{\mathbf{k}'}} \quad (3.20)$$

We take a static limit ( $\omega \rightarrow 0$ ) to understand the effect of dimensions on the susceptibility. In some systems near critical points or phase transitions, the susceptibility might diverge or exhibit anomalous behavior. The imaginary part  $\text{Im } \chi_0(\mathbf{q}, 0) = 0$  and the real part,  $\text{Re } \chi_0(\mathbf{q}, 0)$  can then be evaluated for all cases [40]. The stability of the electronic system is described by the real part of the susceptibility function

3D case:

$$\text{Re } \chi_0(\mathbf{q}, 0) \propto - \left[ 1 + \frac{1 - (q/2)^2}{q} \ln \left| \frac{1 + q/2}{1 - q/2} \right| \right] \quad (3.21)$$

2D case:

$$\text{Re } \chi_0(\mathbf{q}, 0) \propto \begin{cases} - \left( 1 - \sqrt{1 - (2/q)^2} \right) & \text{if } q \geq 2k_F \\ -1/E_F & \text{if } q < 2k_F \end{cases} \quad (3.22)$$

1D case:

$$\text{Re } \chi_0(\mathbf{q}, 0) \propto - \frac{1}{2q} \ln \left| \frac{1 + q/2}{1 - q/2} \right| \quad (3.23)$$

A perfect FSN leads to divergence at  $\mathbf{q} = 2k_F$  in 1D case shown in Figure 3.5. Fermi surface nesting puts a bound on energy gained by the system undergoing

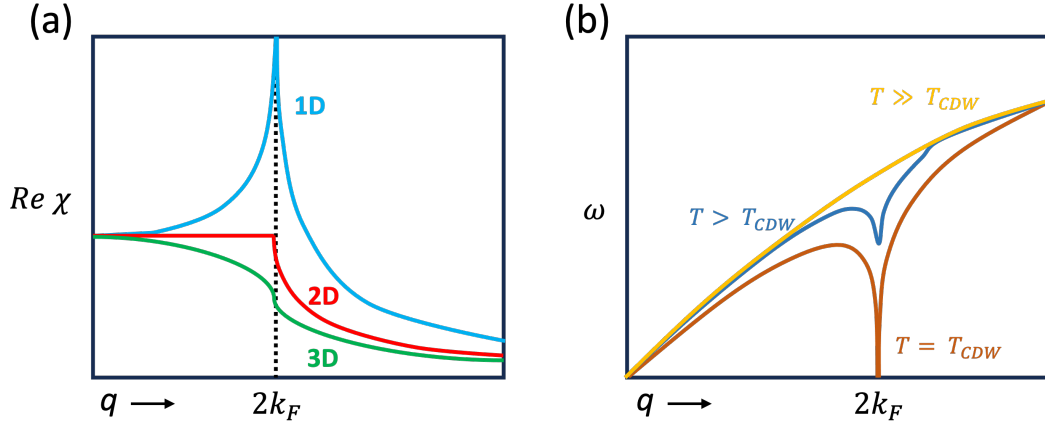


Figure 3.5: Kohn anomaly (a) Free electronic susceptibility,  $\chi(\mathbf{q})$  and (b) Renormalised phonon energy (acoustic branch),  $\omega(\mathbf{q})$  at different temperature in 1D chain, exhibiting a divergence at  $\mathbf{q} = 2k_F$  below  $T_{CDW}$ . The free phonon dispersion is marked by a dashed line,  $\omega_0$ . Adapted from reference [40]

transition. As the extent of FS nesting increases by  $\mathbf{q}$ , more states are lowered in energy and thus get removed from the Fermi surface. So, a system with more nesting seems to stabilize the CDW more readily. The theoretical treatment presented in this section describes how an idealized case of a 1D metal would be unstable to CDW formation as a result of FS nesting, evidenced by the strong divergence in the electronic susceptibility and phonon dispersion near the nesting vector,  $\mathbf{q} = 2k_F$ .

For real materials in two or three dimensions, the weak divergence in  $Re \chi_0(\mathbf{q}, \omega)$  is hard to explain. The static limit, i.e.,  $\omega \rightarrow 0$ , is hardly applicable. In real systems, the susceptibility function's imaginary and real parts are important to describe a quantitative picture of FSN. [40]. The condition for the Fermi surface nesting in real materials translates into the requirement of peaks in both imaginary and real parts of Lindhard function  $\chi_0(\mathbf{q}, \omega)$  at  $\mathbf{q} = \mathbf{q}_{CDW}$ , and divergence of full electron susceptibility [47].

### 3.4 Type II CDW

CDW transition always happens in tandem with lattice distortion. Type II CDW is driven by strong electron-phonon coupling (EPC) without Fermi surface nesting or metal-to-insulator transition. In this scenario, electron and lattice are tied to each other, as the phonon mode of wavevector  $\mathbf{q}_{CDW}$  becomes soft at temperature  $T_{CDW}$  phase transition occurs. The physics of CDW transition is not qualitatively different from Peierls' model discussed in section 3.2. CDW with strong electron-lattice

coupling has a larger distortion amplitude and energy gap than weakly coupled systems. The ratio of the electron energy gap to the energy of the specific phonon mode sets the dividing line between strongly and weakly coupled systems. Strongly coupled systems are characterized by  $\Delta/\hbar\omega_D \approx 1$ , where  $\Delta$  is electron energy gap and  $\omega_D$  is Debye phonon frequency [6].

A simplified expression for the Hamiltonian of electron gas coupled to underlying lattice via electron-phonon coupling was given by Frohlich [48] as mentioned in equation 3.8 rewritten here for ease of reference.

$$H = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} + \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{q}} g_{\mathbf{k}\mathbf{q}} a_{\mathbf{k}+\mathbf{q}}^{\dagger} a_{\mathbf{k}} (b_{-\mathbf{q}}^{\dagger} + b_{\mathbf{q}})$$

here  $\epsilon_{\mathbf{k}}$  is the energy of electronic state,  $a_{\mathbf{k}}^{\dagger}$  and  $a_{\mathbf{k}}$  are the creation and annihilation operator for an electron in state  $\mathbf{k}$ ,  $\omega_{\mathbf{q}}$  is the frequency of phonon mode,  $b_{\mathbf{q}}^{\dagger}$  and  $b_{\mathbf{q}}$  are the phonon creation and annihilation operators,  $N$  is the number density and  $g_{\mathbf{k}\mathbf{q}}$  is momentum  $\mathbf{q}$ -dependent electron-phonon coupling (EPC) parameter. EPC parameter leads to the renormalization of the phonon mode, as mentioned in the previous section

$$\tilde{\omega}_{\mathbf{q}}^2 = \omega_{\mathbf{q}}^2 + 2\omega_{\mathbf{q}}^2 |g_{\mathbf{k}\mathbf{q}}|^2 \text{Re}\chi(\mathbf{q}, \omega) \quad (3.24)$$

$\omega_{\mathbf{q}}$  is bare phonon frequency in absence of EPC and  $\chi(\mathbf{q}, \omega)$  is interacting susceptibility function, renormalized phonon frequency is  $\tilde{\omega}_{\mathbf{q}}$ . EPC coupling constant  $g_{\mathbf{k}\mathbf{q}}$  is strongly dependent on momentum  $\mathbf{q}$  and also anisotropic. The Type II CDW with strong EPC usually does not lead to strong Kohn anomaly and FSN but softens the phonon modes. The reason behind the absence of FSN and weak Kohn anomaly is hidden in the electronic energy gain. For weakly coupled systems with a small energy gap ( $\Delta/E_F \ll 1$ ), gain in electronic energy is of the order of  $(\Delta^2 \ln \Delta)$  with contribution mostly from  $\mathbf{k}_F$ , in contrast strongly coupled system with large gap ( $\Delta/E_F \leq 1$ ) entire Brillouin zone contribute to the electronic energy gain proportional to  $\Delta$  emphasizing the reduced contribution from Fermi surface. Larger atomic displacements in systems with strong coupling mean nonlinear terms in electron-lattice interaction play an important role.

The thermodynamic behavior of weak and strongly coupled CDW systems are very different [49, 50]. In weak coupling systems, charge density and lattice modulation diminish above a transition temperature. Electronic entropy mainly contributes

to the thermal disorder. On the other hand, in a strong EPC system, the lattice entropy contributes more to the thermal disorder, leading to a reduction in long-range coherence between lattice and charge density modulation above the transition temperature without affecting the energy gap much. Localized charge modulation persists in a system with a strong EPC above the transition temperature. One of the Type II CDW systems studied in this work is transition metal dichalcogenide  $2H\text{-NbSe}_2$ .

### 3.5 Type III CDW

Electronic correlations play an essential role in systems with Type III CDW. This class's microscopic mechanism of CDW formation can not be derived from the electron-phonon coupling or Fermi surface nesting. Overhauser developed an unconventional approach to CDW in correlated systems [51, 52]. This theory emphasizes the exchange-correlation interactions between itinerant electrons forming heterogeneous states in charge density, spin density, or both. The spin-up and spin-down densities are given by

$$\rho_{\uparrow}(\mathbf{r}) = \frac{1}{2}\rho_0[1 + \bar{p} \cos(\mathbf{k} \cdot \mathbf{r} + \phi)] \quad (3.25)$$

$$\rho_{\downarrow}(\mathbf{r}) = \frac{1}{2}\rho_0[1 + \bar{p} \cos(\mathbf{k} \cdot \mathbf{r} - \phi)] \quad (3.26)$$

The wavevector  $\mathbf{k}$  of spatial oscillation is close to magnitude  $\mathbf{k}_F$ ,  $\rho_0$  is the average electron density,  $\bar{p}$  is the fractional modulation of wave and  $\phi$  is a relative phase difference in spin up and spin down density oscillations. For  $\phi = 0$  is a pure CDW with uniform spin density, for  $\phi = \pi/2$ , is pure spin density wave (SDW) with uniform charge density, while for  $0 < \phi < \pi/2$  is a mixed CDW-SDW [40]. Fermi surface with spherical symmetry favors Overhauser's CDW states in contrast to Peierls' picture, where Fermi surface anisotropy is needed. We will discuss two different classes of subsystems under the Type III CDW arising from electron correlations.

#### 3.5.1 CDW in unconventional superconductors

In the earlier attempts to understand superconductivity, Frohlich proposed a model where the movement of charge density waves manifested as superconductivity [48]. This model failed to explain the microscopic mechanism of superconductivity and was superseded by Bardeen-Cooper-Schrieffer's (BCS) theory [53]. Unexpected

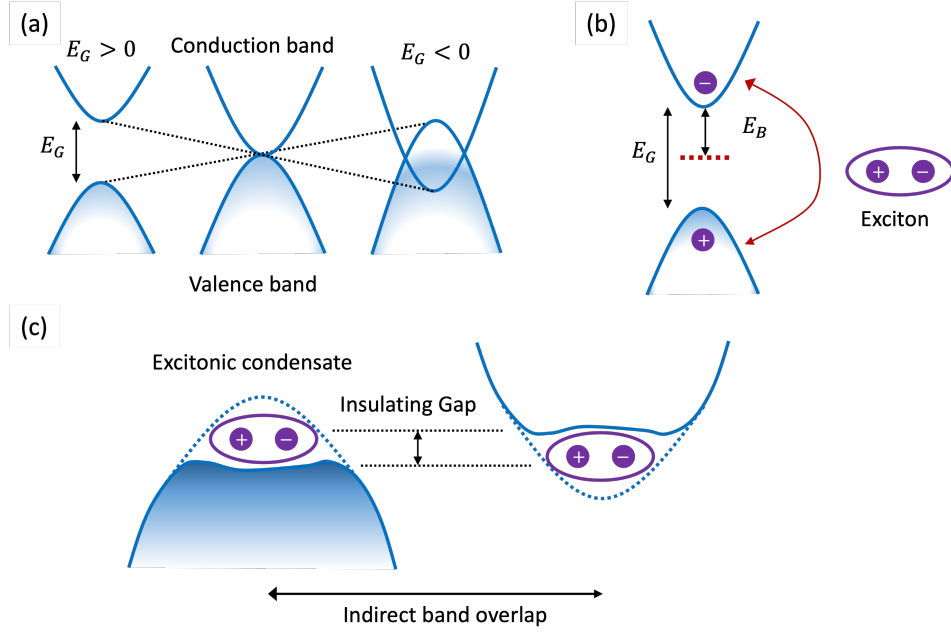


Figure 3.6: Excitonic condensation (a) Electronic band dispersion in the normal phase ( $E_G > 0$ ) and in the excitonic insulator phase ( $E_G < 0$ ), after the bandgap  $E_G$  has become smaller than the binding energy of the exciton state  $E_B$ . (b) Excitons are bound states of valence band holes and conduction band electrons. (c) After exciton-ic condensation, a small gap opens, transitioning to the excitonic insulator phase. Adapted from reference [58].

connections have emerged after the discovery of superconductivity in cuprates at high temperatures between CDW and the superconducting phase [54]. Cuprates are quasi-2D materials. Stripes, checker-board phase, and long and short-range charge fluctuation have been observed as charge-ordered phases of different materials.

Scanning tunneling microscopy study of under-doped cuprates showed that CDW modulation is unconventional as antiferromagnetic and Coulomb interaction may play a key role [55]. A dimensional crossover of CDW from 2D to 3D has been observed in certain cuprates at higher magnetic fields, complicating the current picture [56]. The interplay between CDW, magnetic ordering, and superconductivity is still an exciting and active area of research [57].

### 3.5.2 CDW in excitonic insulators

In Peierls' model, CDW transition is driven by electron-lattice interaction and can be understood through a single metallic band picture. Charge density ordering in the excitonic insulator is driven by electron-electron interactions in two bands

with a small indirect band overlap [59, 60]. Excitons are bound states of electrons and holes, neural quasiparticles in semiconducting, semi-metallic, or insulating systems [61]. Let us assume a two-band semiconducting system with energy gap  $E_G$  with valence band maxima at wavevector  $\mathbf{k} = 0$  and conduction band minimum at  $\mathbf{k} = \mathbf{q}_0$ . For energy,  $\epsilon_{\mathbf{k}}^v$  and  $\epsilon_{\mathbf{k}}^c$  of electrons in valence and conduction band, respectively, the effective Hamiltonian for the modeling of the excitonic insulator phase can be written as

$$H_{EI} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}}^v a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \sum_{\mathbf{k}'} \epsilon_{\mathbf{k}'}^c b_{\mathbf{k}'}^\dagger b_{\mathbf{k}'} + \sum_{\mathbf{k}', \mathbf{k}} \Delta_{\mathbf{k}} (b_{\mathbf{k}'}^\dagger a_{\mathbf{k}} + a_{\mathbf{k}}^\dagger b_{\mathbf{k}'}) \quad (3.27)$$

$a_{\mathbf{k}}^\dagger, b_{\mathbf{k}}^\dagger$  are creation operators for state  $\mathbf{k}$  and  $a_{\mathbf{k}}, b_{\mathbf{k}}$  are anihilation operators,  $\Delta_{\mathbf{k}}$  is energy gap after reconstruction of electronic structure. We will discuss a qualitative picture of two cases  $E_G > 0$  and  $E_G < 0$  as the Coulomb interaction is taken into account. The energies of the electrons in valence ( $\epsilon_{\mathbf{k}}^v$ ) and conduction bands ( $\epsilon_{\mathbf{k}}^c$ ) are

$$\epsilon_{\mathbf{k}}^v = -\frac{1}{2}E_G - \frac{\hbar^2}{2m_v}\mathbf{k}^2, \quad \epsilon_{\mathbf{k}}^c = \frac{1}{2}E_G + \frac{\hbar^2}{2m_c}(\mathbf{k} - \mathbf{q}_0)^2 \quad (3.28)$$

where  $m_v$  and  $m_c$  are effective masses of particles in corresponding bands.

### Case I $E_G > 0$

We start with the semiconducting situation. Let  $E_B$  be the binding energy of exciton such as  $E_G > E_B > 0$ . We assume tunability of band gap  $E_G$  with some external parameters. If the binding energy of exciton remains the same, reducing  $E_G$  leads to a reduction in the excitation energy of exciton, i.e.,  $E_G - E_B$ . As the quantity  $E_G - E_B$  goes to zero excitons start to form spontaneously, and electronic instability occurs.

### Case II $E_G < 0$

Semimetals have small indirect band overlap (negative band gap- maxima of the valence band is higher than conduction band minimum). The critical value of band overlap ( $E_c$ ) plays a significant role in the formation and stability of the excitonic insulator phase. In materials where the conduction band minimum lies above the valence band maximum, there's a positive band overlap ( $E_c > 0$ ). This configuration typically favors the standard metal or semiconductor behavior. When the conduction band minimum shifts below the valence band maximum, resulting in a negative



band overlap ( $E_c < 0$ ), it can lead to the formation of an excitonic insulator phase. For certain critical values ( $E_c < 0$ ) of band overlap, instability occurs due to the screening effect. If electrons and holes in the system are insufficiently screened, they facilitate the formation and stabilization of excitons, promoting their condensation into an excitonic insulator.

The exciton insulator phase leads to the formation of electron density waves. Charge density wave have wavelength  $\lambda_0 = 2\pi/|\mathbf{q}_0|$  corresponds to soft electronic mode. Sometimes, the CDW is accompanied by lattice distortion with the same periodicity, but the primary excitonic insulator instability is electronic in nature. The most important example of an excitonic insulator-induced CDW state is 1T-TiSe<sub>2</sub>. We will discuss this material in detail in the following chapters.

### 3.6 Experimental techniques for CDW characterization

| Features of CDW             | Experimental technique                                                           |
|-----------------------------|----------------------------------------------------------------------------------|
| Fermi surface nesting (FSN) | ARPES                                                                            |
| Susceptibility Function     | ARPES                                                                            |
| Structural transition       | Neutron diffraction<br>X-ray diffraction<br>Electron diffraction<br>STM          |
| Kohn anomaly                | Inelastic neutron scattering<br>Inelastic X-ray scattering<br>He atom scattering |
| Charge modulation           | STM                                                                              |
| Electronic transition       | STM and STS                                                                      |

Table 3.2: List of experimental tools utilized to study different features associated with the CDW transition. Abbreviations: **ARPES**: Angle-resolved photoemission spectroscopy, **STM**: Scanning tunneling microscopy, **STS**: Scanning tunneling spectroscopy [40]

Real materials show variations of the above-mentioned charge density wave phase transformation models. No universal mechanism can be applied to all materials as the CDW transitions are strongly system-dependent. A myriad of techniques is employed to experimentally characterize the features associated with the CDW in real materials. The experimental techniques used to study specific features of CDW are listed in the table 3.2. In this work, we investigated the Type II and Type III CDW systems with scanning tunneling microscopy (STM). The direct real-space observation of electron density modulation can be performed using STM topography

imaging. Scanning tunneling spectroscopy can gain local density of states (LDOS) information. All electronic systems' phase transition dynamics occur around the Fermi level. STM is ideal for studying CDW and energetics near the Fermi level. More details on the STM technique are mentioned in Chapter 4.

## *Chapter 4*

### EXPERIMENTAL METHODS AND SETUP

*“There is plenty of room at the bottom.”*

— Richard Feynman

#### 4.1 An overview

Scanning Tunneling Microscopy (STM) has an intriguing history that marks significant advancements in the visualization and understanding of materials at the atomic scale. The idea behind STM traces back to the quantum mechanical principles of tunneling, which were proposed in the early 20th century. In 1928, physicist Friedrich Hund first described electron tunneling phenomena [62, 63], which suggested the possibility of studying surfaces at an atomic level. Building upon this theoretical groundwork, in the 1970s, the concept of STM began to take shape. Physicists like Gerd Binnig and Heinrich Rohrer (at IBM Zurich) developed the theoretical framework for an instrument that could visualize individual atoms on a surface by leveraging the tunneling effect. In 1982, Gerd Binnig and Heinrich Rohrer reported the first-ever topographic picture of a surface at an atomic scale [64]. The topografiner [65] and the electron tunneling experiments [66] paved the path toward the invention of scanning tunneling microscopy. Topografiner used a field emission current by accelerating electrons to a few kV and mapping the surface from a distance of 100nm, with a resolution of sub-micron scale [65]. Teague’s apparatus demonstrated vacuum tunneling between two gold electrodes, without a raster scan mechanism but fine adjustment for gap width [66].

The realization of STM was a breakthrough not only in the field of surface science to image the atoms on a metal or a semiconductor surface but also to make nanostructures using a bottom-up approach from the single atoms or molecules with the STM tip-based manipulation techniques and probe their electronic properties using the very local spectroscopic method. The STM is based on the principle of the quantum tunneling of electrons through a potential barrier. In this effect, a particle can tunnel from one metal to another if placed very close such that the gap is  $< 10 \text{ \AA}$ . The lateral resolution of STM depends on how sharp a tip is; the atomic resolution is achieved when a single tip atom on the apex is nearer to the sample than other tip

atoms. The tunneling probability decays exponentially with the width of the barrier so that the tunneling current mainly flows through the narrowest parts of the barrier. The first STM image of Si( $7 \times 7$ ) reconstruction was reported by Binnig et al. in 1983 [67].

The introduction of STM revolutionized nanoscience and nanotechnology. It enabled scientists to explore surface structures and properties in unprecedented detail. Subsequent developments included variants of STM such as Atomic Force Microscopy (AFM) and Scanning Tunneling Spectroscopy (STS), expanding its applications in studying material properties, surface reactions, and even biological samples. Several advances in surface science, materials science, and physics have undoubtedly established the powerful utility of STM in investigating the topography and the local electronic properties with atomic-scale precision. It is a unique technique that provides the structural properties and the corresponding electronic properties of the surface. STM provides a real space image compared to other techniques like x-ray diffraction (XRD) and low energy electron diffraction (LEED). A scanning electron microscope (SEM) resolution is limited by the incident energy and the electron beam cross-section and cannot resolve atoms or molecules. STM analyses the local electronic properties of the surface with fine energy resolution. A few examples of the utility of STM probe in material science include measurements of the surface states [68], surface potential [69, 70], the Kondo effect [71], Dirac cone-like dispersion in graphene [72] and topological insulator [73], and the vibrational energy spectrum [74] as well as electron spin [75].

This chapter briefly introduces the scanning tunneling microscopy (STM) principle, experimental setup, and sample preparation and data acquisition methods. In particular, the general working principle, data acquisition, and theoretical models are discussed.

## 4.2 Theoretical aspects of scanning tunneling microscopy and spectroscopy

Here we will discuss the basics of STM. The fundamental principle of STM is the quantum tunneling of electrons through a vacuum barrier. There are several theoretical approaches to explain the tunneling effect. J. Bardeen's quantitative theory of tunneling was published in 1961 [76] and applied to the scanning tunneling microscope in 1983 by Tersoff and Hamann [77]. For ease of understanding, we begin with a simple one-dimensional model, move on to the Bardeen model of tunneling, and finally to the Tersoff-Hamann approach to the Bardeen model.

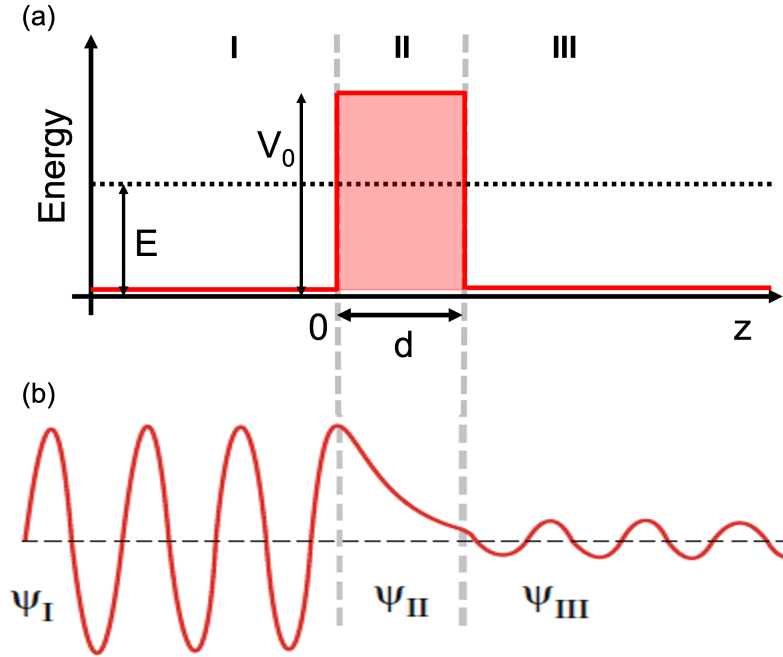


Figure 4.1: One dimensional tunneling barrier junction with barrier height  $V_0$  and width  $d$ . The real part of a complex wave function is plotted for different regions.

#### 4.2.1 Potential barrier model for 1D

The 1D model for tunnel junction (tip-vacuum-sample) is considered as a finite square potential barrier  $V(x)$  of height  $V_0$ , in a region between  $x = 0$  and  $x = d$  (as shown in Figure 4.1). The time-dependent Schrodinger equation for the electron of energy  $E$  is

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left( -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right) \Psi(\mathbf{r}, t) \quad (4.1)$$

As the barrier potential is not explicitly dependent on time, we can write the solution as a product of spatial and temporal factor, i.e.,  $\Psi(\mathbf{r}, t) = \phi(t)\psi(\mathbf{r})$ , where  $\phi(t) = e^{-iEt/\hbar}$  is time dependent part. The time-independent Schrodinger equation for our case is

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x) \psi(x) = E \psi(x) \quad (4.2)$$

Barrier divide the space into region I ( $x < 0$ ), region II ( $0 \leq x \leq d$ ) and region III ( $x > d$ ). If we assume electrons travel from left to right and insert the *ansatz*  $\psi(x) = e^{ikx}$  into equation 4.2, we will get

$$-\frac{\hbar^2 k^2}{2m} + V(x) = E \quad k = \sqrt{\frac{2m}{\hbar^2} [E - V(x)]}. \quad (4.3)$$

Outside the barrier in regions I and III,  $V = 0$ , the solution takes an oscillating waveform.

$$\psi(x) = e^{ikx} \quad \text{with} \quad k = \sqrt{\frac{2mE}{\hbar^2}} \quad (4.4)$$

Inside the barrier  $V = V_0$  in region II  $k$  in equation 4.3 becomes imaginary, as  $E - V_0 < 0$ . We define  $k = i\kappa$  with real value  $\kappa$ .

$$\kappa = \sqrt{\frac{2m}{\hbar^2} [V_0 - E]} \quad (4.5)$$

The *ansatz*  $\psi = e^{ikx}$  for Schrodinger equation becomes non-oscillating solution  $\psi = e^{-\kappa x}$  for an electron with energy  $E$  less than the barrier of height  $V_0$  inside the barrier. The potential barrier is forbidden for classical particles, but in quantum mechanics, particles can enter and cross the barrier region in a process known as tunneling [78].

We only considered right-moving particles in the *ansatz*, but there is also an independent, left-moving solution. We must consider the general solution for a particle with energy  $E < V_0$  valid for three regions and all values of  $x$ . The general solution in different regions takes a form,

$$\psi(x) = \begin{cases} \psi_I(x) = Ae^{ikx} + Be^{-ikx} & x < 0 \quad \text{region I} \\ \psi_{II}(x) = Ce^{-\kappa x} + De^{\kappa x} & 0 \leq x \leq d \quad \text{region II} \\ \psi_{III}(x) = Fe^{ikx} & x > d \quad \text{region III} \end{cases} \quad (4.6)$$

$A$ ,  $B$ ,  $C$ ,  $D$ , and  $F$  are complex coefficients. In region I ( $x < 0$ ), the incoming wave of amplitude  $A$  is accompanied by the reflected wave of amplitude  $B$ . In region II ( $0 \leq x \leq d$ ), wavefunction tunnels into the barrier with a term proportional to  $C$  and  $D$  as a reflected term. No wave travels to the left in region III ( $x > d$ ) as we assume only right-moving particles. The wave function and its first derivative must be continuous at the boundary separating the three regions. The conditions at

position  $x = 0$  and  $x = d$  are

$$\psi_I(0) = \psi_{II}(0) \quad (4.7)$$

$$\frac{\partial}{\partial x}\psi_I(0) = \frac{\partial}{\partial x}\psi_{II}(0) \quad (4.8)$$

$$\psi_{II}(d) = \psi_{III}(d) \quad (4.9)$$

$$\frac{\partial}{\partial x}\psi_{II}(d) = \frac{\partial}{\partial x}\psi_{III}(d) \quad (4.10)$$

Assume  $A = 1$ ; equation 4.9-4.12 gives four complex equations that can fix four complex coefficients.

$$1 + B = C + D \quad (4.11)$$

$$ik(1 - B) = \kappa(D - C) \quad (4.12)$$

$$Ce^{-\kappa d} + De^{\kappa d} = Fe^{ikd} \quad (4.13)$$

$$\kappa(De^{\kappa d} - Ce^{-\kappa d}) = ikFe^{ikd} \quad (4.14)$$

We are interested in the amplitude  $F$  of the wavefunction. Solving the above system of equations, we get

$$F = 2e^{-ikd} \left[ \frac{k\kappa}{2k\kappa \cosh(\kappa d) + i(\kappa^2 - k^2) \sinh(\kappa d)} \right] \quad (4.15)$$

Absolute square of  $F$  is the probability of a particle appearing past the barrier, represented as transmission factor  $T$

$$T = |F|^2 = \frac{4k^2\kappa^2}{(k^2 + \kappa^2)^2 \sinh^2(\kappa d) + 4k^2\kappa^2} \quad (4.16)$$

For  $kd \gg 1$  limit  $\sinh^2$  term can be approximated by  $\sinh^2(\kappa d) \approx \frac{1}{4}e^{2\kappa d}$ , so the transmission coefficient becomes

$$T \approx \frac{16k^2\kappa^2}{(k^2 + \kappa^2)} e^{-2\kappa d} \approx \frac{16E(V_0 - E)}{V_0^2} \exp \left[ -2d \sqrt{\frac{2m}{\hbar^2}(V_0 - E)} \right] \quad (4.17)$$

The transmission coefficient  $T$  is exponentially dependent on the barrier width ( $d$ ). The probability current density  $J$  is velocity times the absolute square of wavefunction amplitude in region III  $J = |F|^2 v = T \cdot v$ . The next section will use the Bardeen model to discuss a more realistic picture of tunneling between the metals across a vacuum barrier.

### 4.2.2 Bardeen model of tunneling

The scanning tunneling microscopy image is interpreted as a topography of the surface. A topography image reflects the surface charge density to the first approximation. Bardeen developed a model for tunneling between metal junctions separated by an insulating barrier [76]. The complete system of Schrodinger equations for the tip-barrier-sample junction is very complicated, even in a single electron approximation picture. Bardeen approached this problem by dividing a system into two independent subsystems. The solution for small subsystems can be found more efficiently, and these solutions are then combined to solve the complete system using time-dependent perturbation theory. The Bardeen theory's predictions are reliable when the tip-sample distance is significant and for small bias. There are two general approaches to the Bardeen theory: (i) using the nonequilibrium Green function (NEGF) and (ii) Oppenheimer's theory of ionization of hydrogen.

The nonequilibrium Green functions (NEGF) approach to tunneling theory was developed by Caroli et al. [79], and Feuchtwang [80–82]. The theory is the exact formulation developed to handle electron-electron and electron-phonon interactions. NEGF current formula is more general than the Bardeen current formula, which approximates the former. Oppenheimer's perturbation theory differs from standard time-dependent perturbation theory [83]. The Bardeen theory begins with a few assumptions: 1. tip and sample states are orthogonal, 2. tunneling is small and treated to a first approximation, other assumptions are 3. independent electron approximation (no electron-electron interaction), 4. Tip and sample are at the same chemical potential, and 5. The probabilities of occupation of states for the tip and sample are constant and independent.

The figure shows that we begin with a tip and sample separated by an imaginary surface, choosing inside the tunneling gap. A potential of the system is divided into the tip and sample potential with a condition  $V_{tot}(\mathbf{r}) = V_T(\mathbf{r}) + V_S(\mathbf{r})$ , such that tip potential  $V_T(\mathbf{r}) = 0$  in a sample and sample potential  $V_S(\mathbf{r}) = 0$  inside the tip shown in Figure 4.2. The time-dependent Schrodinger equation of the above-defined tip-sample system is as follows.

$$i\hbar \frac{\partial \Psi_{T,i}(\mathbf{r}, t)}{\partial t} = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V_T(\mathbf{r}) \right] \Psi_{T,i}(\mathbf{r}, t) \quad (4.18)$$

$$i\hbar \frac{\partial \Psi_{S,j}(\mathbf{r}, t)}{\partial t} = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V_S(\mathbf{r}) \right] \Psi_{S,j}(\mathbf{r}, t) \quad (4.19)$$



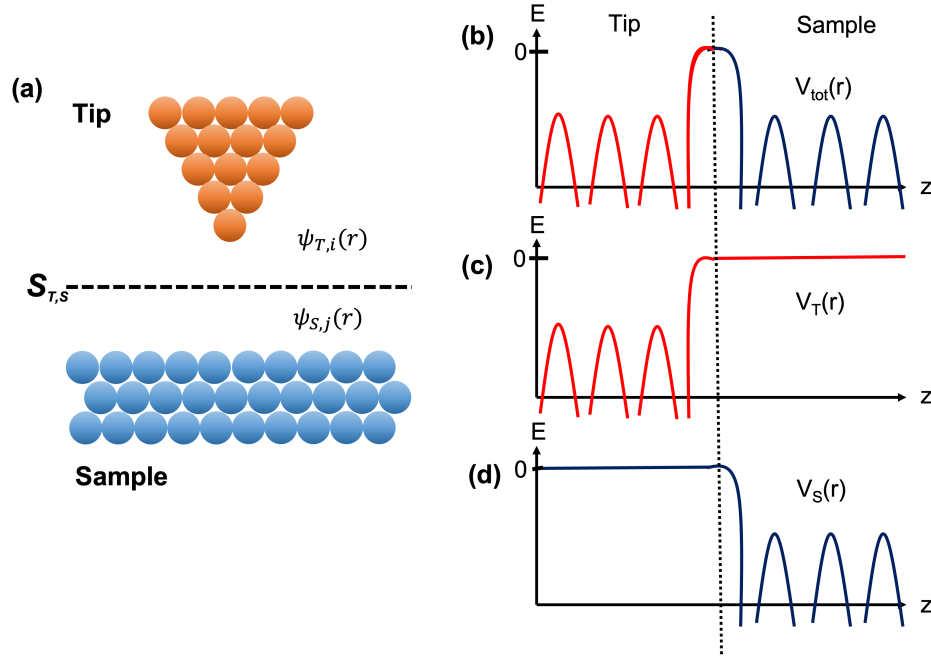


Figure 4.2: Schematics of tip and sample system. (a) According to the Bardeen model, a tip-sample system can be split into two parts separated by surface  $S_{T,S}$ . (b) Total potential  $V_{tot}$  is split into two simple systems with potential (c) tip potential  $V_T$  and (d) sample potential  $V_S$

for tip and sample, respectively. Solution for time-dependent Schrodinger equation for state  $i$  of tip and state  $j$  of sample for potential  $V_T(\mathbf{r})$  and  $V_S(\mathbf{r})$  respectively is

$$\Psi_{T,i}(\mathbf{r}, t) = \psi_{T,i}(\mathbf{r}) e^{\frac{-iE_i t}{\hbar}} \quad (4.20)$$

$$\Psi_{S,j}(\mathbf{r}, t) = \psi_{S,j}(\mathbf{r}) e^{\frac{-iE_j t}{\hbar}} \quad (4.21)$$

The time-independent equations takes following form for  $i$  tip and  $j$  sample state

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_T(\mathbf{r}) \right) \psi_{T,i}(\mathbf{r}) = E_i \psi_{T,i}(\mathbf{r}) \quad (4.22)$$

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_S(\mathbf{r}) \right) \psi_{S,j}(\mathbf{r}) = E_j \psi_{S,j}(\mathbf{r}) \quad (4.23)$$

If we consider the tip, a separate system, the electron in a specific state will stay forever. Now, we consider the tunneling (or scattering) of an electron from state  $i$  in a tip to the final  $j$  state of the sample. Tunneling causes a minimal perturbation; the

final state is almost identical to the initial one. The wavefunction in the final form can be written as initial state  $\Psi_{T,i}(\mathbf{r}, t)$  plus sum over functions  $\Psi_{S,j}(\mathbf{r}, t)$  multiplied with  $a_j$  being the probability amplitude of electron being in this state.

$$\Psi_{final}(\mathbf{r}, t) = \Psi_{T,i}(\mathbf{r}, t) + \sum_j a_j(t) \Psi_{S,j}(\mathbf{r}, t) \quad (4.24)$$

We are interested in the tunneling rate of  $i$  to  $j$ , i.e., the time dependence of  $a_j$ . The wavefunction in equation 4.24 is a solution of the complete system

$$i\hbar \frac{\partial \Psi_{final}(\mathbf{r}, t)}{\partial t} = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V_T(\mathbf{r}) + V_S(\mathbf{r}) \right] \Psi_{final}(\mathbf{r}, t) \quad (4.25)$$

insring equation 4.24 into equation 4.25

$$i\hbar \frac{\partial \Psi_{T,i}(\mathbf{r}, t)}{\partial t} + i\hbar \sum_j \frac{da_j(t)}{dt} \Psi_{S,j}(\mathbf{r}, t) + i\hbar \sum_j a_j(t) \frac{\partial \Psi_{S,j}(\mathbf{r}, t)}{\partial t} \quad (4.26)$$

$$= \left[ \frac{-\hbar^2}{2m} \nabla^2 + V_T(\mathbf{r}) + V_S(\mathbf{r}) \right] \left( \Psi_{T,i}(\mathbf{r}, t) + \sum_j a_j(t) \Psi_{S,j}(\mathbf{r}, t) \right) \quad (4.27)$$

using equation 4.18-4.23, we can simplify the above equation to rewrite it as

$$i\hbar \sum_j \frac{da_j(t)}{dt} \Psi_{S,j}(\mathbf{r}, t) = V_S(\mathbf{r}) \Psi_{T,i}(\mathbf{r}, t) + V_T \sum_j a_j(t) \Psi_{S,j}(\mathbf{r}, t) \quad (4.28)$$

replacing  $\Psi_{T,i}(\mathbf{r}, t)$  and  $\Psi_{S,j}(\mathbf{r}, t)$  from equation 4.20-4.21

$$i\hbar \sum_j \frac{da_j(t)}{dt} \psi_{S,j}(\mathbf{r}) e^{\frac{-iE_j t}{\hbar}} = V_S(\mathbf{r}) \psi_{T,i}(\mathbf{r}) e^{\frac{-iE_i t}{\hbar}} + V_T \sum_j a_j(t) \psi_{S,j}(\mathbf{r}) e^{\frac{-iE_j t}{\hbar}} \quad (4.29)$$

In this model, we assume that the final states are orthonormal. Multiplying by the complex conjugate of the specific final state, i.e.,  $\psi_{S,f}^*(\mathbf{r})$  and integrating over space gives

$$i\hbar \frac{da_f(t)}{dt} e^{\frac{-iE_f t}{\hbar}} = \int d^3\mathbf{r} \psi_{S,f}^*(\mathbf{r}) V_S(\mathbf{r}) \psi_{T,i}(\mathbf{r}) e^{\frac{-iE_i t}{\hbar}} + V_T a_f(t) e^{\frac{-iE_f t}{\hbar}} \quad (4.30)$$

The last term on the right-hand side is small, and we neglect it. We obtained the differential equation for the time-dependent co-efficient  $a_f(t)$

$$\frac{da_f(t)}{dt} = -\frac{1}{i\hbar} \int d^3\mathbf{r} \psi_{S,f}^*(\mathbf{r}) V_S(\mathbf{r}) \psi_{T,i}(\mathbf{r}) e^{\frac{i(E_f - E_i)t}{\hbar}} \quad (4.31)$$

We define transition matrix elements as following with integral over whole space

$$M_{fi} = \int d^3\mathbf{r} \psi_{S,f}^*(\mathbf{r}) V_S(\mathbf{r}) \psi_{T,i}(\mathbf{r}) \quad (4.32)$$

we can limit the integral only to the sample region. The result of integrating equation 4.31 is

$$a_f(t) = \frac{1}{i\hbar} M_{fi} \int_0^t dt' \exp \left[ \frac{i(E_f - E_i)t'}{\hbar} \right] \quad (4.33)$$

$a_f(t)$  is the probability amplitude of finding a state  $f$  at time  $t$ . We assumed a small current means a small transition rate, such that the initial state is fully occupied and the final state is almost empty. Simplifying the integral

$$\begin{aligned} a_f(t) &= -M_{fi} \frac{\exp [i(E_f - E_i)t/\hbar] - 1}{(E_f - E_i)} \\ &= -2iM_{fi} \exp [i(E_f - E_i)t/2\hbar] \frac{\sin [(E_f - E_i)t/2\hbar]}{(E_f - E_i)} \end{aligned}$$

using formula  $\exp(ia) - 1 = 2i \exp(i\frac{a}{2}) \sin \frac{a}{2}$  to simplify the quantity in the last line. By squaring the above equation, we get the probability tip state  $i$  transitioning (tunneling) to the sample state  $f$  as

$$|a_f(t)|^2 = 4|M_{fi}|^2 \frac{\sin^2 [(E_f - E_i)t/2\hbar]}{(E_f - E_i)^2} = |M_{fi}|^2 \frac{2t}{\hbar} \frac{\sin^2 [(E_f - E_i)t/2\hbar]}{(E_f - E_i)^2 t/2\hbar} \quad (4.34)$$

Using the specific functional form of Dirac delta distribution

$$\delta(x) = \lim_{a \rightarrow \infty} \frac{1}{\pi} \frac{\sin^2 ax}{ax^2} \quad (4.35)$$

The probability of an electron in state  $E_i$  jumping to  $E_f$  becomes narrow and high with increasing  $t$ . Identifying terms with Dirac delta function from equation 4.35 (identity  $x = E_f - E_i$  and  $a = t/2\hbar$ ), in the large time limit

$$\lim_{t \rightarrow \infty} |a_f(t)|^2 = \frac{2\pi}{\hbar} |M_{fi}|^2 \delta(E_f - E_i) t \quad (4.36)$$

the transition rate of electrons from initial tip state  $i$  to final sample state  $f$  is given by

$$w_{fi} = \frac{2\pi}{\hbar} |M_{fi}|^2 \delta(E_f - E_i) \quad (4.37)$$

The Bardeen model with elastic energy condition (obeying Dirac delta function) gives a tunneling transition rate proportional to the matrix element. The only term we need to calculate for transition probability is the matrix element (expressed

in equation 4.32). However, Bardeen matrix elements depend on wavefunctions of electrons in tip and sample and sample potential  $V_S$ . We can rephrase the terms so that matrix elements will depend on the value of wavefunction at the separation surface between the tip and sample, as defined earlier. Starting with expression for matrix elements

$$M_{fi} = \int_{sample} d^3\mathbf{r} \psi_{T,i}(\mathbf{r}) V_S(\mathbf{r}) \psi_{S,f}^*(\mathbf{r}) \quad (4.38)$$

Taking complex conjugate of equation 4.22 for a state  $f$  and replacing  $V_S(\mathbf{r}) \psi_{S,f}^*(\mathbf{r})$  in the integral with remaining terms

$$M_{fi} = \int_{sample} d^3\mathbf{r} \psi_{T,i}(\mathbf{r}) \left( E_f + \frac{\hbar^2}{2m} \nabla^2 \right) \psi_{S,f}^*(\mathbf{r}) \quad (4.39)$$

Tunneling transition occurs when  $E_i = E_f$ .

$$M_{fi} = \int_{sample} d^3\mathbf{r} \left( E_i \psi_{T,i}(\mathbf{r}) \psi_{S,f}^*(\mathbf{r}) + \psi_{T,i}(\mathbf{r}) \frac{\hbar^2}{2m} \nabla^2 \psi_{S,f}^*(\mathbf{r}) \right) \quad (4.40)$$

Using the Schrodinger equation from 4.22, and setting  $V_T(\mathbf{r}) = 0$  as the integration is extended over sample volume only we get

$$M_{fi} = \frac{\hbar^2}{2m} \int_{sample} d^3\mathbf{r} \left( \psi_{T,i}(\mathbf{r}) \nabla^2 \psi_{S,f}^*(\mathbf{r}) - \psi_{S,f}^*(\mathbf{r}) \nabla^2 \psi_{T,i}(\mathbf{r}) \right) \quad (4.41)$$

converting volume integral into surface integral using Green's identity, we write the matrix elements over the arbitrary surface separating tip and sample

$$M_{fi} = \frac{\hbar^2}{2m} \int_{surface} dS \mathbf{r} \left( \psi_{T,i}(\mathbf{r}) \nabla \psi_{S,f}^*(\mathbf{r}) - \psi_{S,f}^*(\mathbf{r}) \nabla \psi_{T,i}(\mathbf{r}) \right) \quad (4.42)$$

Tunneling from any tip state to any sample state is given by summing all pairs of initial and final states (using equation 4.37)

$$w_{T \rightarrow S} = \frac{2\pi}{\hbar} \sum_{i,f} |M_{fi}|^2 \delta(E_f - E_i) \quad (4.43)$$

Multiply by electron charge; the transition rate gives the tunneling current. taking spin degeneracy into account, we multiply by a factor of two

$$I = \frac{4\pi e}{\hbar} \sum_{i,f} |M_{fi}|^2 \delta(E_f - E_i) \quad (4.44)$$

Instead of using the wave function, we use the density of states of the tip and sample for an energy-dependent approximation of the Bardeen model. We use an identity  $\int_{-\infty}^{\infty} d\epsilon f(\epsilon) \delta(\epsilon - x) = f(x)$  to calculate energy dependent matrix elements

$$|M(E_f)|^2 \delta(E_f - E_i) = \int_{-\infty}^{\infty} d\epsilon |M(\epsilon)|^2 \delta(\epsilon - E_i) \delta(\epsilon - E_f) \quad (4.45)$$

We can now calculate the current using equation 4.44 and integrating over a bias window only

$$\begin{aligned} I &= \frac{4\pi e}{\hbar} \sum_{i,f} \int_0^{eV} d\epsilon |M(\epsilon)|^2 \delta(\epsilon - E_i) \delta(\epsilon - E_f) \\ &= \frac{4\pi e}{\hbar} \int_0^{eV} d\epsilon |M(\epsilon)|^2 \sum_i \delta(\epsilon - E_i) \sum_f \delta(\epsilon - E_f) \end{aligned} \quad (4.46)$$

The number of electronic states in a certain energy range is called the density of states. The density of states of a system for  $n$  discrete states are given by  $\rho(E) = \sum_n \delta(E - E_n)$ . For  $\rho_T(E)$  tip density of states and  $\rho_S(E)$  sample density of state at energy,  $E$  and choosing sample Fermi energy as a reference point tunneling current according to above equation will be

$$I = \frac{4\pi e}{\hbar} \int_0^{eV} d\epsilon \rho_T(\epsilon) \rho_S(\epsilon) |M(\epsilon)|^2 \quad (4.47)$$

Rather than setting energy reference to sample Fermi level, we can set tip Fermi energy as its own reference.  $\rho_T(\epsilon)$  at bias  $V$  will become  $\rho_T(\epsilon - eV)$  then the equation modify to become

$$I = \frac{4\pi e}{\hbar} \int_0^{eV} d\epsilon \rho_T(\epsilon - eV) \rho_S(\epsilon) |M(\epsilon)|^2 \quad (4.48)$$

The tunneling current is a convolution of the density of states of the tip and sample if the density of states of the tip is known the tunneling current maps the surface density of states of the sample.

### 4.2.3 Tersoff-Hamann approximation

Bardeen proposed his tunneling model for a metal-insulator-metal junction in 1961, well before the development of STM [76]. Tersoff-Hamann applied this model

to realistic surface wavefunctions to first approximation and small bias voltages [77]. It is hard to calculate the tunneling matrix elements in the Bardeen model, Tersoff-Hamann calculated the matrix elements in the small bias voltage limit near Fermi energy. In this method, explicit wavefunctions of the surface and tip have to be inserted. Tersoff-Hamann used Fourier plane wave expansion for the surface wavefunction and considered the tip as a point located at  $\mathbf{r}$  from the surface such that the tunneling current at a small voltage is

$$I \propto \sum_n |\psi_n(\mathbf{r})|^2 \delta(\epsilon_n - E_F) \quad (4.49)$$

The tunneling current is then proportional to the sample states of energy  $E_F$  at the location of the tip

$$I \propto \rho_S(E_f, \mathbf{r}) \quad (4.50)$$

This led to a simple interpretation of tunneling current as the local density of states (LDOS) of the surface at the position of the tip.

#### 4.2.4 Scanning tunneling spectroscopy (STS)

The compelling utility of a scanning tunneling microscope (STM) is its ability to acquire spectroscopic data with angstrom scale spatial resolution. Our discussion of the Bardeen model suggests that STM measures the spatial and energy dependence of the local states. Scanning tunneling spectroscopy (STS) is the direct measure of LDOS. The current-voltage relation of the tunneling junction accomplishes this task. Small changes in the bias voltage lead to an additional tunneling current. We define transmission factor in terms of matrix elements  $T(\epsilon, V, d) = |M(\epsilon)|^2$  then the expression for the tunneling current at temperature  $T = 0K$  can be written as

$$I = \frac{4\pi e}{\hbar} \int_0^{eV} d\epsilon \rho_T(\epsilon - eV) \rho_S(\epsilon) T(\epsilon, V, d) \quad (4.51)$$

To the first approximation small change in current  $dI$  per unit change in bias voltage  $dV$ , taken at upper limit  $\epsilon = eV$  gives

$$\frac{dI}{dV} \approx \frac{4\pi e}{\hbar} \rho_T(0) \rho_S(eV) T(eV, V, d) \quad (4.52)$$

The differential conductance is proportional to the product of sample density of states at energy  $eV$  to the sample density of the state at Fermi energy. If the tip LDOS and transmission factor are considered constant and independent of voltage (see Figure 4.3).

$$\frac{dI}{dV} \propto \rho_S(eV) \quad (4.53)$$

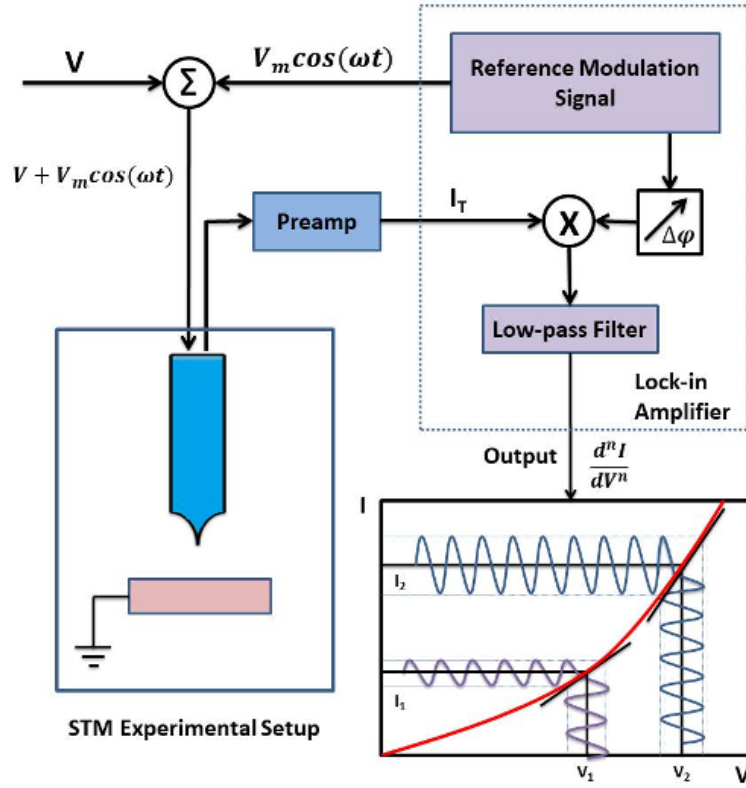


Figure 4.3: Schematics of spectroscopy measurements. Graphical representation of the  $I - V$  curve. The voltage modulation is applied around value  $V_1$  or  $V_2$ . The measured tunneling current is then proportional to the slope of the  $I - V$  curve ( $dI/dV$ ) at  $V_1$  or  $V_2$ , respectively. Adapted from [84]

The differential conductance is measured by fixing a tip-sample distance for a certain bias and at a certain current. The primary signal measured is the current as a function of applied voltage  $I = f(V)$ . The lock-in technique is used to reduce the noise in the measurements. In the lock-in technique, small AC signal of frequency  $\omega$  was generated ( $V_m \cos(\omega t)$ ) and added to the applied bias voltage  $V$ ; this changes the current  $I(t) = f(V + V_m \cos(\omega t))$ . The Taylor expansion of modulated current as a polynomial function of  $V$  can be written as

$$I = \sum_{k=0}^{\infty} \frac{V_m^k}{k!} \frac{d^k f(V)}{dV^k} \cos^k(\omega t) \quad (4.54)$$

If we expand the sum and group the terms in the Taylor series with the same multiples of modulation frequency, we get

$$I = f(V) + V_m \cos(\omega t) \frac{df(V)}{dV} + \frac{V_m^2}{4} \cos(2\omega t) \frac{d^2 f(V)}{dV^2} + \frac{V_m^3}{24} \cos(3\omega t) \frac{d^3 f(V)}{dV^3} + \dots \quad (4.55)$$

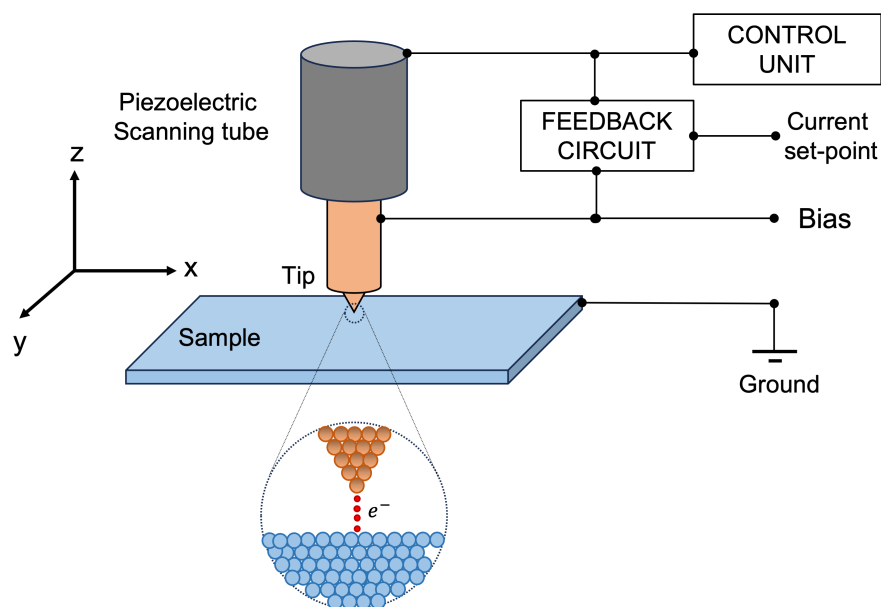


Figure 4.4: Working principle of STM - A small voltage is applied to the tip while a sample is grounded. The piezoelectric scanning element can then move the tip in  $x$ ,  $y$ , and  $z$  directions while recording the tip height, and a feedback loop is used to maintain the barrier width in the tunnel junction.

Taylor expansion becomes the harmonic sum of frequencies with  $n$ th derivative of the  $I - V$  curve. By measuring  $n$  times modulation frequency, we obtain the  $n$ th derivative of amplitude. The filtered output via a low pass filter corresponds to the  $n^{th}$  derivative of the  $I - V$  curve.

#### 4.2.5 Design and the operational modes of STM

As discussed earlier, the central part of an STM is a quantum mechanical tunnel junction of two metal electrodes separated by vacuum, where two metal electrodes represent the tip and the sample. Figure 4.4 shows a schematic to understand the basic design of STM. A sharp tip with approximately a single atom at its end scans the sample to achieve a high lateral resolution of sub-Angstrom. High spatial resolution can only be achieved if the tunneling occurs through a single atom. The STM tunnel junction is shown in the Figure. The STM image is acquired by moving the tip laterally in the  $X - Y$  plane by a piezoelectric scanner, and a feedback loop in place to maintain the tip height in  $Z$  direction, simultaneously detecting the variation in the tunneling current by applying a small DC bias between the tip and the sample.

STM topographic images can be recorded in two basic operational modes, constant height, and current modes, as shown in Figure 4.5. In the constant height



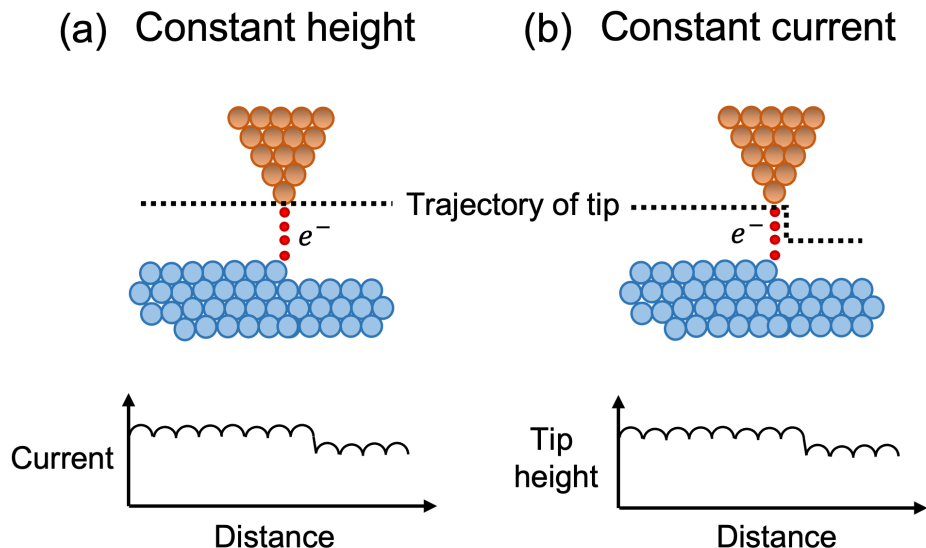


Figure 4.5: Operational modes of STM. In constant height mode tip hovers over the sample at a fixed distance and measures the variation of current as a function of position while a feedback loop is switched off; on the other hand, in constant current mode, the feedback loop adjusts the height to maintain constant current and variation in height is measured as a function of position.

mode, the STM tip scans the conducting surface by maintaining a constant height within the tunneling range. Therefore, plotting the tunneling current change in the  $X - Y$  plane gives the real space topographic image. The main disadvantage of performing experiments in this mode is that if the surface roughness is more than the fixed gap between the tip and the surface, the tip crashes on the surface. The tip must be stable in the  $Z$  direction against thermal noise and external mechanical vibration. The constant current mode is the other operation mode, the most commonly used for STM imaging. A feedback loop maintains the constant current by moving the tip up and down in the  $Z$  direction. Which means effectively varying the barrier width. The real space STM image in this mode is recorded by plotting the variation in the height with respect to the lateral displacement during scanning. The advantage of this mode is that the tip follows the surface electron density contour, and there is no chance of the tip crashing over the surface as the feedback loop ensures stability. In this thesis, we used the constant current operation mode, and the feedback loop was turned off only during spectroscopy.

Figure 4.6 represents the energy level diagram of the tunnel junction and electron tunneling mechanism under applied bias. When the tip and sample are far

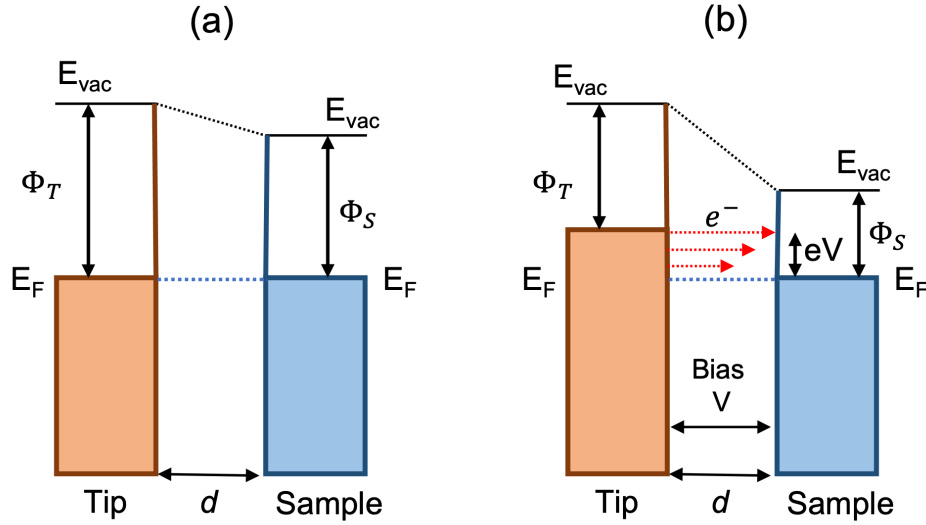


Figure 4.6: Energy level diagram of the tunneling junction. (a) Tip and sample are in the tunneling range without any bias; tunneling of electrons between tip and sample results in an equilibrium state with no net tunneling current. (b) The applied bias shifts the Fermi level by  $eV$ , and net electron flow manifests as a tunneling current.

apart, effective tunneling does not occur, as illustrated in Figure 4.6(a). As the tip approaches within the tunneling range, random tunneling events between the tip and sample commence, resulting in no net tunneling current. A bias is applied between the tip and the sample to establish a net tunneling current. When a positive bias is applied to the sample, as depicted in Figure 4.6(b), electrons begin tunneling from the tip to the sample. Consequently, the tunneling current probes the unoccupied states of the sample. Conversely, when a negative bias is applied to the sample, electrons tunnel from the sample to the tip, allowing the tunneling current to probe the occupied states of the sample, this explanation assumes a constant density of states for the tip, often achieved by utilizing a metallic tip.

#### 4.2.6 Atom manipulation using STM

Scanning Tunneling Microscopy (STM) is an incredible tool that also allows manipulate of individual atoms on surfaces. Atoms physically adsorbed on the metallic substrate can be manipulated with ease using STM. When the STM tip approaches the surface, the interplay of van der Waals and electric forces occurs between the tip and atoms. Tunneling electrons facilitate the transmission of both charge and energy from the tip to the atoms. Manipulation occurs due to the involvement of multiple interactions. Even the basic lateral movement of an atom

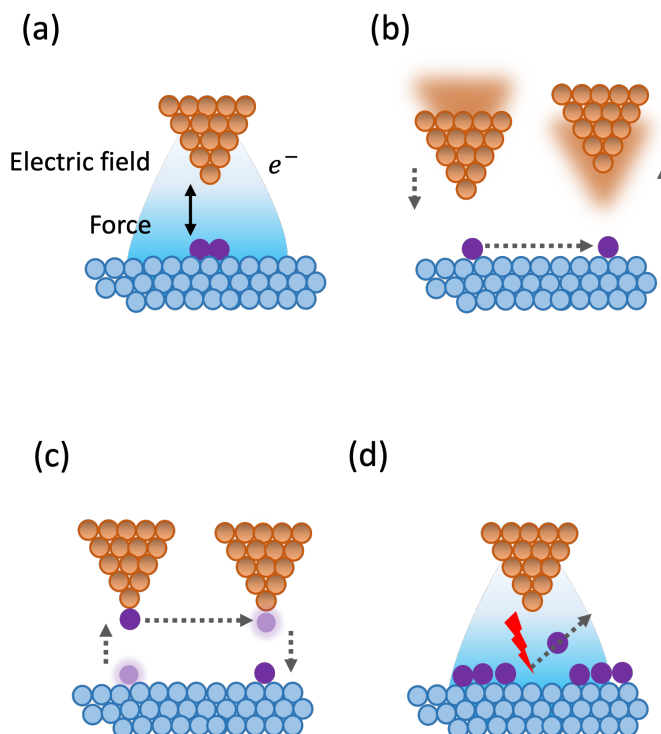


Figure 4.7: Schemes for atom manipulation (a) Interaction between adatoms and tip via electric field (b) Lateral manipulation (c) Vertical manipulation (d) extraction of adatom by applying voltage bias

on a metal surface engages various mechanisms, contingent upon the tip-sample distance, bias voltage, and tunneling current. Figure 4.7(b) depicts a common technique for lateral manipulations, where an STM tip either pushes or pulls the adsorbed atom on the surface. It's important to note that lateral manipulation employs a small bias, typically tens of millivolts, to avoid stimulating the adsorbates and maintaining the atoms adhered to the surface. While in vertical manipulation adsorbates are excited using a substantial bias voltage, typically a few volts. This process aims to transfer adsorbates from the sample to the tip as shown in Figure 4.7(c). These adsorbates attached to the tip are relocated to a different position and subsequently released using another bias voltage pulse. Application of substantial bias can lead to the dissociation of chemical bonds between the adsorbates and the surface, inducing their diffusion or complete removal (depicted in Figure 4.7(d)).

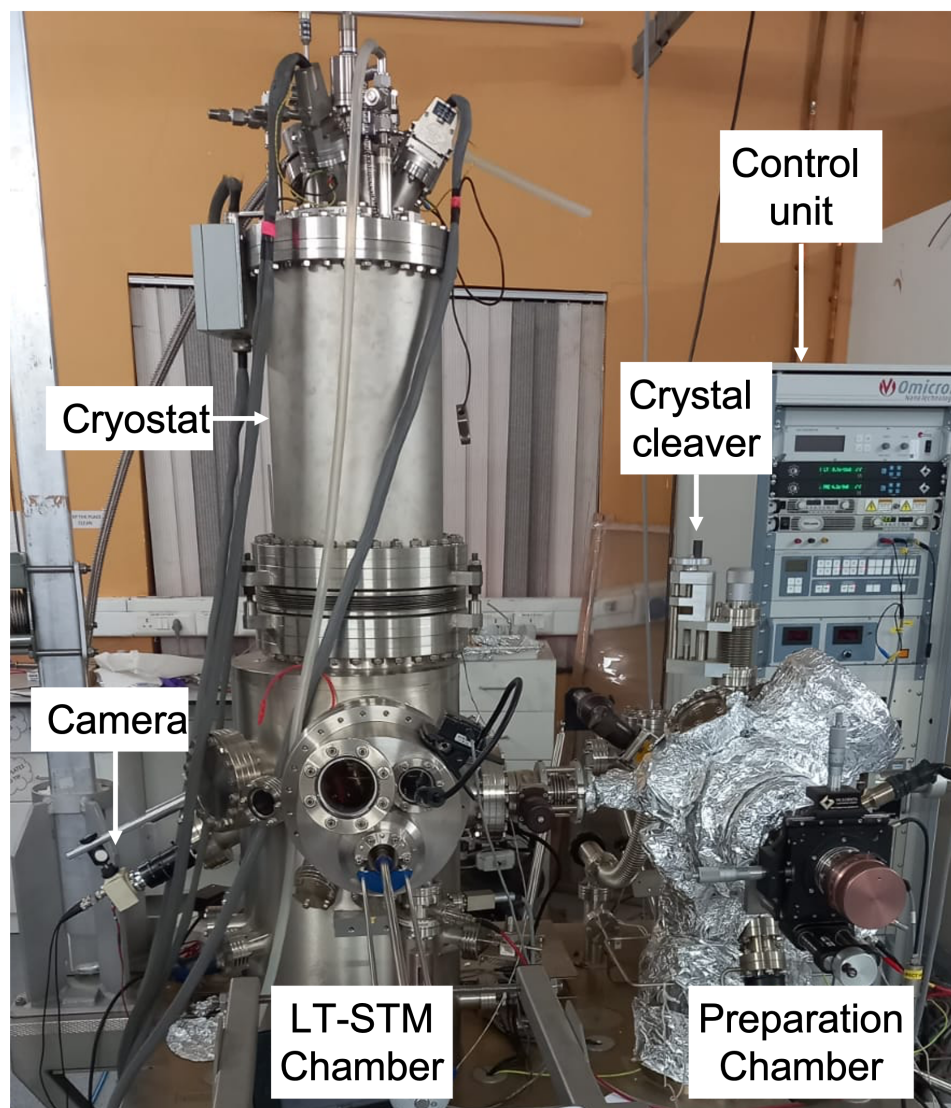


Figure 4.8: UHV LT-STM and preparation chamber picture. A valve separates both chambers.

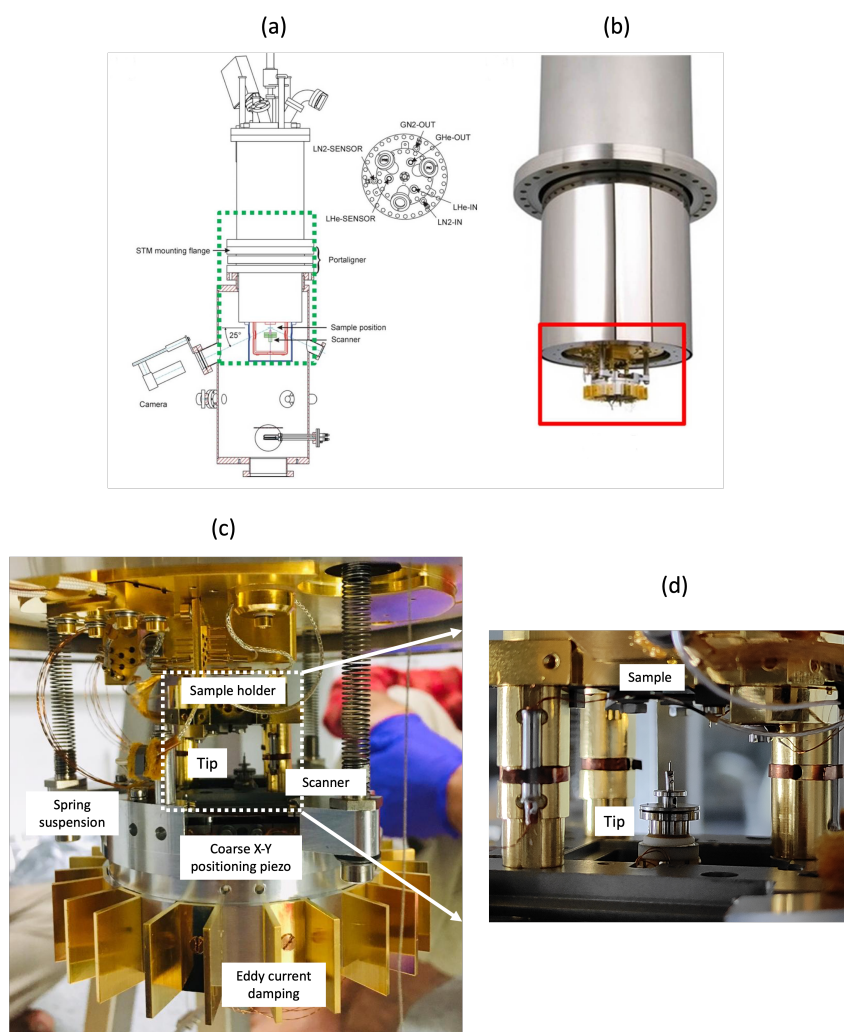


Figure 4.9: (a) Schematic design of LT-STM chamber and location of STM scanning head inside the chamber. (b) Picture of actual STM at the cryostat base marked by the red rectangle. (c) Enlarged picture of scanning head marked by red in (b). (d) Close-up of tip mounted on a fine scanning in close proximity to sample plate.

### 4.3 Ultra High vacuum Low-Temperature Scanning Tunneling Microscope (UHV LT-STM)

All the research detailed in this thesis was conducted using the UHV LT-STM manufactured by Omicron (now ScientaOmicron) Nanotechnology GmbH. This system allows scanning tunneling microscopy (STM) measurements at three different temperatures: 4.2 K (liquid helium), 77 K (liquid nitrogen), and 300 K (room temperature). The STM is maintained under ultra-high vacuum conditions, attained through a sequence of vacuum pumps. The combination of a rotary pump, turbomolecular pump, and ion pump helps to establish these stringent conditions, reaching a pressure as low as  $10^{-11}$  mbar. The system configuration is depicted in figure 4.8. It comprises two sections: the main LT-STM chamber on the left in figure 4.7 for conducting measurements and a preparation chamber on the right for substrate preparation. The STM's cooling mechanism involves thermal contact with a bath cryostat, enabling simultaneous cooling of both the tip and the sample. This ensures that the tip and sample maintain identical temperatures during measurements, reducing thermal noise. Maintaining a very low tip temperature is particularly advantageous for obtaining stable STM images, as it minimizes the thermal diffusion of the apex atom. Additionally, the system can sustain a temperature of 4 K for approximately 60 hours with a single filling liquid helium (LHe) and 77 K for approximately 72 hours with liquid nitrogen ( $\text{LN}_2$ ), facilitating uninterrupted long-term experiments.

To get a clear understanding of the UHV LT-STM setup, refer to figure 4.9. The cryostat comprises two concentric dewars, illustrated in the figure. The outer one holds  $\text{LN}_2$ , while the inner dewar accommodates  $\text{LN}_2$  or LHe filling. Inset in the figure 4.8(a) are the liquid inlet, gas outlet, and the LHe sensor. The STM scanning head is situated at the bottom of the cryostat, directly linked to the inner LHe dewar. When the inner dewar is filled with LHe alone, the STM maintains a temperature of 4.2 K. However, if both the inner and outer dewars contain  $\text{LN}_2$ , the temperature is 77 K. The outer dewar is always filled with  $\text{LN}_2$  and acts as a thermal shield for the inner dewar. A low-temperature sensor at the STM stage that measures the temperature. In the diagram, the STM's position is indicated. An external CCD camera enables the observation of the STM tip and sample on a screen by focusing through one of the viewports.

The STM scanning stage is adjustable using the knob atop the cryostat. It can be lifted to touch the LHe dewar directly for cooling purposes. During tunneling



measurements, the stage is released to hang freely via three springs, effectively isolating it from external vibrations. The LT-STM, particularly the tip and sample unit, is further detailed in figure 4.8(c). The sample stage is supported by three suspension springs. To minimize mechanical vibrations and thermal loss, the entire stage must hang freely without contacting the LHe dewar or the side wall once the stage is cooled. Additional noise reduction is achieved through the eddy current damping unit. The diagram identifies the Scanner, tip holder reception, and sample holder unit. The sample faces downward while the tip approaches from below. The diagram delineates the STM sample plate, highlighting the maximum scanning area with a red square. An image of a tip holder and a tungsten tip is included for reference.

#### **4.4 Other characterization techniques**

Understanding the properties and behavior of materials relies heavily on characterization techniques. In addition to scanning tunneling microscopy (STM), various other methods play a role in this field. The following are additional techniques employed in this study:

##### **4.4.1 Transport Properties**

Material transport properties involve how different quantities move within a substance. These properties hold significance in unraveling the mechanisms through which materials conduct heat, electricity, and other forms of energy or mass. Studying these properties provides valuable insights into how material functions in terms of transmitting and distributing various quantities [85]. Various techniques are employed to measure the transport properties of materials. The choice of technique depends on the specific properties being investigated (e.g., thermal conductivity, electrical conductivity) and the characteristics of the material under consideration.

Electrical resistivity is the inverse of electrical conductivity and serves as an indicator of a material's resistance to the flow of electric current. The study of electrical resistivity as a function of temperature is particularly valuable in gaining insights into the phase transitions and the nature of different phases within a material. As temperature changes, the electrical resistivity can undergo variations, providing crucial information about the material's behavior at different temperature ranges. This relationship between electrical resistivity and temperature serves as a valuable tool for understanding how the material transitions between different phases and sheds light on the underlying physical transformations occurring within it.

In this thesis, the utilization of electrical resistivity measurements is applied to unravel the anomalous resistivity peak, which is contingent on the growth temperature of  $\text{TiSe}_2$ . The emergence of this peak is attributed to the charge density wave phase transition, and its manifestation depends on the concentration of  $Ti$  intercalants. The suppression of the peak signifies a high concentration of  $Ti$  atoms.

#### 4.4.2 Raman Spectroscopy

Raman spectroscopy is a powerful tool in materials science. The technique is named after Sir C.V. Raman, who won the Nobel Prize in Physics in 1930 for the discovery of the Raman effect [86]. It involves the interaction of monochromatic light with a sample, typically a laser, and the subsequent analysis of the scattered light. The scattered light undergoes a frequency shift, known as the Raman shift, which is caused by the inelastic scattering of photons. The Raman effect occurs when incident photons interact with molecular vibrations, rotations, and other low-frequency modes in a sample. Most of the scattered light retains the energy of the incident photons (Rayleigh scattering), but a small fraction of the scattered light undergoes a change in energy due to interactions with the sample's structure. This energy shift is characteristic of the vibrational and rotational modes of the molecules in the sample. Raman spectroscopy provides valuable information about the chemical composition, structure, and other properties of a material. It is non-destructive, meaning it doesn't alter the sample during analysis.

Raman spectroscopy is widely used for strain analysis in materials. The technique is particularly valuable for studying the structural and vibrational changes in a material induced by mechanical strain or stress. When a material experiences strain, the interatomic distances and bond angles may change, leading to alterations in vibrational frequencies. Raman spectroscopy can detect these changes in the form of shifts in the Raman peaks. The shift in the Raman peak positions provides information about the strain-induced modifications in the material's lattice structure.

In this thesis, Raman spectroscopy was employed as a powerful analytical tool to comprehensively investigate the induced strain in  $\text{NbSe}_2$ , providing valuable insights into the vibrational and structural changes of this material under varying mechanical conditions.

#### 4.4.3 Electron Backscatter Diffraction (EBSD)

Electron diffraction and Electron Backscatter Diffraction (EBSD) are techniques used in materials science and condensed matter physics to study the crystal-



lographic structure of materials at the micro- and nanoscale. Both techniques utilize the wave nature of electrons, providing valuable information about the arrangement of atoms in a material. In electron diffraction, a beam of electrons is directed onto a crystal. The interaction of electrons with the crystal lattice results in diffraction patterns, similar to X-ray diffraction patterns. Electron diffraction provides information about the crystal structure, lattice spacing, and orientation of the crystal planes in the material.

Electron Backscatter Diffraction (EBSD) is a scanning electron microscopy (SEM) technique that utilizes the backscattered electrons to obtain crystallographic information. When electrons from the SEM beam interact with the crystal lattice, they undergo elastic scattering and can be used to determine crystallographic orientation [87]. In EBSD, an SEM is used along with a specialized detector to collect backscattered electrons. A phosphor screen or semiconductor detector captures the diffraction pattern formed by the backscattered electrons. It provides information about crystal orientation, phase identification, grain boundaries, and microstructural features at the micrometer scale. EBSD allows for the analysis of bulk materials without the need for thin sections. It provides high spatial resolution and is capable of mapping large areas.

The Electron Backscatter Diffraction (EBSD) is used to study strain in NbSe<sub>2</sub> at a smaller scale and its local variation.

## Chapter 5

### 1T-TiSe<sub>2</sub>: CHARGE DENSITY WAVES, EXCITONS AND DEFECTS

*"In the material sciences, these are and have been,  
and are most surely likely to continue to be heroic  
days."*

— J. Robert Oppenheimer

#### 5.1 Overview of properties

Transition metal dichalcogenides (TMDC) are versatile materials that exhibit phenomena like strongly correlated phases to multifaceted tunable properties for applications in flexible electronics, optoelectronics, spintronics, and energy harvesting [88–91]. 1T-TiSe<sub>2</sub> is a standout among TMDC due to its remarkable characteristics. It is known for its unique properties, such as its ability to undergo a charge density wave (CDW) transition, making it a fascinating material for exploring unconventional electronic behaviors. This compound also exhibits strong correlations between its electronic and structural properties, contributing to its significance in the realm of condensed matter physics. Its distinct behavior underlines its potential in various applications, from novel electronic devices to fundamental studies in quantum phenomena.

##### 5.1.1 Structural properties

1T-TiSe<sub>2</sub> crystal is a stack of monolayers bonded by van der Waals interaction. Each monolayer consists of titanium (*Ti*) atoms sandwiched between two sheets of selenium (*Se*) atoms (Fig.1(a)). Each *Ti* atom is surrounded by six *Se* atoms in octahedral coordination, as shown in figure 5.1. The hexagonal Bravais lattice of 1T-TiSe<sub>2</sub> has a space group  $P\bar{3}m1$  (*no.*164,  $D_{3d}^3$ ). The first Brillouin zone (BZ) is hexagonal with three high-symmetry points  $\Gamma, M$ , and  $K$ , as illustrated in figure 5.2(a). The 3*d* and 4*s* valence electrons from Ti atoms transfer to the 4*p* orbitals of the Se atoms, forming ionic bonding in such a way that the valence and conduction bands mainly come from Se 4*p* and Ti 3*d* orbitals respectively.

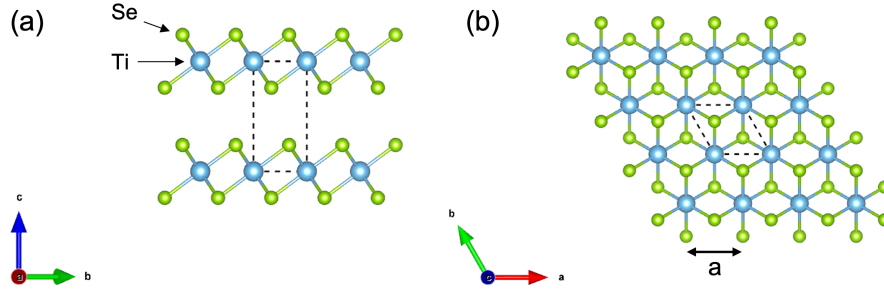


Figure 5.1: 1T-TiSe<sub>2</sub> lattice (a) As viewed along the  $a$ -axis,  $Ti$  atoms are blue and  $Se$  atoms are in green (b) viewed along the  $c$ -axis. A unit cell is drawn with a dotted line.

### 5.1.2 Electronic properties

1T-TiSe<sub>2</sub> (henceforth TiSe<sub>2</sub> in short) is a semimetal with a small indirect bandgap [92]. It has a semiconductor-like electronic structure near the Fermi energy, but its valence and conduction bands overlap slightly through an indirect gap. However, Angle-resolved photoemission spectroscopy (ARPES) experiments were inconclusive about whether the system is a semimetal with a small band overlap [93] or a semiconductor with a small indirect band gap [94]. This difficulty arises from the extremely small occupation of the conduction band in the normal state, with the fact that the transition takes place at very high temperatures to allow the necessary resolution in the ARPES spectra. According to *ab initio* density functional theory (DFT) band calculations, the TiSe<sub>2</sub> is a semimetal with an indirect band with valence band maxima near the  $\Gamma$  point of the Brillouin zone (BZ) and conduction band minimum near the  $M$  point (for bulk  $L$  point can be projected in a plane to  $M$  point) [95, 96]. Figure 5.2(b) a visual representation illustrating the Fermi surface. It displays an electron pocket located near the  $M$  point alongside a hole pocket positioned around the  $\Gamma$  point.

At temperature  $T_{CDW} \sim 200K$  TiSe<sub>2</sub> undergoes a second-order phase transition to the charge density wave (CDW) phase [97]. Charge density wave is a many-body, correlated electron phenomenon where a periodic distortion modulates electron density. CDW, depending on the ratio of their wavelength and lattice parameters, are classified as commensurate (CCDW), nearly commensurate (NCCDW), or incommensurate (ICDW) [38, 98]. Pristine 1T-TiSe<sub>2</sub> shows CCDW order below 200K [97]. Charge carrier doping via electrochemical ionic gating in TiSe<sub>2</sub> leads to suppression of CCDW, giving way to the emergence of ICDW and the superconducting phase at lower temperature [99]. The CDW transition temperature

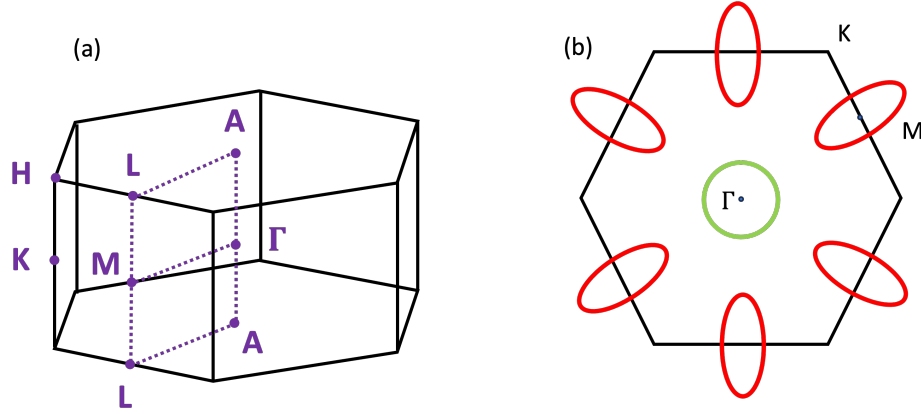


Figure 5.2: (a) Brillouin zone (BZ) of undistorted TiSe<sub>2</sub> lattice with high symmetry point. After  $2 \times 2$  modulation, BZ reduces to a smaller hexagon. (b) Fermi Contours (Energy map near  $E_F$ ) in the plane parallel to  $\Gamma - M - K$  plane.

drops significantly for TiSe<sub>2</sub> doped with copper. Superconductivity emerges in Cu<sub>x</sub>TiSe<sub>2</sub> for  $x \sim 0.04$ , maxima of superconducting transition temperature reaches at  $x \sim 0.08$  acquiring a dome shape in the phase diagram [100]. ICDW phase coexists with the superconducting phase under applied pressure [101, 102] and copper doping [103]. In the above-mentioned experiments, the CDW phase transitions were identified through transport measurements, i.e., resistivity versus temperature curve. Close to the onset of superconductivity, the CDW undergoes a transition to an incommensurate state and continues to persist even at significantly high doping levels. Remarkably, the entire region exhibiting superconductivity falls within this incommensurate CDW (ICDW) phase. This unique behavior positions TiSe<sub>2</sub> as an ideal platform for investigating the coexistence of CDW and superconductivity, presenting a compelling opportunity to explore the interplay between these multiple orders in a single material system.

## 5.2 CDW in 1T-TiSe<sub>2</sub>

The formation mechanism of CDW in TiSe<sub>2</sub> is still debatable. At  $T_c \approx 200$  K, the system was observed to undergo a second-order phase transition to a commensurate CDW phase. In the triangular hexagonal lattice of TiSe<sub>2</sub>, the CDW modulation can be described by three wavevectors in a plane oriented at an angle of  $120^\circ$  ( $C_3$  rotations) with respect to each other. A linear combination of three wavevectors ( $\mathbf{Q}'_1$ ,  $\mathbf{Q}'_2$  and  $\mathbf{Q}'_3$ ) characterizes the general charge density modulation:

$$\rho(\mathbf{r}) = \rho_0 + \rho_{\mathbf{Q}'_1}(\mathbf{r}) + \rho_{\mathbf{Q}'_2}(\mathbf{r}) + \rho_{\mathbf{Q}'_3}(\mathbf{r}) \quad (5.1)$$

This CDW state is known as the triple- $\mathbf{q}$  phase. In bulk crystal, CDW has  $2 \times 2 \times 2$  modulation with periodic lattice distortion, represented by wavevector  $\mathbf{Q}'_1$  along  $\Gamma L$  direction with other vectors  $\mathbf{Q}'_2, \mathbf{Q}'_3$  related by  $C_3$  rotation.

As there is, no evidence for Fermi surface nesting and the existence of periodic lattice distortion (PLD) points at either strong electron-phonon coupling (EPC) or electron-electron interaction mediating CDW transition. So there are two favored mechanisms: band type Jahn-Teller effect (related to EPC) [104] and excitonic insulator phase (electronic correlation) [105]. A Jahn-Teller-like mechanism is independent of free carrier concentration. *Ab initio* calculations, taking EPC into account, show ion-ion interaction can lead to softening of  $L_1^-(1)$  phonon [106]. In the Jahn-Teller effect, the lattice spontaneously distorts to lift the degeneracy and reach the lower symmetry state because of the interaction between phonons and degenerate electron states. The pressure dependence of CDW transition temperature and the nature of the superconducting dome also point toward strong EPC [107]. But it was soon challenged [108] and pointed out that the results in the calculations are sensitive to the electronic correlations taken into account [95]. On the other hand, due to the small overlap between the electron and hole pockets separated in the normal state band structure, the Coulomb interaction is expected to be poorly screened. This leads to the formation of excitons by an electron from a conduction band and holes in the valence band.

### 5.2.1 Excitonic nature of CDW

Excitons are bound states of electrons and holes. Excitons are bosons as their overall spin is zero or an integer. Bosons tend to form a Bose-Einstein condensate under favorable conditions [109–112]. The small negative band overlap in the  $\text{TiSe}_2$  system tends to favor the spontaneous exciton condensation [105, 113]. This leads to the opening of a band gap and the formation of an excitonic insulator phase in  $\text{TiSe}_2$ . The excitonic insulator phase can emerge within a narrow bandgap semiconductor or semimetal, where excitons spontaneously form due to a low carrier density that fails to screen the attractive Coulomb interaction between electrons and holes. This instability often presents as a CDW phase. The crucial debate lies in understanding whether phonons play any role in CDW formation, or are they just spectators. Or does the electron-phonon coupling (EPC) play a dominant role? As theoretical models suggest, we need to consider EPC to calculate acoustic phonon energy accurately. This makes it harder to disentangle the exact mechanism of CDW formation.

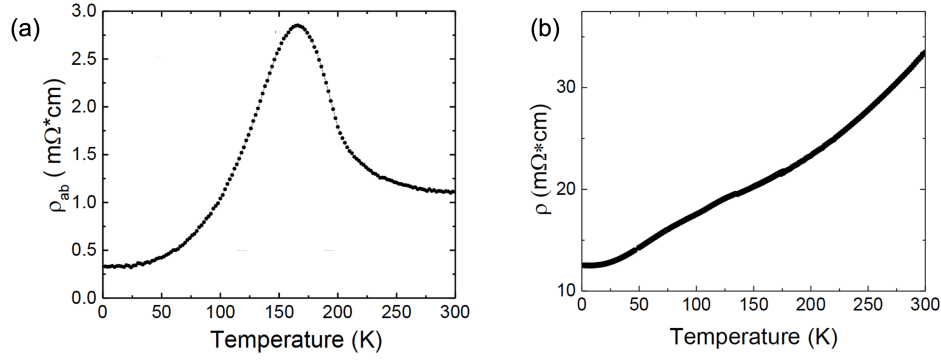


Figure 5.3: (a) Resistivity of TiSe<sub>2</sub> sample grown at lower temperature. An anomalous resistivity peak can be identified in the normalized resistivity curve. (b) For TiSe<sub>2</sub> grown at a higher temperature, the anomalous resistivity peak is suppressed.

Given this complexity, our proposal uses defects within the sample to investigate CDW formation and manipulate its nature. By leveraging these defects, we aim to gain insights into the mechanisms underlying CDW formation and potentially modulate its characteristics. This approach offers a promising avenue to disentangle the role of various factors in driving CDW formation amidst the interplay of excitonic interactions, electron-phonon coupling, and other contributing elements.

### 5.3 Intrinsic defects in 1T-TiSe<sub>2</sub>

TiSe<sub>2</sub> belongs to the category of nonstoichiometric compounds. This means that its composition doesn't strictly adhere to a fixed ratio between the constituent elements, titanium (Ti) and selenium (Se). The deviations from a perfect stoichiometric ratio occur due to variations in the crystal growth process. The concentration of *Ti* in a crystal depends on the temperature at which the crystal is grown. A commonly used method for TMDC crystal growth is chemical vapor transport (CVT). Higher growth temperature generates higher chalcogen pressure, resulting in a crystal with intercalation of *Ti* metal atoms [114]. An indirect inference of the presence of excess *Ti* can be carried out through temperature-dependent resistivity measurements. 1T-TiSe<sub>2</sub> shows an anomalous resistivity peak near the CDW phase transition (see figure 5.3(a)). As the growth temperature increases, the crystal becomes more metallic due to excess *Ti*, suppressing the anomalous resistivity peak [97, 115] (see figure 5.3(b)). 1T-TiSe<sub>2</sub> shows a small indirect band gap above the transition temperature  $T_{CDW} \sim 200\text{K}$  [116, 117]. Experimental evidence suggests excitonic insulator mechanism [93, 95, 118–121]. Theoretical investigations suggest that excitonic condensation can be either superfluid [122] or an insulator [123]. Sup-

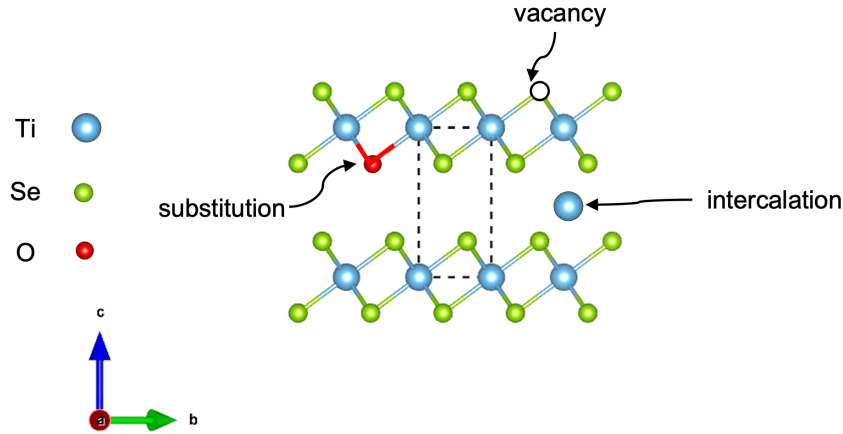


Figure 5.4: Schematics of types of intrinsic defects in  $\text{TiSe}_2$

pression of CDW results via electrostatic gating [99] or with Cu intercalation, [100] or Pd intercalation [124].  $\text{TiSe}_2$  becomes insulating after Pt doping [125]. These experimental and theoretical studies imply that doping affects the nature of CDW and electronic properties of  $1T\text{-TiSe}_2$ . A correlated phenomenon, like CDW, is sensitive to defects. In our study, we employed low-temperature STM to specifically examine how the CDW behaves at the atomic scale in the presence of intrinsic defects. Our primary focus was on understanding the correlation between the conditions under which crystals were grown and the presence of these intrinsic defects. By analyzing crystals synthesized through various routes, we aimed to explore the relationship between growth conditions and the formation of intrinsic defects, shedding light on how different synthesis methods might influence the nature and prevalence of these defects within the crystal structure. We referred to them as sample A (crystal was grown by chemical vapor transport (CVT) using iodine ( $\text{I}_2$ )) and sample B (crystal was grown using  $\text{Se}$  as self-flux) in the subsequent discussion.

The crystal cleaves along (001) planes exposed  $\text{Se}$  atoms in a hexagonal symmetric pattern. In constant current topography images, STM tip probes the topmost  $\text{Se}$  atoms [126, 127]. The tunneling current is mainly due to the contribution from the  $4p$  orbital of  $\text{Se}$  atoms. The preferred site for  $\text{Ti}$  atom intercalation,  $\text{O}$  substitution site schematically shown in figure 5.5. Iodine is used as a transport agent in a CVT crystal growth method. Substitution of  $\text{Se}$  atom by  $\text{I}$  is another defect commonly found in CVT-grown samples.  $\text{I}$  substitution occupies same sites as  $\text{O}$  substitution. Defects in the STM topography image of samples are in figure 5.5 show up as localized bright regions.



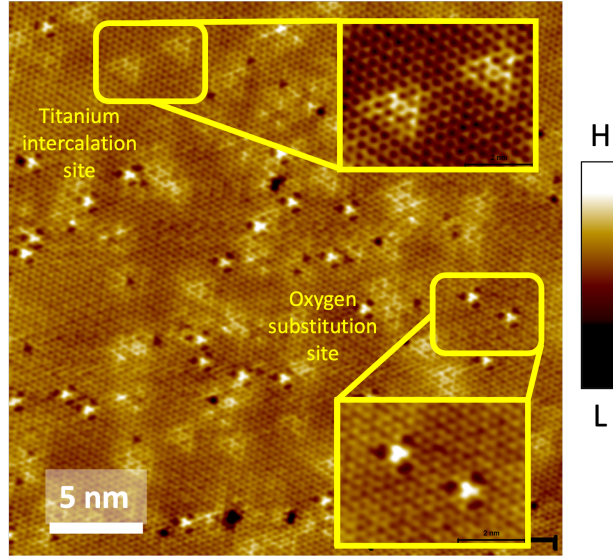


Figure 5.5: Intrinsic defects in  $\text{TiSe}_2$  a constant current STM image of  $30\text{nm} \times 30\text{nm}$  area of sample A. Enlarged view of  $Ti$  intercalation sites and  $O$  substitution sites are in yellow rounded rectangle inset in sample A.  $V_{bias} = 300\text{ mV}$  and  $I_{set} = 300\text{ pA}$  at base temperature of  $T = 77\text{ K}$ . This image lacks any visible CDW modulation.

Voltage-dependent imaging in STM involves capturing images of a sample surface while varying the voltage applied between the STM tip and the sample. This technique allows for the observation of changes in the sample's electronic structure and surface properties at different voltages. By altering the bias voltage, STM can reveal voltage-induced modifications in surface topography, electronic states, or the presence of specific features like defects. In our voltage-dependent imaging, we aimed to comprehend intrinsic defects behavior. Interestingly, vacancy defects were easily discernible and easily located at both positive and negative bias voltages. This suggests their consistent visibility and stability across varying electrical conditions. At negative biases, electronic states exhibit localization for the  $Ti$  intercalant, whereas at positive biases, they adopt their characteristic triangular appearance. This distinctive change in behavior depending on the polarity of the bias showcases the intriguing duality of its electronic states. Locating  $O$  defects proves challenging at negative bias, yet they become visible and identifiable at positive bias settings. This polarity-dependent visibility supports the electronegative character of oxygen. In the Fast Fourier Transform (FFT) analysis of voltage dependent STM images (insets in Figure 5.6), Charge Density Wave (CDW) signal shows notable weakening at higher biases or when moving away from the Fermi energy. This weakening occurs due to the increased contribution of other electronic states,



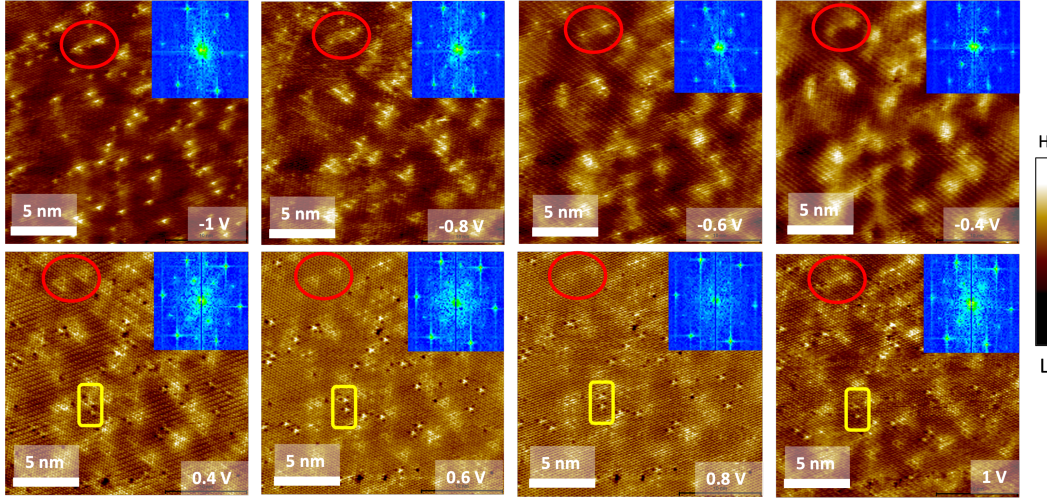


Figure 5.6: Voltage dependent imaging of intrinsic defects in  $\text{TiSe}_2$  at  $T = 77$  K. The red circles highlight  $Ti$  defects, exhibiting variations at different biases. Meanwhile, the yellow squares indicate  $O$  defects, visible only at positive bias, proving challenging to discern at negative biases. The insets show the FFT of each image. Notably, the intensity of the CDW peaks diminishes at higher biases.

overshadowing the distinctive CDW signal. As the bias voltage moves away from the Fermi level, states beyond the CDW start to dominate the signal, thereby reducing the apparent intensity or clarity of the CDW peaks in the FFT analysis.

STM with  $dI/dV$  spectroscopy technique allows for the investigation of local density of states (LDOS) on a surface. It helps identify energy levels, revealing details about the electronic structure, the presence of quantum states, and the energy distribution of surface states or defects. This method is particularly useful in studying the behavior of materials at the atomic scale, providing insights into their electronic behavior and properties. Point spectroscopy serves as a tool to comprehend the behavior of intrinsic defects. In the Figure 5.7, point spectra obtained at  $O$  defects reveal the addition of states above the Fermi energy without impacting the CDW gap. Conversely, spectra gathered at vacancies exhibit no observable alterations in the measured states. This distinction highlights how  $O$  defects introduce additional electronic states above the Fermi energy, yet the CDW gap remains unaffected, while vacancies do not elicit any discernible changes in the spectra.

#### 5.4 Interplay between defects and CDW

The amplified atomic-scale image of the defect, depicted in Figure 5.5, exhibits  $Ti$  intercalation sites. STM primarily investigates defects located within or near the

surface layer of the material. Titanium (Ti) atoms intercalate the space between the layers of  $\text{TiSe}_2$ , the van der Waals gap. Since STM is primarily surface-sensitive, it detects electronic states solely from the top layer of the crystal. The detection of the imprint left by the intercalated Ti atoms is confined to the layer just beneath the uppermost monolayer. The bias voltage and tunneling current used in operation exclusively probe the topmost layer and specifically the  $p$  orbitals of selenium (Se) atoms in  $\text{TiSe}_2$ . At lower bias voltages, the tunneling current predominantly originates from near-surface regions, allowing for the imaging of surface features. Higher bias voltages, on the other hand, enable tunneling from deeper within the material, providing information about subsurface structures or electronic states below the surface. Therefore, the choice of bias voltage in STM experiments directly influences the depth from which the tunneling current predominantly originates, affecting the spatial resolution and the specific layers or features that are probed and imaged. Within the van der Waals gap, intercalated atoms tend to occupy either octahedral or tetrahedral sites. In the case of  $Ti$ , the octahedral sites are preferred due to their higher coordination number, and the spacing between adjacent octahedral sites surpasses that of tetrahedral sites, as discussed by Fan et al. [128]. The distinctive appearance of intercalated  $Ti$  sites is attributable to alterations in the local density of states, as noted by May et al. [129]. These defects manifest as bright features in filled-state STM images, observed specifically at negative bias voltages.

There were defects with a strongly localized density of states (DOS) at the topmost  $Se$  atoms surrounded by depleted regions in empty-states STM images can be identified with oxygen ( $O$ ) substitution of the  $Se$  atom in the lower layer.  $I$  substitution of  $Se$  in lower sites are hard to recognize as they appear very faint compared to  $O$  sites [127]. Substitution of  $Se$  by  $O$  or  $I$  on the topmost layer is not favored energetically [127]. Oxygen, present as an impurity in iodine and selenium precursor during growth, acts as a native dopant. Sample A has been observed to possess more  $Ti$  intercalation sites than sample B Figure 5.8. The average number of intercalation sites was counted using STM images in different regions of both samples. Employing this method, we found that the count of  $Ti$  intercalation sites per unit cell for sample A is 0.6% compared to 0.2% sites per unit cell of sample B. This observation supports the dependence of  $Ti$  intercalation sites' concentration on sample growth conditions [97]. In samples grown via chemical vapor transport (CVT), there tends to be a higher presence of oxygen ( $O$ ) substitution. This occurrence often arises from the initial presence of oxygen in the precursor

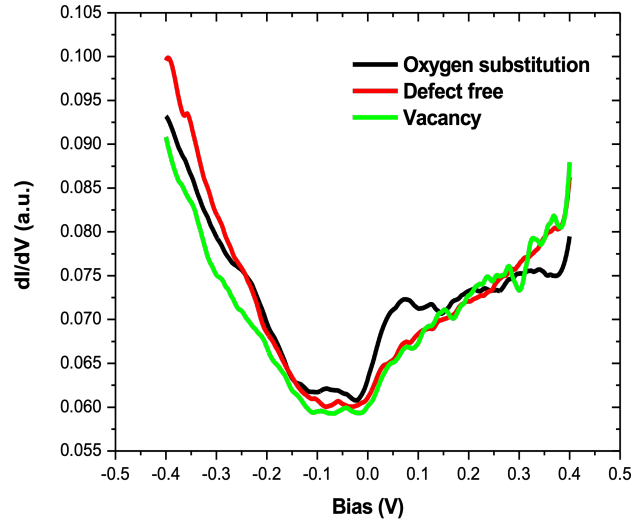


Figure 5.7:  $dI/dV$  spectra of intrinsic defects in  $\text{TiSe}_2$ . All the data presented in the figure has been obtained at  $T = 77$  K.

materials used during the growth process, where oxygen acts as an impurity.

Intercalation and substitution change the material carrier concentration, changing the material's electronic properties. Correlated states like CDW are sensitive to external factors like mechanical stress, external pressure, and carrier concentration. Point defects can affect CDW by changing carrier density locally and introducing localized distortions in lattice [114]. STM topography images were obtained at different bias voltages, spatially resolving the CDW. figure 5.8(a) and (d) show STM images of samples A and B with different concentrations of  $Ti$  intercalation and  $O$  substitution densities. The real space topography shows the clear  $2 \times 2$  superlattice of CDW. Figure 5.8(b) is an enlarged image with atomic resolution showing CDW forming a superstructure (marked by yellow circles). Fourier transforms (FT) of topography images (Figure 5.8(a) and (d)) yield contributions of lattice and CDW superlattice as six-fold symmetry peaks. Peaks in FT images affirm that the wavelength of CDW is twice the lattice spacing (first-order Bragg peak).

To reduce background noise and understand the spatial variation of CDW amplitude, we performed an inverse transform of CDW FT peaks. Inverse Fourier transforms (IFT) image clearly shows diminishing CDW amplitudes in the presence of  $Ti$  defects in Figure 5.8(c) and (e). In the presence of a large number of defects, CDW-modulated regions can be easily visually identified from IFT images (Figure

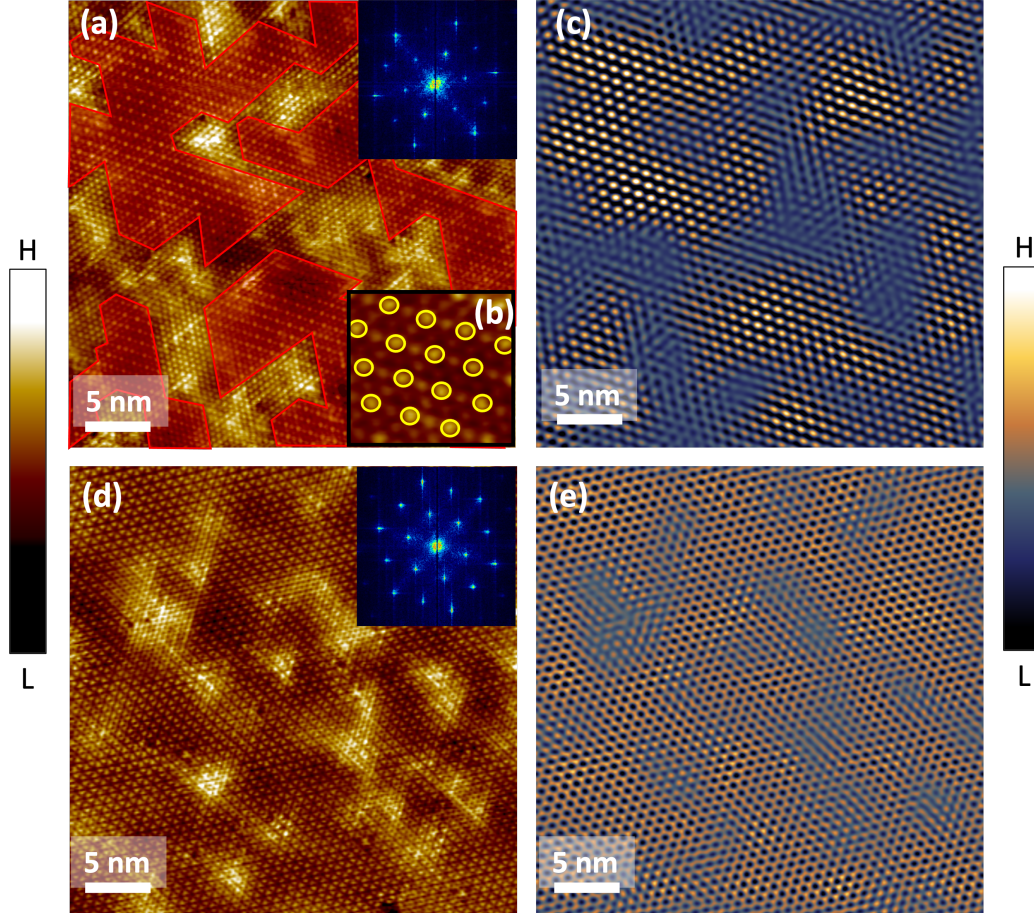


Figure 5.8: (a) A constant current STM image of 30 nm X 30 nm area of sample A,  $V_{bias} = -400$  mV  $I_{set} = 300$  pA. Areas marked by red are CDW domains, separated by non-modulated regions induced by *Ti* intercalation sites. Fourier transform of topography image in the right upper corner. (b) An enlarged image shows a  $2 \times 2$  superstructure with CDW peaks marked by yellow circles. (c) Selective inverse Fourier transform of CDW peaks in (a). (d) A constant current STM image of 30 nm X 30 nm area of sample B (grown by flux method),  $V_{bias} = -300$  mV  $I_{set} = 400$  pA, with Fourier transform of topography. (e) Selective inverse Fourier transform of CDW peaks. There is no suppression of CDW amplitude or formation of domains. All the data presented in the figure has been obtained at  $T = 77$  K



5.8(c)). In  $\text{TiSe}_2$  with more  $Ti$  intercalation density, the presence of defects forms domains of CDW.  $2 \times 2$  superstructure of CDW changes to  $1 \times 1$  modulation near intercalation sites, which forms the boundaries of CDW modulated region. Also, the IFT image is used as a guide to locate these boundaries. Different CDW modulated regions are marked in red in Figure 5.8(a). CDW-modulated regions separated by boundaries were not observed in Figure 5.8(d) containing fewer intercalation sites. IFT in Figure 5.8(e) shows the reduced amplitude of CDW in the presence of intercalation sites but no formation of separate regions.  $\text{TiSe}_2$  thin flakes are reported to oxidize quickly in atmospheric conditions and disrupt the CDW phase [130]. The oxidation of  $1T\text{-TiSe}_2$  was minimized by cleaving the crystals in our UHV sample preparation chamber (refer to section II. METHODS).  $O$  and  $I$  substitution sites increase the local density of states in the unoccupied states away from the Fermi energy [127]. The CDW gap near the Fermi level remains unaffected by  $O$  or  $I$  substitution.

Metal intercalation of  $\text{TiSe}_2$  at certain doping concentrations shows a phase shift of CDW modulation across the domain walls [118, 131].  $Cu$  intercalation in  $1T\text{-TiSe}_2$  results in an incommensurate CDW phase with localized commensurate CDW separated by domain walls at critical doping concentration [132].  $Ti$ , like  $Cu$ , is electropositive and suppresses the CDW phase.  $Cu$  intercalation into van der Waals gap of  $\text{TiSe}_2$  was stabilized by transfer of charge from  $Cu$  to  $Se$  atoms in the adjacent layers [133]. Similarly, the  $Ti$  intercalant gets stabilized by charge transfer. A significant overlap between the atomic orbitals of intercalated  $Ti$  and  $Se$  atoms in the layer results in the intercalant sites' peculiar appearance in the STM images. To better understand the phase shift of CDW across domain boundaries, IFT of both lattice Bragg peaks and CDW peaks of Figure 5.8(a) were obtained, as shown in Figure 5.9(a). A line section of electron density indicates the suppression of CDW modulation at the boundary (Figure 5.9(b)).

Interestingly, we observed no phase shift in the CDW modulation across the boundaries. We can infer that the increased concentration of  $Ti$  intercalation leads to the disruption of CDW and reduces long-range order to short-range [134]. The distinction between the mechanisms driving CDW formation—strong electron-phonon coupling versus electron-electron interaction—is important, considering the observed phase insensitivity. The phase insensitivity might serve as a distinguishing factor between the impact of electron-phonon coupling and electron-electron interaction on CDW formation. If strong electron-phonon coupling is the leading

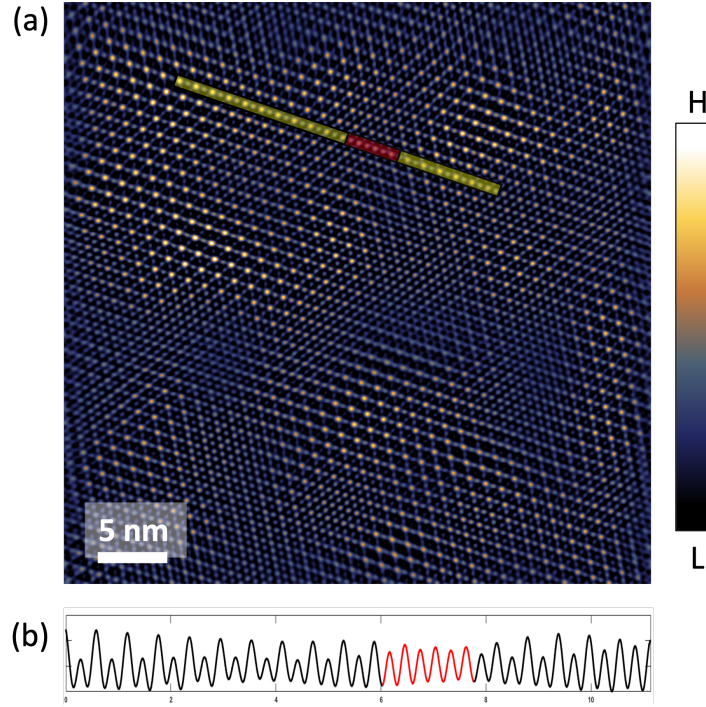


Figure 5.9: (a) Inverse Fourier transform the image of Bragg peaks and CDW peaks of STM image shown in figure 5.8 of sample A. Line sections passing through domain boundary (marked by red region) plotted in (b) Red part of line section indicates no CDW modulation as indicated by the reduced amplitude in red region of line section. No phase shift was observed across the domain wall.

mechanism for CDW formation, local alterations in electronic density induced by Ti defects might disrupt the phase coherence by inducing phase slips. On the other hand, the robustness of the phase coherence of excitonic bound pairs within condensate might endure and remain unaffected by these local changes in electronic density. The behavior of CDW in the presence of intercalated *Ti* provides a fundamental distinction between the formation mechanisms, as suggested by the phase insensitivity.

The electropositive nature of *Ti* intercalation defect and formation of CDW modulated regions and non-modulated boundaries in excess *Ti* intercalation may provide some insight into the mechanism of the formation of CDW. Considering the above-mentioned results, we offer a hypothesis for the suppression of CDW by *Ti* intercalation. Semimetals or small gap semiconductors at lower temperatures can undergo CDW phase transition by excitonic condensation mechanism. For  $\text{TiSe}_2$ , a small carrier density and a weakly screened Coulomb interaction can result in exciton formation. Excitons are formed from electrons in the pocket at the *M* (or *L*)

point in the Brillouin zone (BZ) and holes from the pocket at  $\Gamma$  point in the energy band structure of  $1T$ -TiSe<sub>2</sub>. Being a composite boson, it undergoes condensation at  $T_{CDW} \sim 200K$  as the number of excitons increases. Excitonic condensation leads to a periodic modulation of charge density, a CDW state. The extent to which CDW are modulated in  $1T$ -TiSe<sub>2</sub> is intercalation dependent. If we assume excitonic condensation as the mechanism of the CDW state in TiSe<sub>2</sub>, the suppression of CDW and formation of domain boundaries can be explained by the electropositive nature of *Ti* intercalation. By altering the electronic structure or the local environment around the Se atoms, this intercalation might interfere with the interactions that lead to CDW formation.

First-principles energy band calculations have demonstrated the origin of specific electronic pockets within the Brillouin Zone in TiSe<sub>2</sub>. It has been established that the electron pocket at the *M* point primarily arises from *Ti* 3*d* states (Three *t*<sub>2g</sub> derived conduction bands), whereas the hole pockets at  $\Gamma$  derive from *Se* 2*p* states (two *p* valence bands) that are hybridized with *Ti* 3*d* states [135]. Moreover, the density of states (DOS) at the Fermi energy is predominantly contributed by *Ti* states, constituting over half of the total DOS, with the remaining portion attributed to *Se* [133]. The electropositive nature of *Ti* intercalation leads to the introduction of additional electrons into the system. These added electrons predominantly occupy *Ti*-derived states around the Fermi level due to the higher density of states associated with *Ti*. Consequently, the inclusion of *Ti* through intercalation results in an augmentation of electronic states specifically around the Fermi energy. This augmentation significantly screens the Coulomb interaction between electrons and holes, thereby leading to the reduction in excitonic pairs and subsequent suppression of the charge density wave (CDW) in the material.

The characterization of the charge density wave (CDW) order was further advanced by computing the translational autocorrelation. This method allowed for the calculation of the CDW's autocorrelation length, offering insights into the intricate relationship between CDW and intercalant density. In our analysis, STM (Scanning Tunneling Microscopy) topographic images proved instrumental in identifying the non-modulated boundaries within CDW-modulated regions. This distinction was particularly evident in areas with a heightened concentration of defects, as depicted in Figure 5.8(a). Utilizing the correlation length provided a valuable means to assess the impact of intercalation on the CDW order. This measurement enabled the detection of disruptions in the CDW order that might not have been readily discernible

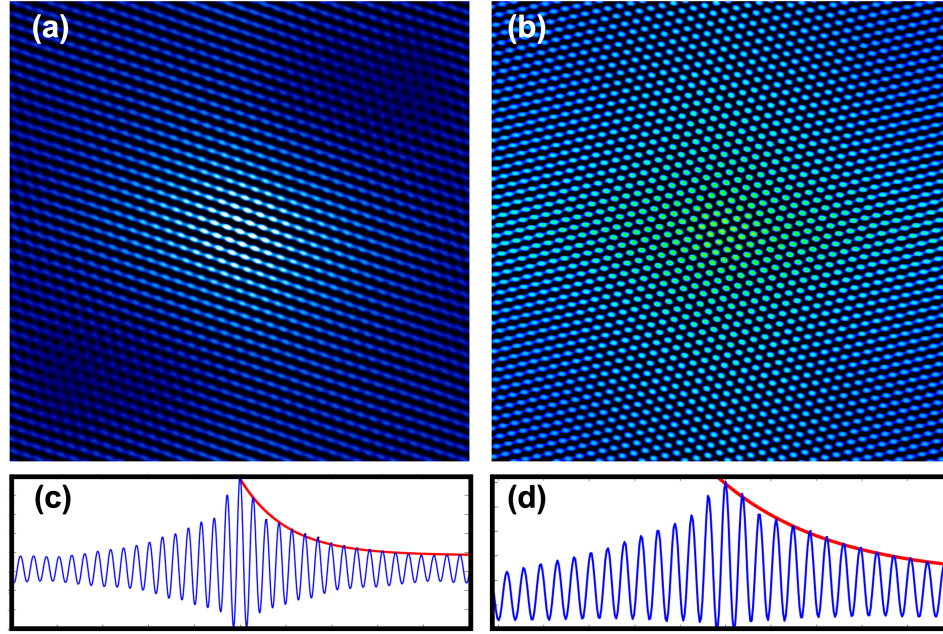


Figure 5.10: (a) Autocorrelation of  $30\text{nm} \times 30\text{nm}$  area of sample A, (b) Autocorrelation of  $30\text{nm} \times 30\text{nm}$  area of sample B, (c) and (d) Line section of autocorrelation of sample A and autocorrelation of sample B shown in along the CDW direction respectively, the red curve indicates the rate of decay of CDW amplitude as function of distance. The correlation length determined for image (a) of sample A is  $\xi = 2$  nm, while for image (b) of sample B,  $\xi = 7$  nm.

through visual examination of STM images alone. Specifically, the presence of intercalants was found to significantly disturb the CDW order, leading to a reduction in the translational correlation length. Consequently, the measurement of correlation length served as a sensitive indicator of alterations in the CDW order induced by the presence of intercalants.

The assessment of the CDW order involved multiple steps, including the selection of CDW peaks in the Fourier transform (FT) of topography images, and the subsequent application of an inverse Fourier transform (IFT). This resulted in the generation of an IFT image portraying CDW amplitudes as a function of position, as illustrated in Figure 5.10(a) and (b). Calculating autocorrelation on these IFT images provided a means to extract information regarding the translational autocorrelation length of the CDW. The autocorrelation length was then determined by analyzing the change in amplitude along line sections within the autocorrelation of the IFT images, employing the following formula [136].



$$A(x) = A_0 e^{-x/\xi} \cos(k_{\text{cdw}}x) + B_0 \quad (5.2)$$

Where  $A(x)$  is the amplitude,  $\xi$  is autocorrelation length,  $k_{\text{cdw}}$  wave vector of CDW along  $x$  direction,  $B_0$  is average random noise in autocorrelation obtained from IFT and  $A_0 = 1 - B_0$ . The finite correlation length is a consequence of the in-homogeneity and finite scanning area [136]. Autocorrelation of STM topography image of the area with more defects in Figure 5.8(a) is shown in Figure 5.10(a), and the area with less number of defects in Figure 5.8(d) is shown in Figure 5.10(b). A line section along the axis in the autocorrelation image, that is, the amplitude of CDW as a function of  $x$  was plotted. The autocorrelation length was calculated by a fitting curve to the amplitude decay rate in the line section. In Figure 5.10(c) and (d) blue curve is a line section along CDW direction, indicating its amplitude, and the red curve fitted using (5.2) shows the rate of change of CDW amplitude. The correlation length obtained from fitting indicates that the correlation length is smaller for images with more intercalant sites than those with fewer. This implies the long-range coherence of CDW has broken into small domains because of intercalation. A sharp decline of CDW amplitudes means a smaller correlation length, a sign of the reduced long-range order.

The correlation length of the CDW appears to correlate intricately with the concentration of  $Ti$  intercalation. This relationship is meticulously depicted in Figure 5.11, where a clear dependence of the correlation length on the density of  $Ti$  intercalation is demonstrated. The approach to comprehensively understand this relationship involved the capture of atomically resolved images, enabling the enumeration of  $Ti$  intercalation sites. Simultaneously, the CDW's correlation length was determined from the autocorrelation of the IFT images, as previously outlined. Comparing Samples A and B, it's evident that Sample B, characterized by a lower  $Ti$  intercalation concentration, exhibits a notably larger correlation length. This observation aligns with the overarching trend identified: a decrease in the correlation length of the CDW as the density of  $Ti$  intercalation increases. This trend strongly supports our earlier hypothesis regarding the excitonic origin of the CDW, particularly emphasizing its sensitivity to the electron-doping nature of the  $Ti$  intercalant. Considering the image sizes, we attained a maximum correlation length of approximately  $\xi \approx 7$  nm for a 20 nm image and low  $Ti$  defect density. Conversely, a smaller correlation length of around few nm was observed for a higher  $Ti$  intercalation concentration.

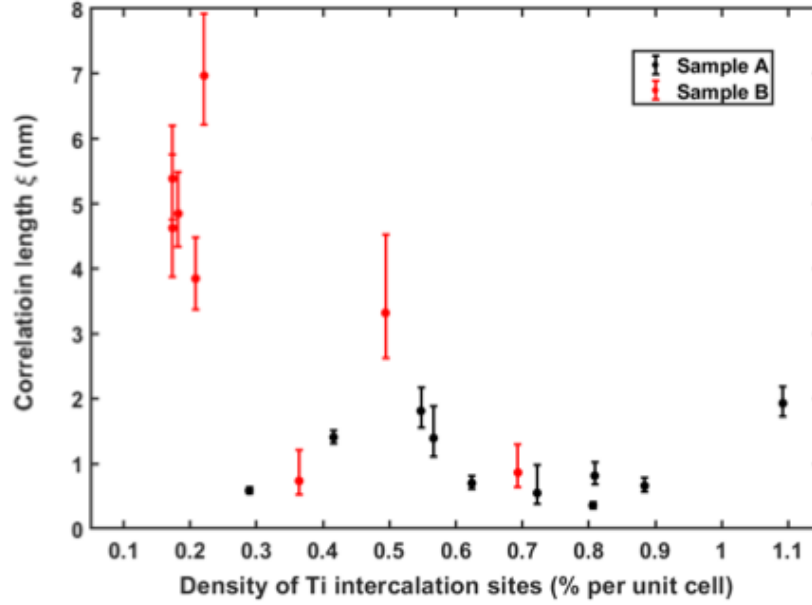


Figure 5.11: Correlation length obtained by fitting the CDW amplitudes for topography images of different  $Ti$  intercalation concentrations. Sample A contains more intercalation sites than sample B. (The average density of intercalation sites for sample A is 0.6% and for sample B is 0.2%.) The correlation length of CDWs in sample B seems to be higher than that of CDWs in sample A. All the data presented in the figure has been obtained at  $T = 77$  K

However, a nuanced feature emerges within the trend: a gradual increase in correlation length at a defect concentration of 0.3%, reaching a maximum at 0.5%, followed by a subsequent decrease. This intriguing pattern might be associated with the presence of inequivalent  $Ti$  defect sites resulting from CDW modulation, as indicated in [134]. We posit that these findings will stimulate further model building. Such a model could shed light on and help explain the underlying mechanisms governing this distinct pattern observed in the correlation length.

## 5.5 Conclusions

The study of defects at the atomic scale in  $1T$ - $TiSe_2$  crystals grown through different methods has revealed crucial insights. Specifically, the intercalation of  $Ti$  atoms within the van der Waals gap exerts a profound influence on the long-range order of the charge density wave (CDW). As the concentration of intercalated  $Ti$  atoms increases, the CDW structure undergoes a transformation, compelling the formation of distinct domains. Notably, these domain boundaries exhibit no phase shift.

A significant finding is the inverse relationship between the correlation length of the CDW and the density of intercalated  $Ti$  atoms. This observation underscores that the intercalation of  $Ti$  in  $1T\text{-TiSe}_2$  actively suppresses the CDW and facilitates the creation of domain boundaries. This suppression phenomenon aligns with the electron-doping nature of  $Ti$ , which leads to a reduction in the number of holes within the system.

Drawing from the excitonic condensation model, the reduction in hole concentration induced by intercalated  $Ti$  atoms plays a pivotal role. This reduction results in the depletion of excitonic bound states, directly influencing the suppression of the CDW. Consequently, the dependence observed between the correlation length and  $Ti$  intercalation strongly corroborates the excitonic condensation model underlying the formation of the CDW in  $1T\text{-TiSe}_2$ . This study serves as a compelling demonstration of this relationship and its alignment with the theoretical framework of excitonic condensation governing CDW formation in this material.

## *Chapter 6*

### 1T-TiSe<sub>2</sub>: CHIRAL NATURE OF CHARGE ORDERING

*"Who ordered that?"*

— Isidore I. Rabi

#### 6.1 Introduction to chirality

Parity, a fundamental symmetry in nature, involves transforming spatial coordinates by flipping their signs or reflecting them in a mirror (as shown in Figure 6.1). When an object's mirror image differs from itself, it's referred to as a chiral object. At a fundamental level, nature exhibits chirality, as demonstrated by the violation of parity in weak interactions [137, 138]. Chirality manifests across various scales, from the subatomic level with parity violation in weak interactions to the molecular realm with homochirality in biomolecules. Geometrical chirality arises from the arrangement of atoms or molecules within a crystalline lattice that lacks certain symmetry elements like mirror planes or inversion centers. As a result, the crystal itself is chiral, leading to distinct physical properties based on its handedness. In some materials, interactions between particles (such as electrons) can lead to a phase transition where the system spontaneously adopts a chiral state [139]. This phenomenon, known as chiral symmetry breaking, occurs when the material exhibits macroscopic chirality without the underlying molecular structure being inherently chiral. In topological materials, certain arrangements of atoms or electrons give rise to emergent phenomena with chiral properties. This can manifest in conducting edge states or surface states that display chirality due to the material's topological characteristics.

Understanding and manipulating chirality in condensed matter systems have implications in various fields such as electronics, photonics, and materials science. For instance, chirality can influence the behavior of light passing through certain materials (chiral optics) and affect the conductivity in electronic systems.

#### 6.2 Chirality and CDW

A charge density wave (CDW) refers to an ordered correlated state that disrupts translational symmetry within a material. It signifies a modulation in the

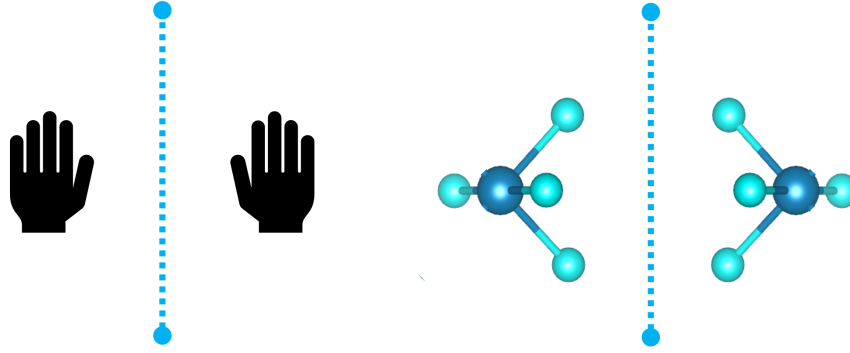


Figure 6.1: Mirror reflection of an object is not similar to itself then it is chiral.

electronic charge density, often corresponding to alterations in the spacing of the atomic lattice beneath it. Various energy-reducing interactions, such as Peierls transition (Fermi surface nesting instability) [4], the Jahn-Teller effect (orbital degeneracy lifting) [140] and excitonic insulator (bound states of electrons and holes) [105] contribute to the formation of CDWs, as extensively discussed in chapter 3. Generally characterized by a scalar order parameter, CDWs typically lack an inherent helical configuration. However, chiral patterns within charge order can emerge through the coupling of electronic density, orbital orientations, and lattice deformation [141]. The superposition of multi-directional CDWs within the same material either disrupts or restores additional symmetries [142]. Charge density wave exhibits chirality, it means that the modulation in the electron density pattern shows handedness or asymmetry. In other words, the charge density wave breaks the mirror symmetry, resulting in a distinct directionality or preference in its structure. A CDW in which the modulation direction of charge density and atomic displacements diverge breaks spatial symmetries in dual ways: via its wave vector (indicating the modulation direction) and its polarization (denoting the atomic displacements' direction). The breaking of inversion symmetry due to displaced lattice results in a polar CDW [143]. The emergence of a chiral CDW can have significant consequences for the material's properties. It may lead to unique electronic behaviors, such as the emergence of novel conducting states or influence the material's response to external stimuli like temperature or magnetic fields.

### 6.3 Chirality and CDW in 1T-TiSe<sub>2</sub>

Figure 6.2 illustrates the unit cell configuration of TiSe<sub>2</sub>. Within this unit cell, the *Ti* atom functions as an inversion center, establishing TiSe<sub>2</sub> as achiral due to the presence of inversion symmetry. While the CDW transition disrupts translational

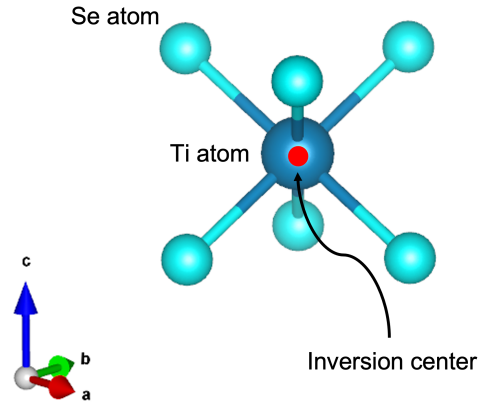


Figure 6.2: The unit cell of 1T-TiSe<sub>2</sub> has a inversion center. Rendering the unit cell achiral.

symmetry, it does not affect the inversion symmetry. Consequently, an achiral TiSe<sub>2</sub> material is anticipated to maintain its lack of chirality even after undergoing the CDW transition. However, experimental observations contradict this assumption. Studies utilizing polarized optical reflectometry and scanning tunneling microscopy (STM) by Ishioka et al. report the manifestation of chiral properties in both pristine and Cu-doped TiSe<sub>2</sub> [144–146]. Their research employing STM and optical polarimetry techniques highlights the definite chirality present in the charge density waves within the layered transition metal dichalcogenide TiSe<sub>2</sub> [144]. This chiral structure originates from the amalgamation of three directional CDWs, introducing a fixed relative phase difference that disrupts mirror symmetry. The STM experiments reveal a helical charge density distribution, where the displacements' orientation in one layer continuously transitions into the next due to their in-plane distortions. The observed chiral phase in TiSe<sub>2</sub>, as demonstrated by Ishioka et al., constitutes a combination of three distinct CDWs.

The experimental study delves into the intriguing phase transition that leads to the formation of a chiral order within a charge density wave (CDW) as a function of energy. According to insights from the Ginzburg-Landau theory (as referenced in [141]), a proposed phase diagram outlines the transformation of the material's state. At higher temperatures, the material exists in a uniform phase, transitioning to an achiral triple-**q** CDW state at a critical temperature  $T_{CDW}$ . As the temperature decreases further, the CDW state transforms once again, giving rise to a chiral phase

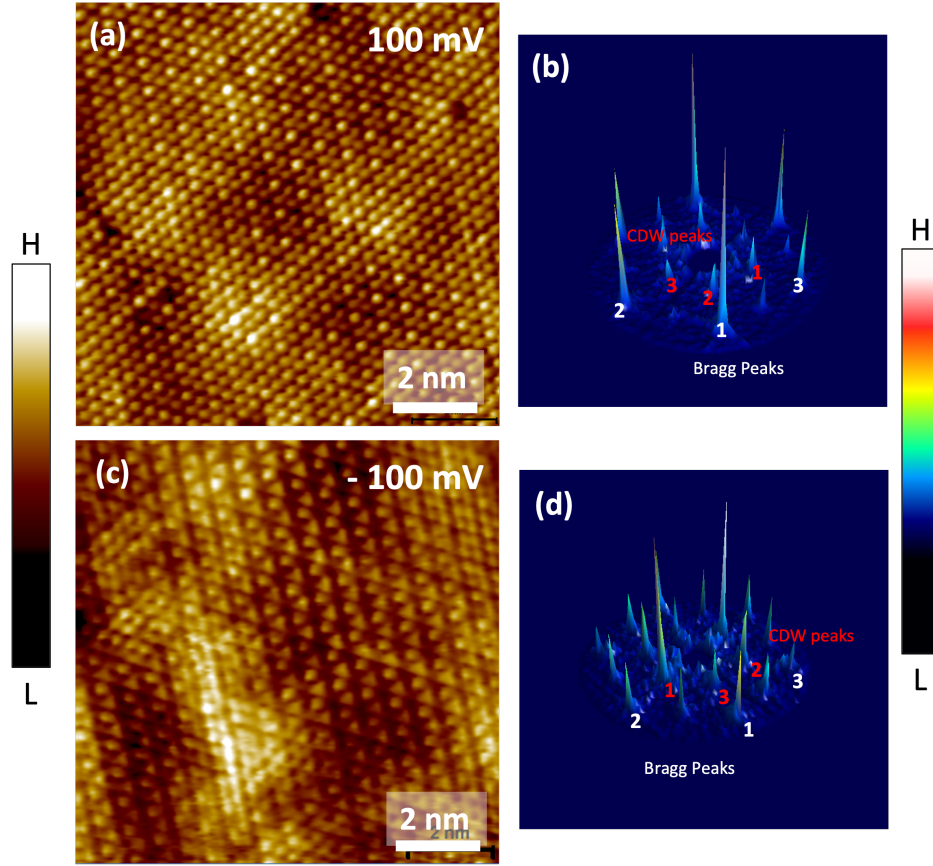


Figure 6.3: (a)  $\text{TiSe}_2$  STM image at 100 mV. (b) The Contour FT of image (a) is plotted to visualize the CDW peaks and their unequal intensity along different directions. Peaks marked in descending order of CDW and lattice Bragg peak intensities. (c) is the STM image of the same area in (a) but at negative bias. (d) Intensity peaks of FT show different ordering. All the data presented in the figure has been obtained at  $T = 4.5$  K well below CDW transition temperature.

at a lower temperature denoted as  $T_{\text{Chiral}}$ .

Interestingly, the temperature range indicating the emergence of the chiral phase lies between approximately 84 K and the critical temperature  $T_{\text{CDW}}$ , which is estimated to be around 202 K. This signifies that within this temperature window, the material undergoes a transformation from an achiral CDW state to a chiral phase. To directly observe this transition into the chiral phase, the experimental approach involves imaging the sample at temperatures below  $T_{\text{Chiral}}$ . This enables researchers to directly visualize and study the emergence of the chiral order within the charge density wave, offering valuable insights into the nature and properties of this intriguing phase transition.

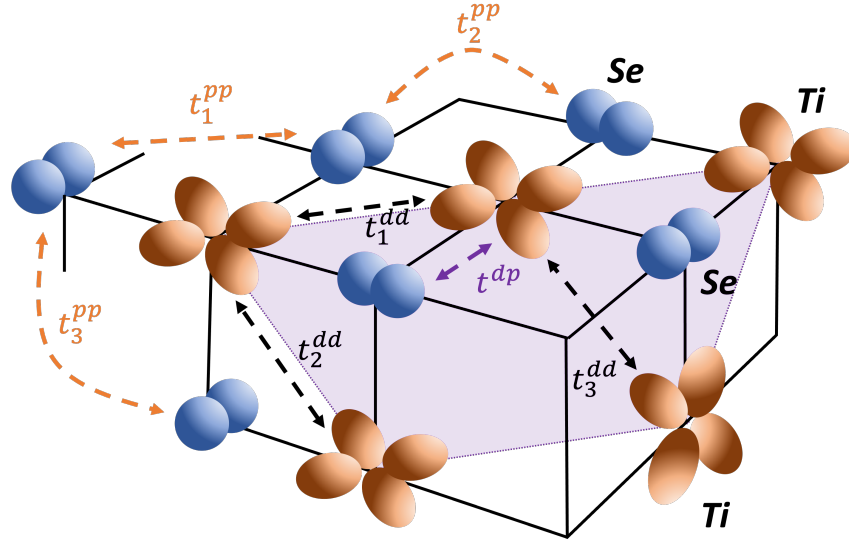


Figure 6.4: The tight-binding description: seven distinct hopping pathways are schematically shown here, All remaining overlap integrals are either zero by symmetry or expected insignificantly small. Adapted from [147]

The space group of  $\text{TiSe}_2$  above CDW transition temperature is  $P\bar{3}m1$ , after CDW transition in the triple- $q$  state, it lowers to  $P\bar{3}c1$ , chiral phase breaks and reduces this symmetry further to  $P2$  space group. The cause of the relative phase differences is still unclear. The chirality might appear because of the coupling of CDW to some other preexisting or induced chiral structure in the  $\text{TiSe}_2$ . The directional order can arise from ordering in an orbital degree of freedom. We must first understand the orbital contribution of  $\text{Ti}$  and  $\text{Se}$  atoms to bands.  $\Gamma$ -point valence band contribution comes from Se  $4p$  orbitals and  $L$ -point contribution of conduction band electrons comes from Ti  $3d$  orbitals. Coordination of  $\text{Se}$  atoms breaks the  $3d$  orbital degeneracy to form two groups of energies  $e_g$  and  $t_{2g}$ . CDW transition in  $\text{TiSe}_2$ , irrespective of the mechanism, results in a shift of electronic states from the maximum of the Se  $4p$  band at the center of the Brillouin zone ( $\Gamma$  point) to the three minima of the Ti  $3d$  bands at the zone boundaries. The  $M$ -point contribution of electrons comes from Ti  $t_{2g}$  orbitals and hole contribution from Se  $4p$  orbitals at  $\Gamma$ -point resulting in three CDW vectors ( $\Gamma - L$  vectors) associated with different orbitals [141].

The tight binding Hamiltonian for the  $\text{TiSe}_2$  can be written as follows



$$\begin{aligned}
H = & \sum_{i,\alpha} \frac{\Delta}{2} \left( d_{i,\alpha}^\dagger d_{i,\alpha} - p_{1i,\alpha}^\dagger p_{1i,\alpha} - p_{2i,\alpha}^\dagger p_{2i,\alpha} \right) \\
& + \sum_{\langle i,j \rangle, \alpha, \beta} \left\{ t_{\alpha, \beta, i-j}^{dd} d_{i,\alpha}^\dagger d_{j,\beta} \right. \\
& + t_{\alpha, \beta, i-j}^{pp} \left[ p_{1i,\alpha}^\dagger p_{1j,\beta} + p_{2i,\alpha}^\dagger p_{2j,\beta} \right] \\
& + t_{\alpha, \beta, i-j}^{pd} \left[ d_{i,\alpha}^\dagger p_{1j,\beta} + d_{i,\alpha}^\dagger p_{2j,\beta} + \text{H.c.} \right] \\
& \left. + t_{\alpha, \beta, i-j}^{pp} \left[ p_{1i,\alpha}^\dagger p_{2j,\beta} + \text{H.c.} \right] \right\}. \tag{6.1}
\end{aligned}$$

Here,  $d_i^\dagger$ ,  $p_{1i}^\dagger$ , and  $p_{2i}^\dagger$  create electrons on the Ti, upper Se, and lower Se atoms (as shown in Figure 6.4), respectively, in the unit cell centered at position  $\mathbf{R}_i$ . The labels  $a$  and  $b$  encompass all possible orientations of the Ti  $t_{2g}$  and Se  $p$ -orbitals, and  $i, j$  denote neighboring sites within and between unit cells. The chemical potential difference between the orbitals is denoted by  $\Delta$ , while the various hopping pathways are encompassed in the matrices  $t^{dd}$ ,  $t^{pd}$ , and  $t^{pp}$ . By fitting the established band structure of  $\text{TiSe}_2$ , we can ascertain the orbital characteristics of these bands through a tight-binding approach [147].

The asymmetry arises due to different occupations of  $\text{Ti } t_{2g}$  orbitals [148]. The occupation number changes as a function of energy. The chirality in CDW results from the occupation of  $\text{Ti}$  orbitals. Different electron filling causes asymmetric lattice distortion as well. This induces phase differences among the three directional CDW. This implies an orbital-ordered state. The detailed energetics of the interaction between phononic, orbital, and electronic degrees of freedom is required to uncover the exact character of chirality. We used STM to determine the orbital character of CDW at low temperatures and its dependence on energy. The best way to determine the phase difference between the three CDW directions is to check the intensity peaks in the Fourier transform of the topography image. If  $V$  is a bias voltage for the topography image, then the contribution to the tunneling current is the integrated density of states from the Fermi level to  $eV$ . Topography images at different bias voltages correspond to different integrated densities of states. Voltage-dependent imaging can shed some light on the energy dependence of chirality reflected in FT peak intensities.

If there is no phase difference in CDW in different directions, then all FT peaks should be symmetrical and of similar intensity. The variation in the peak intensities can also arise from the shape of the tip. We scanned the same areas in different

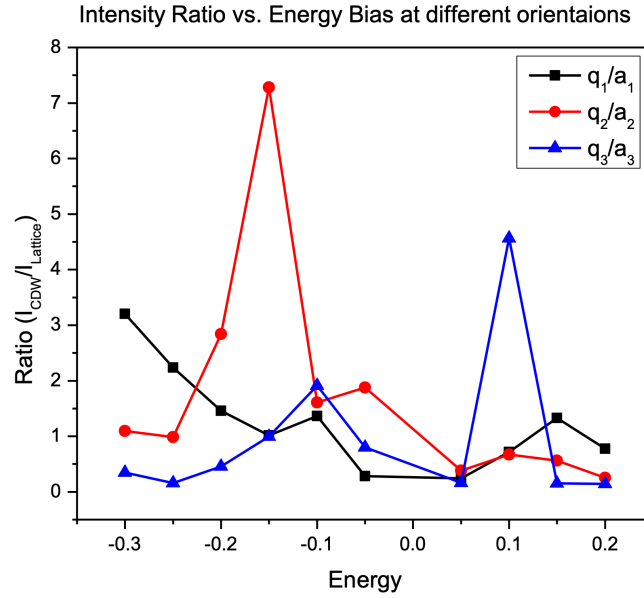


Figure 6.5: Plot of normalized intensities along three different CDW directions as a function of the bias voltage applied. All measurements were performed at  $T = 77$  K, below CDW transition temperature.

directions to ensure the measurements were free of tip artifacts. We checked the dependence of peak intensities as a function of the scanning angle. The same regions were scanned at different bias voltages. As the CDW peaks also lie along the lattice, we first normalized CDW peak intensity with Bragg peak intensities to compare the intensities of the peaks. The results are plotted in Figure 6.5. CDW peak along  $q_1$  direction was more intense at  $-0.3V$ , with intensity gradually decreasing, reaching a minimum at  $0.5V$  to increase again. This implies the filling fraction of  $Ti$  orbital is energy-dependent, and this orbital chiral structure influences scalar CDW.

## 6.4 Conclusions

The system under study manifests a fascinating intertwining of scalar charge density wave (CDW) order and chiral order, leading to the emergence of a chiral CDW phase. This unique phase arises from the coupling between the scalar CDW order and the breaking of chiral symmetry within the system, a result of an electronic transition occurring precisely at the CDW transition. In the specific case of  $TiSe_2$ , the chirality observed in its CDW pattern is intricately linked to orbital ordering. This material exhibits three crucial CDW instabilities that collectively generate the chiral pattern observed in its CDW phase. The essential factor contributing

to this chirality lies in the relative phase differences among the three CDW order parameters, originating directly from the orbital ordering within the material.

Our detailed analysis, particularly focusing on the energy dependence of the orbital ordering's effect on the intensity peaks of CDW observed in scanning tunneling microscopy (STM) topography images, has led us to a significant conclusion. We've found that the microscopic energetics of the occupied states within the system play a crucial role in shaping the CDW intensity peaks, superseding any overarching physical principles at play. This understanding of the chirality within the charge density wave of  $\text{TiSe}_2$  opens doors for further exploration. It provides a rich ground for delving into its implications, especially in comprehending similar behaviors observed in high-temperature superconductors. By unraveling the intricacies of the chiral CDW phase in  $\text{TiSe}_2$ , we aim to glean insights that might shed light on analogous phenomena in other materials, particularly those exhibiting high-temperature superconductivity.

## Chapter 7

### 2H-NbSe<sub>2</sub>: INTERPLAY OF STRAIN AND CHARGE DENSITY WAVES

*"A method is more important than a discovery since the right method will lead to new and even more important discoveries."*

— Lev Landau

#### 7.1 Overview

As discussed in previous chapters, transition metal dichalcogenides (TMDC) as well as organic and inorganic linear chain compounds, charge density waves (CDW) are associated with phenomena like Peierls distortion [149], Fermi surface nesting [150–152], excitonic insulators [153–155], or electron-phonon coupling [156, 157]. The transport measurements in the CDW phase indicate anomalous electric and magnetic behavior, indicating its correlated electronic nature [158, 159]. Interestingly CDW is an electronic order resembling the superconducting phase [160], and it competes with other ordered phases in some materials [161–163]. Focusing on TMDC, the debate over the formation mechanism of CDW still persists. The interplay of CDW with other coexisting electronic states is complex and less understood. Another interesting dimension to the study of CDW is the tunability of CDW, an emergent phenomenon awaiting discovery and subsequent investigation. Here we focus on 2H-NbSe<sub>2</sub>, the metallic, layered TMDC towards an open-ended probe of CDW in this material in its pristine form and under the influence of strain.

#### 7.2 Structural properties

NbSe<sub>2</sub> is a prominent transition metal dichalcogenide (TMDC) featuring a layer of Nb atoms nestled between Se layers, as depicted in Figure 7.1. This compound exhibits various polymorphs including 1H, 2H, 4H, and 3R, among which the 2H variant stands as the most stable configuration. Notably, the van der Waals (vdW) interaction between layers in 2H-NbSe<sub>2</sub> facilitates its facile exfoliation. The reduction in the number of layers within 2H-NbSe<sub>2</sub> has been observed to elevate the transition temperature of charge density waves (CDW) while concurrently dampen-

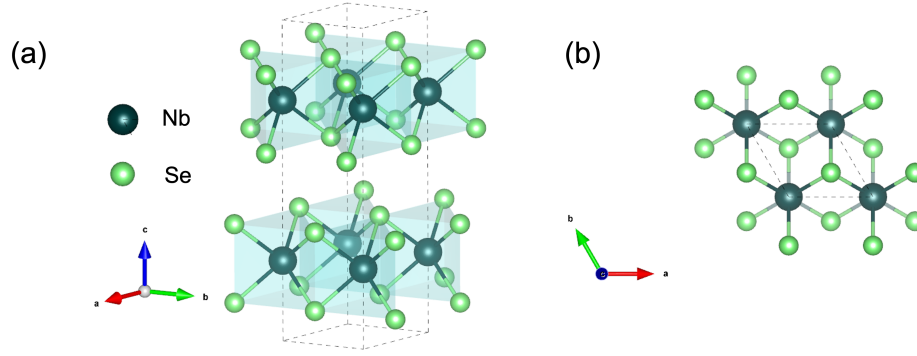


Figure 7.1:  $2H$  polymorph of NbSe<sub>2</sub> consists of two layers per unit cell. A unit cell of  $2H$ -NbSe<sub>2</sub> is indicated by a dashed line with the  $c$ -axis perpendicular to the layers. Nb atoms are surrounded by Se atoms in trigonal prismatic coordination. (b) The view along the  $c$ -axis shows hexagonally packed Se atoms.

ing the occurrence of superconductivity [164]. Intriguingly, Bemol Incorporation in the USA has pioneered the synthesis of NbSe<sub>2</sub> as a conductive lubricant for vacuum applications due to its notably low degassing properties [165]. This unique dual characteristic of NbSe<sub>2</sub>—as both a material sensitive to layer thickness in electronic phenomena and as a functional lubricant—underscores its versatile applications across diverse domains.

### 7.3 Electronic Properties

At room temperature,  $2H$ -NbSe<sub>2</sub> exhibits metallic properties. Upon reaching a critical temperature  $T_{CDW} = 34$  K, it undergoes a second-order phase transition, forming a nearly commensurate CDW. This transition marks a fascinating phenomenon observed in STM images, revealing a distinctive  $3 \times 3$  modulation of charge density (Figure 7.2). Notably, this material showcases a dual nature, coexisting as both a superconductor below  $T_c = 7.2$  K and a host for the CDW phase [166–168]. Understanding the intricacies of the CDW formation in  $2H$ -NbSe<sub>2</sub> remains a subject of ongoing debate [156, 169]. While some theories attribute the energy gap opening at the transition temperature to the nesting mechanism [170], recent theoretical calculations challenge this notion, suggesting that Fermi surface (FS) nesting might play a negligible role in the origin of CDW in  $2H$ -NbSe<sub>2</sub> [171, 172].

The strong electron-phonon coupling emerges as a pivotal factor in the existence of CDW in  $2H$ -NbSe<sub>2</sub> [10, 173]. Recent insights from STM studies have pointed towards electron-lattice coupling as a significant contributor to CDW formation,

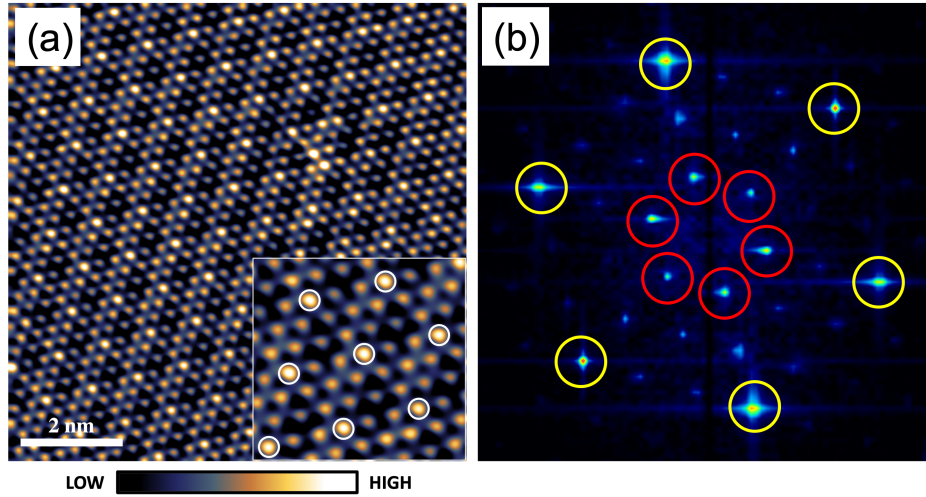


Figure 7.2: (a) High resolution STM image of unstrained  $2H\text{-NbSe}_2$  showing  $\sim 3a_0$  periodic triangular ( $3Q$ ) CDW. The lower right corner inset is the enlarged part of the image where CDW peaks are encircled white to show the  $3a_0 \times 3a_0$  modulation clearly. (b) Fourier transforms (FT) of the STM image. The peaks due to the lattice (Bragg peaks) are encircled in yellow, and the peaks due to the CDW ordering are circled in red. STM images are taken at  $V_{bias} = 40$  mV and  $I_{set} = 100$  pA. Data collected at the base temperature of  $T = 4.5$  K, below CDW transition temperature  $T_{CDW} = 33$  K

contrasting the earlier emphasis on Fermi surface physics [136]. Moreover, in the presence of defects, localized strong modulation weakly affects the long-range order of CDW, resulting in the formation of a Bragg glass phase. This phase acts to pin the CDW in  $2H\text{-NbSe}_2$ , illustrating the intriguing interplay between local distortions and the overall CDW structure [174]. This multifaceted interplay between different mechanisms underscores the complexity of the CDW phenomenon in  $2H\text{-NbSe}_2$  and highlights the intricate balance between various contributing factors in its manifestation.

#### 7.4 Strain and CDW in $2H\text{-NbSe}_2$

Electronic properties are interlinked with the geometric structure of the lattice. Strain, defined as the geometric response of a material to an applied force, has been a knob to tune a wide spectrum of properties from bulk materials to lower dimensional materials [175, 176]. Strain influences the properties of functional materials like superconductors [177], transition metal oxides [178], and transition metal dichalcogenides [179]. Applying strain by pressure or stretch can provide

insight into electron-electron and electron-lattice dynamics. It can change the CDW transition temperature by modifying phonon interactions [180–182]. The strain in vdW layered materials is responsible for the phonon mode softening [183–185]. The CDW ordering vector depends on the electron-phonon coupling [157, 186] and the CDW transition corresponds to the softening of acoustic phonon mode that is related to incommensurate CDW ordering wave vector  $q_{CDW}$  [187–189]. The charge density distribution depends on the Lindhard response function, whose imaginary component identifies with contributions from electron-electron interaction and electron-phonon interaction [190]. Overall, the CDW order that is dependent on either electron-electron or electron-phonon interaction gets affected by strain. Sub-angstrom changes in the lattice can affect the band structure and electronic mobility by inducing changes in the electron hopping parameter or electron-phonon coupling.

Recent studies centered on  $2H$ -NbSe<sub>2</sub> highlight the significant influence of strain, demonstrating its capability to induce a quantum phase transition, consequently altering the CDW ordering vector  $q_{CDW}$ . The application of local strain has been observed to create distinct domains exhibiting commensurate CDW wavevectors aligned with the lattice directions [172, 191, 192]. To comprehensively grasp the impact of strain, exploring the phase space encompassing all possible commensurate and incommensurate CDW wavevectors becomes pivotal. The theoretical modeling of the CDW phase using Landau phase transition theory indicates a distinct behavior, with commensurate CDW being firmly pinned to lattice sites while incommensurate phases exhibit greater flexibility [193].

Understanding the intricate relationship between the CDW wavevector, the periodicity of charge order, and the changes in electron-electron or electron-phonon interactions under strain is essential. The manipulation of strain offers a unique lens to illuminate the microscopic mechanisms governing CDW formation. Specifically, strain-induced manipulations have demonstrated the ability to induce  $1Q$  stripes and  $3Q$  triangular order within  $2H$ -NbSe<sub>2</sub> [172, 191]. This prompts the need to systematically explore various experimental realizations to comprehend how specific CDW wavevectors are determined following strain application. Our work contributes to this exploration by documenting novel CDW ordering in NbSe<sub>2</sub> crystals resulting from strain within the sample.

It has been observed that the induction of small strain in  $2H$ -NbSe<sub>2</sub> drastically changes the CDW ordering [172, 191]. The nanoscale buckling of the sample, or the difference in the substrate's thermal expansion coefficient (TEC) and the NbSe<sub>2</sub>



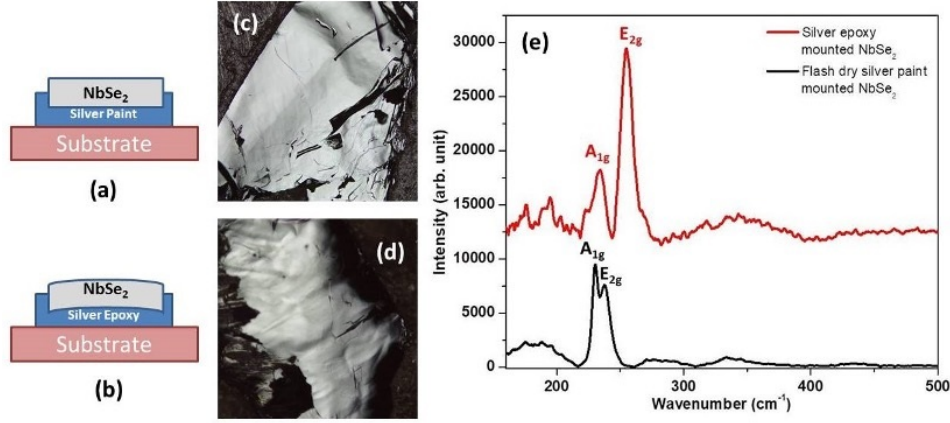


Figure 7.3: Schematic representing the mounting of the unstrained sample (a) and (b) strained sample. (c) The optical image shows the unstrained and (d) the strained samples. (e) The Raman spectra obtained at room temperature of the strained sample showing the peak at the  $230\text{ cm}^{-1}$  and  $238\text{ cm}^{-1}$  unstrained sample showing the peak at the  $233\text{ cm}^{-1}$  and  $255\text{ cm}^{-1}$ . (Raman spectra are vertically shifted for clarity.)

crystal, may cause strain, resulting in a quantum phase transition of proximate ordered phases of CDW. We opted to mount the crystal using flash-dry silver paint and silver epoxy to mount our NbSe<sub>2</sub> crystals to the sample holder to focus our strain-related investigation on the mechanical strain.

Figure 7.3(a) and (b) illustrate how the strain builds in the 2H-NbSe<sub>2</sub> single crystals depending on mounting. Figure 7.3(c) shows the optical microscope image for the sample with flash-dry silver paint, and (d) is for the sample with epoxy after the curing of epoxy at  $150^{\circ}\text{C}$ . The difference in the topography of these samples is seen in their images. Henceforth we identify flash-dry silver paint mounted NbSe<sub>2</sub> as an unstrained sample and silver epoxy mounted and cured as a strained NbSe<sub>2</sub> sample.

Raman spectroscopy serves as a valuable tool for scrutinizing strain effects in 2D materials [194]. In the Raman spectrum of 2H-NbSe<sub>2</sub> mounted with flash-dry silver paint, prominent peaks at  $230\text{ cm}^{-1}$  and  $238\text{ cm}^{-1}$ , corresponding to modes A<sub>1g</sub> and E<sub>2g</sub>, are observed (black curve in Fig. 1(e)) [195, 196]. Additionally, a broad peak centered around  $180\text{ cm}^{-1}$  in the black curve of Fig. 1(e) represents a soft mode that exhibits a shift as the temperature decreases, eventually freezing after the CDW phase transition [197]. These peaks align with the vibrational modes of unstrained NbSe<sub>2</sub> bulk crystals, suggesting that the flash-dry silver paint used for mounting did not induce strain in the sample. Strain effects in 2D materials are



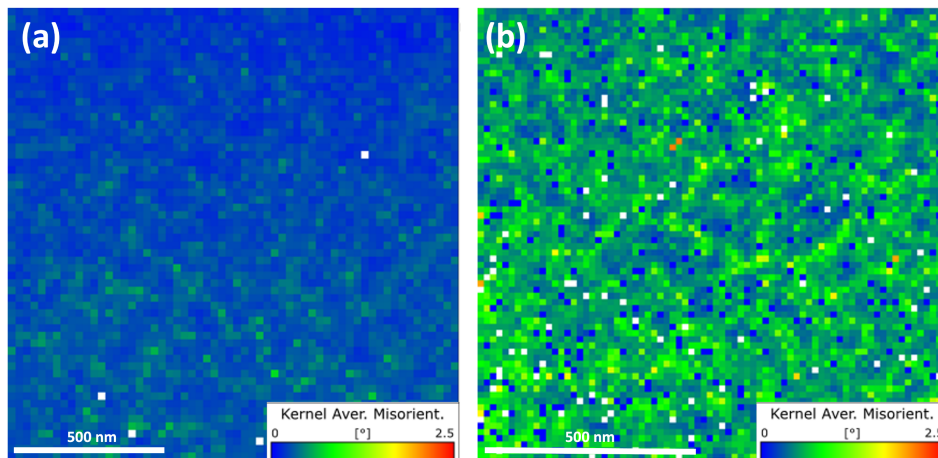


Figure 7.4: The electron backscattered diffraction (EBSD) measurements are performed at ambient temperature to calculate kernel average misorientation (KAM). (a) unstrained  $2H\text{-NbSe}_2$  showing the few variations in KAM as compared to (b) strained sample with large variation across the micron scale region

typically observed through peak broadening or shifting. Applying tensile strain can alter the bond length, consequently affecting the vibrational mode [198]. Notably, Raman spectroscopy of silver epoxy-mounted and cured  $\text{NbSe}_2$  crystals displays broadening and shifting of the  $A_{1g}$  and  $E_{2g}$  peaks (red curve in Fig. 1(e)) to  $233\text{ cm}^{-1}$  and  $255\text{ cm}^{-1}$ . These results qualitatively suggest the induction of global strain in the silver epoxy-mounted  $\text{NbSe}_2$ . However, for a comprehensive understanding of strain's influence, further qualitative assessments are necessary at both macro and microscopic levels.

Understanding spatial variations in the strain field is crucial, and local strain measurements offer valuable insights into these variations. Electron Back Scattered Diffraction (EBSD) stands as a powerful technique for comprehending the crystallographic aspects of materials at the micron scale, aiding in our investigation of strain variations [87]. In our study, EBSD served as a qualitative tool to probe strain variations. Residual strain within a material manifests as local lattice structure variations, which are reflected in the diffraction patterns observed through EBSD. The technique generates Kikuchi lines that are referenced with the crystal structures, and any structural deformation induces broadening and misorientation of these lines compared to the reference structure [199]. These local misorientations observed through EBSD provide a valuable indication of strain distribution across the material.

EBSD maps allow for the comparison of orientations in micron-sized scanning areas with a resolution reaching tens of nanometers. To analyze strain distribution, a kernel, composed of points of a specific size surrounding the point of interest, is employed. The kernel average misorientation (KAM) is a pivotal metric calculated at each point using EBSD data, offering a qualitative depiction of strain [87]. By raster scanning the electron beam, KAM data qualitatively illustrates the strain variation across the crystal surface. In our investigation, we captured KAM data from various areas and sizes for both unstrained and strained NbSe<sub>2</sub> crystals. The KAM map for unstrained NbSe<sub>2</sub> demonstrates minimal variations (Figure 7.4(a)), indicating low or negligible strain within the material. Conversely, the strained NbSe<sub>2</sub> exhibits a substantial variation in KAM map data, uniformly distributed across the surface (Figure 7.4(b)). These substantial variations in the KAM map for strained NbSe<sub>2</sub> signify a notable presence of strain throughout the crystal surface.

From micron-sized scanning areas with a resolution of tens of nanometers that have given us a fair picture of global strain, we move on to nanometer-sized scanning areas with sub-angstrom resolution along with local charge density measurement using scanning tunneling microscope (STM) to investigate the effect of local strain on charge ordering. NbSe<sub>2</sub> is a layered metal TMDC that has different polymorphs like *1T* (1 layer each for trigonal unit cell) and *2H* (2 layers per hexagonal unit cell) [200]. The *2H* polymorph of NbSe<sub>2</sub> is structured such that the *Nb* atoms are in a trigonal prismatic arrangement with the top and bottom sheets of *Se* atoms in a hexagonal unit cell (Fig.3 (a)). Bulk sheets of NbSe<sub>2</sub> have van der Waals interaction between them. Below  $T_{CDW} \approx 34K$  *2H*-NbSe<sub>2</sub> undergoes a second-order electronic phase transition resulting in nearly commensurate triangular (**3Q**) CDW [158]. Various experimental pieces of evidence point to the important role the electron-phonon coupling plays in this CDW transition [187, 201–204].

STM measurements were performed on the strained and unstrained NbSe<sub>2</sub> crystals to compare the difference in CDW geometries. STM topography images of unstrained *2H*-NbSe<sub>2</sub> show top *Se* atoms arranged in a triangular lattice as in figure 7.2(a) ( $|\mathbf{a}| = |\mathbf{b}| = a_0 = 0.33 \text{ nm}$ ). The characteristic superstructure of  $3a_0 \times 3a_0$  triangular (**3Q**) CDW is observed overlaying the lattice (figure 7.2(a)). The periodicity of CDW modulation on the unstrained sample is  $3a_0$ . These commensurate **3Q** CDW has a wavevector oriented along the lattice direction. figure 7.2(b), a Fourier transform (FT) of the image in figure 7.2(a) shows triangular commensurate CDW peaks marked in red circles oriented along the  $\Gamma - M$  direction in reciprocal

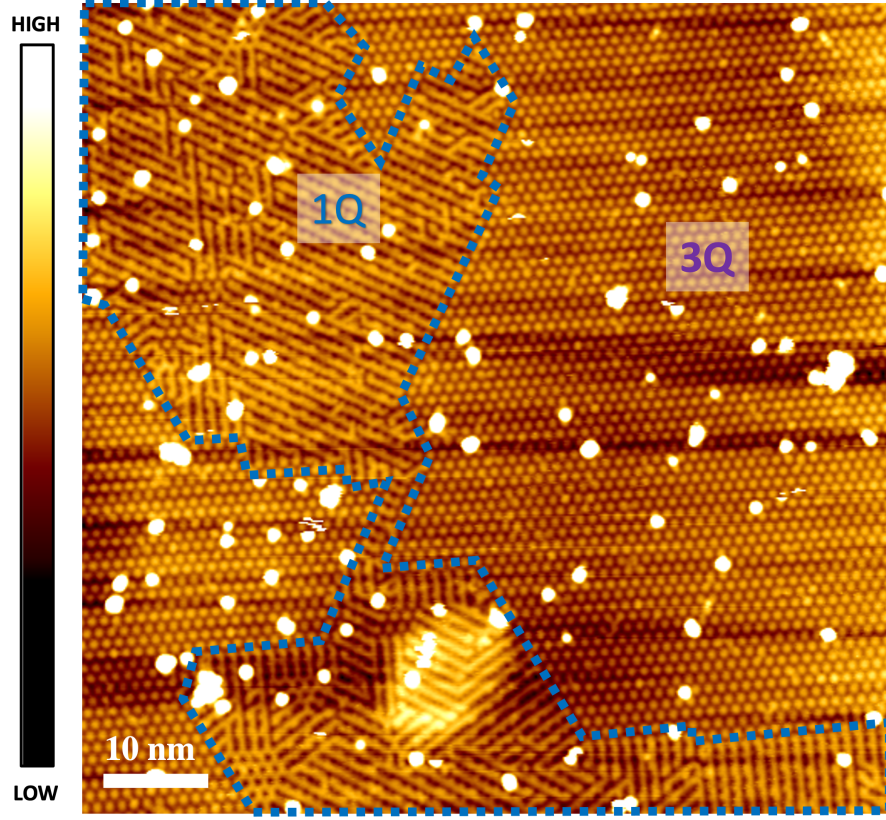


Figure 7.5: Large area STM image of the smooth atomic interface between unidirectional stripes (1Q) and triangular (3Q) CDW order in strained 2H-NbSe<sub>2</sub>. 1Q CDW are marked by blue color for better visualization. Imaging parameters are,  $V_{bias} = -1$  V and  $I_{set} = 100$  pA at  $T = 4.5$  K.

space or Brillouin zone (BZ). Multiple regions were scanned with tens of microns separation. No dispersion of the CDW wavevector has been observed as a function of location or across the imaging parameter space.

In strained 2H-NbSe<sub>2</sub>, a unidirectional "stripe" (1Q) and a triangular or tri-directional(3Q) CDW were formed. Large area images consist of domains of 1Q stripes observed to coexist with domains of 3Q CDW (figure 7.5). Figure 7.6(a), and figure 7.6(d) are representative images of 3Q and 1Q domains, respectively. Interestingly no 3Q CDW of  $3a_0$  periodicity were observed in the strained sample. 1Q CDW is a commensurate phase with  $4a_0 \times 1a_0$  ordering. There are three distinct possibilities for the orientation of 1Q CDW; all were observed in different regions of the same 2H-NbSe<sub>2</sub> crystal. The image in figure 7.6(d) is of a region with stripe orders oriented at  $2\pi/3$  with each other. Origin of the stripe order can be attributed to locally varying strain [172, 191, 204]. The wavevector of 1Q CDW



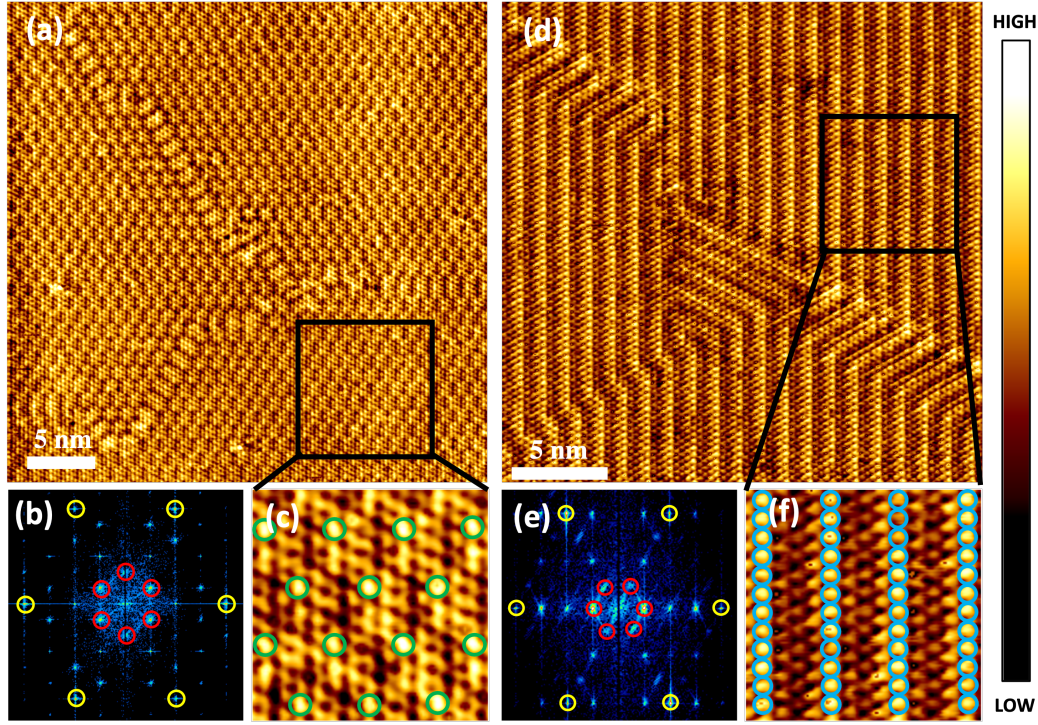


Figure 7.6: (a) Close view of the region in image with  $2\sqrt{3}a_0 \times 2\sqrt{3}a_0$   $R(30^\circ)$  triangular CDW ordering. Imaging parameters are,  $V_{bias} = -500$  mV and  $I_{set} = 10$  pA. The FFT of image (a) is a figure (b); yellow circles mark atomic Bragg peaks, and red circles mark primary CDW order peaks. (c) A small area of the image (b) is enlarged, and real space  $2\sqrt{3}a_0 \times 2\sqrt{3}a_0$  modulation in electron density is marked with green circles. (d) The  $4a_0 \times 1a_0$  stripes of unidirectional CDW ordering are oriented along different directions. STM imaging parameters are,  $V_{bias} = -30$  mV and  $I_{set} = 10$  pA. (e) Yellow circles mark atomic Bragg peaks, and primary CDW peaks are marked by red circles of FT of the image in (d). (f) The enlarged area of the image in (d) to show the  $4a_0 \times 1a_0$  spatial modulation in electron density is encircled blue. All the data presented in the figure has been obtained at  $T = 4.5$  K.

$\vec{Q}_{4a_0} = \frac{1}{4}\vec{Q}_{Bragg}$  is oriented along the atomic Bragg directions in FT of the image as shown figure 7.6(e). The orientation of commensurate  $1\mathbf{Q}$  CDW wavevector along the lattice direction can be explained by the local directional strain and phonon mode softening occurring along the  $\Gamma - M$  direction. However, the magnitude of the CDW wavevector in strained samples differs from unstrained samples.

We observed  $3\mathbf{Q}$  ordering in STM images of strained NbSe<sub>2</sub> oriented at an angle of  $30^\circ$  to Bragg lattice directions with  $2\sqrt{3}a_0 \times 2\sqrt{3}a_0$   $R(30^\circ)$  periodicity as shown in figure 7.6(a). One of the incommensurate phases in NbSe<sub>2</sub> has  $\sqrt{13}a_0 \times \sqrt{13}a_0$   $R(13^\circ)$ , rotated at  $13^\circ$  to the lattice direction [205, 206]. The primary wave vector of

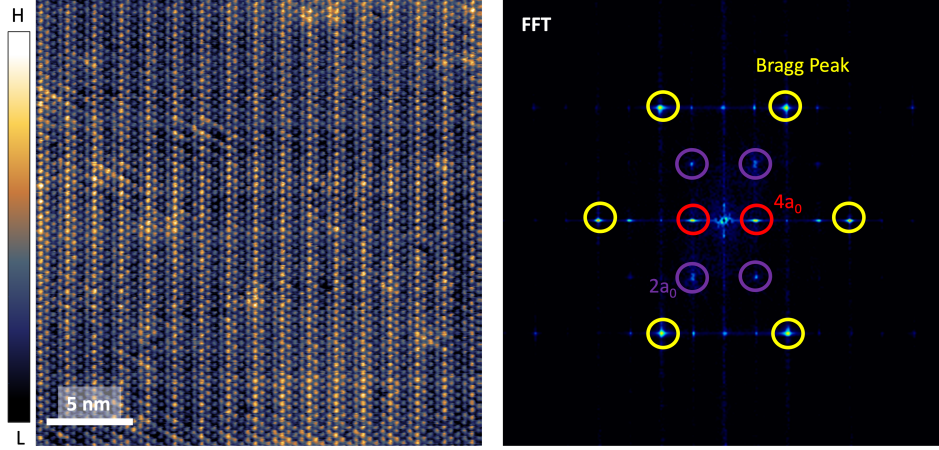


Figure 7.7: Coexistence of hidden  $2a_0 \times 1a_0$  CDW order (marked by peaks in FFT encircled with violet color) within  $4a_0 \times 1a_0$ . The data presented in the figure has been obtained at  $T = 4.5$  K.

incommensurate  $3\mathbf{Q}$  CDW is oriented along the  $\Gamma - K$  direction (figure 7.6(a)) CDW peaks marked by red circles). Difference in the magnitude of  $\sqrt{13}a_0$  and  $2\sqrt{3}a_0$  periodicities is only  $\approx 4\%$ . To measure the magnitude of the incommensurate CDW state accurately, we focused on areas spanned by a single incommensurate phase (figure 7.6(a)). The wavevector addition of two primary CDW wavevectors  $\vec{\mathbf{Q}}_{2\sqrt{3}a_0} = \frac{1}{2\sqrt{3}}\vec{\mathbf{Q}}_{\text{Bragg}}$  of incommensurate phase gives secondary CDW vectors lying along the Bragg direction with a magnitude  $|\frac{1}{2}\vec{\mathbf{Q}}_{\text{Bragg}}|$ . The secondary CDW peaks' location in the image's F.T. (figure 7.6(b)) supports the periodic ordering of magnitude  $2\sqrt{3}a_0$ .

A detailed examination of STM images portraying a  $1\mathbf{Q}$  CDW with a  $4a_0 \times 1a_0$  modulation reveals small areas where a superimposed modulation is evident. Upon Fourier Transform analysis, a faint yet discernible peak emerges, indicating a  $1\mathbf{Q}$  CDW with a  $2a_0 \times 1a_0$  modulation along two distinct directions as shown in Figure 7.7. This coexistence of CDW patterns presents an intriguing observation, shedding light on the critical state of the phase transition. This observation hints at a close proximity of phases within the phase diagram.  $dI/dV$  Spectroscopy conducted on these three phases further highlights the resilience of the Charge Density Wave (CDW) gap in strained samples (as in Figure 7.8). Additionally, it demonstrates how the CDW gap remains nearly identical between the two modulations in strained samples compared to the conventional one.

The presence of distinct CDW in strained single crystals suggests that these

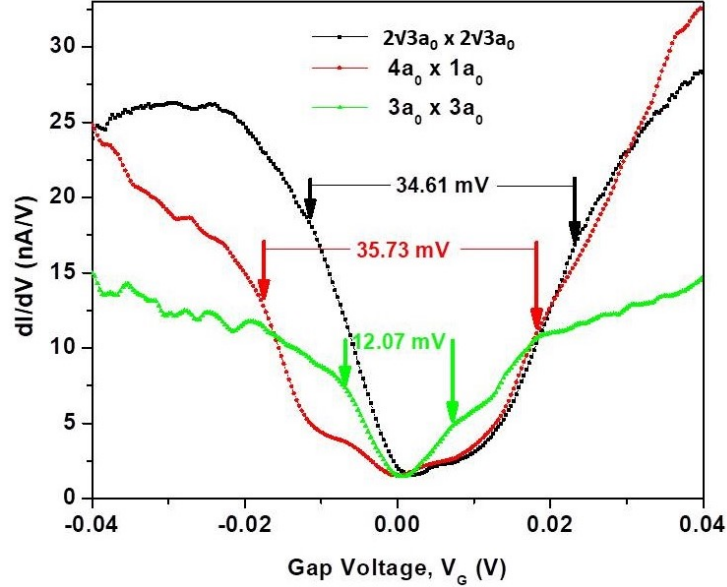


Figure 7.8: Comparison of  $dI/dV$  spectra of three CDW domains. All the data presented in the figure has been obtained at  $T = 4.5$  K

phases may be associated with local variations in the background global in-plane strain. Local variations can arise due to the inhomogeneous granular nature of epoxy glue used for mounting crystals. To better understand the formation of CDW in the presence of strain, it is necessary to understand the spatial variation of the strain. The effect of in-plane strain on the CDW ordering was calculated using the tight-binding model and Random Phase Approximation in Ref. [191], taking into account the modification of hopping integrals because of strain to calculate electronic susceptibility  $D_2(\mathbf{q})$ . This model identifies the CDW ordering vector as the first vector for which electronic susceptibility  $D_2(\mathbf{q})$  exceeds the bare phonon energy  $\Omega(\mathbf{q})$ . Calculations using this model suggest strain effect  $D_2(\mathbf{q})$  significantly can induce different types of CDW wavevector ordering.

To analyze local strain variations, we employed the Lawler-Fujita correction algorithm, as detailed in Appendix B and also discussed in reference [207]. This algorithm yields the two components of the displacement field, namely  $u_x(\mathbf{r})$  and  $u_y(\mathbf{r})$ . The Lawler-Fujita algorithm takes as input the atomic Bragg peak positions derived from the Fourier transform of the topography image, which is obtained through 2D Gaussian fitting. Additionally, a spatial smoothing length scale  $L$  is required, and in this study,  $L$  was set to  $5a_0$  (where  $a_0$  represents the lattice constant), with subsequent conversion to pixel units. Since our interest lies specifically in



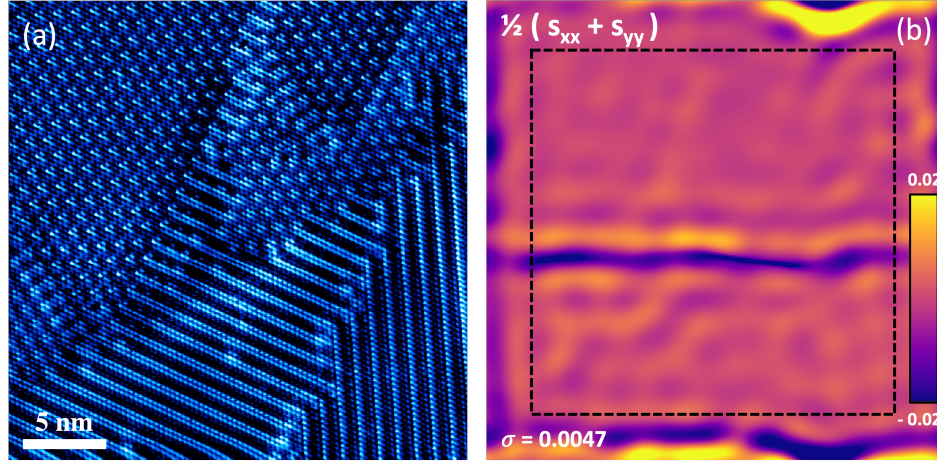


Figure 7.9: (a) Large area STM image of intersecting boundaries of  $2\sqrt{3}a_0 \times 2\sqrt{3}a_0$   $R(30^\circ)$  triangular (3Q) CDW order and  $4a_0 \times 1a_0$  stripes of unidirectional (1Q) CDW ordering. Stripe CDW areas oriented at  $120^\circ$  with respect to each other. The (3Q) CDW orders shifted in phase. (b) Bilateral strain map ( $\frac{1}{2}(s_{xx}(\mathbf{r}) + s_{yy}(\mathbf{r}))$ ) of area is calculated using Lawler-Fujita algorithm. STM data obtained at  $T = 4.5$  K

features of scale  $4a_0$ , we applied smoothing to mitigate higher periodicities in the data. The employed smoothing kernel is a Gaussian function given by  $\frac{1}{2\pi L^2} e^{-\frac{r^2}{2L^2}}$ , defined on a square of side length  $6L + 1$  in pixels [191].

The displacement fields  $u_x(\mathbf{r})$  and  $u_y(\mathbf{r})$  have two primary contributions: (1) the inherent structural strain, denoted as the strain field with components  $s_x(\mathbf{r})$  and  $s_y(\mathbf{r})$ , and (2) experimental artifacts, including piezo-related and thermal effects, referred to as the drift field with components  $d_x(\mathbf{r})$  and  $d_y(\mathbf{r})$ . Thus, the relationships are expressed as  $u_x(\mathbf{r}) = s_x(\mathbf{r}) + d_x(\mathbf{r})$  and  $u_y(\mathbf{r}) = s_y(\mathbf{r}) + d_y(\mathbf{r})$ . The components  $d_x(\mathbf{r})$  and  $d_y(\mathbf{r})$  are determined by fitting a third-order polynomial to  $u_x(\mathbf{r})$  and  $u_y(\mathbf{r})$ . Subsequently, the strain fields are calculated as  $s_x(\mathbf{r}) = u_x(\mathbf{r}) - d_x(\mathbf{r})$  and  $s_y(\mathbf{r}) = u_y(\mathbf{r}) - d_y(\mathbf{r})$ . The partial derivatives, namely  $s_{xx}(\mathbf{r}) = \delta_x s_x(\mathbf{r})$ ,  $s_{xy}(\mathbf{r}) = \delta_x s_y(\mathbf{r})$ ,  $s_{yx}(\mathbf{r}) = \delta_y s_x(\mathbf{r})$ , and  $s_{yy}(\mathbf{r}) = \delta_y s_y(\mathbf{r})$ , represent components of the strain tensor based on elasticity theory. The linear combination  $(s_{xx}(\mathbf{r}) + s_{yy}(\mathbf{r}))/2$  signifies the biaxial strain map, while  $(s_{xx}(\mathbf{r}) - s_{yy}(\mathbf{r}))/2$  serves as an approximate measure of uniaxial strain.

In our analysis, we determined the relative strain between the 3Q and 1Q ordering within the same field of view. We observed no variation across the boundary between the two CDW orders; however, there persists a local variation in strain. As depicted in Figure 7.9(b), the relative variation of strain is not more than 2%

concerning the CDW ordering lattice parameters present in the images. It is crucial to recognize that while the global variation of strain may impact the choice between  $3\mathbf{Q}$  and  $1\mathbf{Q}$ , the local variation is not discernible. This analysis further strengthens our claim of the system being in a quantum-critical state.

We have uncovered new CDW geometry due to global strain and coexisting with closely related stripe geometry. We emphasize that the difference between the two phases arises due to anisotropic phonon contribution. Our analysis can be supplemented in the future by designing experiments for mapping phonon modes in the presence of strain and correlating the CDW geometries. Theoretical study of the proposed mechanism can also lead to a better understanding of energetics and the tunability of CDW order as a function of strain.

## 7.5 Conclusions

The intricate interplay between electrons and phonons plays a pivotal role in orchestrating the formation of Charge Density Waves (CDW). In our exploration of strained  $2H\text{-NbSe}_2$  crystals, we made a significant discovery of a previously unidentified commensurate  $3\mathbf{Q}$  CDW phase-oriented along the  $\Gamma - K$  direction. This revelation sheds light on the profound impact of strain on CDW behavior, particularly in preserving the unit cell volume while being applied along a specific axis, thereby stabilizing the CDW  $3\mathbf{Q}$  geometry with a periodicity of  $2\sqrt{3}a_0$ . This stabilization arises from strain-induced alterations in the electron-electron interaction dynamics, showcasing strain's role in shaping and stabilizing electronic phases.

Moreover, our observations revealed distinct domains exhibiting stripes with a periodicity of  $4a_0$ , stemming from anisotropic phonon interactions influenced by the strain. This microscopic variation in strain manifests as a diverse and rich structure of different geometric phases within the CDW framework. Our findings represent a novel addition to the array of phases known in  $2H\text{-NbSe}_2$ , underscoring the profound influence that even minute strains can exert on charge ordering dynamics.

This exploration into strain-induced effects on CDW formation not only expands our understanding of electronic phase transitions but also highlights the potential for utilizing strain as a precise and tunable axis for manipulating charge ordering in various important materials. These experimental findings reinforce the crucial role of strain as a modifiable factor within the extensive landscape of electronic phases in materials, offering promising avenues for tailoring and controlling their electronic properties.



## *Chapter 8*

### SUMMARY

In condensed matter physics, new properties emerge in a collection of particles due to interaction amongst their constituents. In the case of crystalline solids, the interaction between the electron-electron and electron-lattice generates a variety of phases. Superconductivity is an example of a phase arising from the intersections between electron and lattice. It has been experimentally observed in many elemental solids and different composite materials. Bardeen-Cooper-Schrieffer (BCS) theory is a generalized model of a microscopic mechanism of formation of superconducting states. It is useful to predict superconductivity in new materials. The other interesting phase observed in materials is charge density waves (CDW), a standing wave formed in the otherwise uniform density of electrons. CDW also formed as a result of electron-electron and electron-phonon interaction. The first model proposed to explain 'The Peierls model' - CDW in the 1D atomic chain was based on the interaction between lattice and electrons. This model was used to explain superconductivity without any success. As the field evolved and CDW appeared in different dimensional materials, Peierls' model became inadequate. Search for a general model to explain CDW began without any success to this date. It appears that CDW properties mostly depend on the composition of the material and have a phenomenological explanation. There is no BCS-like theory for CDW. The next best thing is to classify CDW phenomena into groups with materials having similar behavior and microscopic origin of CDW. Materials with strong electron-electron and electron-phonon interaction deviate significantly from the standard Peierls model.

Before formalizing the theory of CDW, we need to separate atypical from mundane. Also, the dependencies of microscopic interactions on the macroscopic parameters. Most atypical materials with CDW belong to high-temperature cuprate and pnictide superconductors and transition metal dichalcogenides (TMDC). The later group found itself in the limelight after the discovery of graphene. Chemical composition, structural polymorphs, and layered nature make TMDC attractive to look for exotic properties and practical applications. Two materials that stand out in this class for their CDW properties are semi-metallic  $1T$ -TiSe<sub>2</sub> and metallic  $2H$ -NbSe<sub>2</sub>. Due to its semi-metallic nature, TiSe<sub>2</sub> is conducive to forming excitons. Excitons are bound pair of electrons and holes, behaving like a boson. The interesting

thing about bosons is their nature to occupy the same state at fixed energy to form a condensate. As we decrease the temperature of  $\text{TiSe}_2$ , all the excitons try to occupy the same energy level and form a condensate making  $\text{TiSe}_2$  ground state unstable and transforming into a CDW phase. Excitonic insulator phase-induced CDW is not a forte of Peierls' model. As for  $\text{NbSe}_2$ , the metallic state gives rise to CDW and a superconducting phase at a lower temperature. CDW coexists with superconductivity. Material properties arise from the dynamics of electrons at the Fermi level. But in  $\text{NbSe}_2$  in CDW state, the role of the Fermi surface is kept at a minimum. The central stage is taken over by electron-phonon interaction. Tuning this interaction even slightly leads to CDW with different periodicities. By tuning it with strain, we explore the rich arena of CDW in  $\text{NbSe}_2$ .

CDW is real space modulation in charge density. The microscopic interaction interplay makes its impression on energy spectra. Considering Maslow's hammer, we used a scanning tunneling microscope (STM) to study two TMDC at an atomic scale to understand these phenomena in a better light. STM is based on the principle of quantum tunneling. When two metals in close proximity, electrons in the metal tunnel through the vacuum barrier between metals. We get a tunneling current if a small bias is applied between the metals. The working principle of STM is based on a sharp metal tip mounted on a piezoelectric drive scanning the surface in close proximity and measuring tunneling current as a function of position on the surface. Tunneling current carries information about the local electronic density of states of materials. By varying bias voltage, we can probe the occupation of energy states of the sample. Differential conductance measurements are performed by fixing the distance between the tip and sample and measuring current by varying the bias voltage. Impurities on the surface act as a scattering center, and by measuring the differential conductance map (spatially resolved map of differential conductance), STM allows us to measure the quasiparticle interference directly. A charge density manifests as a realspace phenomenon and changes in the energy states; STM is the perfect tool to understand CDW materials better. We began our search for microscopic clues for CDW in two TMDC.

We utilized intrinsic defects as a probe to understand the excitonic insulator phase of CDW in  $\text{TiSe}_2$ . The defects influence electronic states locally. We have explored defects at the atomic scale in two crystals of  $1T\text{-TiSe}_2$  grown using different methods.  $Ti$  atoms get intercalated in the van der Waals gap. We find that the density of  $Ti$  intercalation affects the long-range order of CDW. An increased concentration

of intercalant forces CDW to form domains. There is no phase shift across the domain walls. The correlation length of CDW is inversely proportional to the density of intercalated  $Ti$  atoms. Intercalation in  $1T$ - $TiSe_2$  suppresses CDW and forms domain boundaries that can be explained by the electron doping nature of  $Ti$ . Intercalated atoms reduce the number of holes in the system. In the excitonic condensation model of CDW formation, the reduction of hole concentration depletes excitonic bound states. CDW suppression is a direct consequence of excitonic bound state depletion. We demonstrated in our study that the dependence of correlation length on  $Ti$  intercalation supports the excitonic condensation model of the formation of CDW in  $1T$ - $TiSe_2$ .

The order parameter of the excitonic insulator CD state is a scalar entity. The order parameter is always represented as a scalar in all kinds of CDW phase transitions, irrespective of its microscopic origin. This scalar CDW order could couple to a chiral order in the system to generate the chiral CDW order phase. This chiral symmetry breaking happens due to electronic transition occurring at CDW transition. The  $TiSe_2$  CDW pattern's chirality depends mainly on the orbital ordering. The CDW phase in  $TiSe_2$  results from three independent charge density modulations related by  $C_3$  symmetry. Three CDW instabilities with nonzero relative phase difference and non-co-planar displacement patterns are essential for creating a chiral pattern in  $TiSe_2$ . The relative phase difference in three CDW order parameters originated from orbital ordering. Our analysis of the energy dependence of the orbital ordering effect on CDW intensity peaks in STM topography images leads us to conclude that the microscopic energetics of the occupied states also play a role than any overarching physical principle. The chirality of the charge density wave in  $TiSe_2$  can assist in determining the precise character of the driving force behind the transition as the orbital order has energy dependence.

The interplay of electrons and phonons affects and directs the formation of CDW. A strain can change the electron-phonon interaction in non-trivial ways. We uncovered a new commensurate  $3Q$  CDW phase, oriented along the  $\Gamma-K$  direction in strained  $2H$ - $NbSe_2$  crystal. Strain preserving the unit cell volume applied along the axis can stabilize CDW  $3Q$  ( $2\sqrt{3}a_0$  periodicity) geometry by affecting the electron-electron interaction. We also observed domains of the stripes of  $4a_0$  periodicity result from anisotropic phonon interaction. Microscopic variation of strain forms such a rich structure of different geometric phases of CDW. Our results added a new member to the menageries of the phases in  $2H$ - $NbSe_2$ . Illustrating the significant

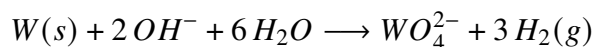
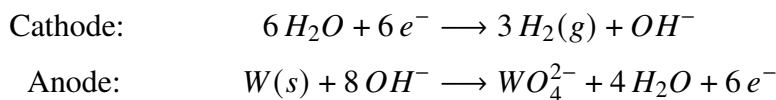
effect of small strain can be helpful in tuning charge ordering in other important materials. Our experimental results reaffirm the importance of strain as a tunable axis in the vast landscape of electronic phases of materials.

This work explored the microscopic mechanisms of the formation of CDW in relation to a broader landscape of CDW research. We begin with  $\text{TiSe}_2$  to understand the exciton insulator phase and its tunability with intrinsic defects. Our work on  $\text{TiSe}_2$  can be naturally extended to build theoretical models of defect and exciton interaction, experimental models, and practical utility for applications. The discovery of new CDW order in  $\text{NbSe}_2$  compelled us to look for a better explanation of phase transition rooted in the interplay of electron-electron and electron-phonon interaction. Strain tuning of CDW in  $\text{NbSe}_2$  changed the current view of its origin in electron-phonon interaction. Without missing the forest for a tree, Our small contribution to the field will help us build a general model for the CDW.

## Appendix A

### TIP PREPARATION

In a scanning tunneling microscope (STM), electrons tunnel across the potential barrier established between a sharp metal tip and conducting or semiconducting surface under an appropriate bias voltage. The resolution of the STM depends upon the quality of the tip. STM tips are generally fabricated from metal wires. Tungsten (W) wire is electro-chemically etched to fabricate good-quality tips. The electrochemical etching procedure involves the anodic dissolution of the metal electrode. For fabricating sharper tips, direct current (dc) etching is preferred. The “Drop off” method is used for dc etching; in this method, etching occurs at the electrolyte metal wire interface, and a portion of the wire drops off when its weight exceeds the tensile strength of the etched region. Schematic of the etching process is shown in the figure below. The electrochemical reaction involves the anodic dissolution of tungsten in aqueous base. The apparatus consists of a film of 2M NaOH solution on a metal ring (silver coated copper or platinum-iridium wire) acting as a cathode, and the W wire pierces the film at the center, acting as an anode. W wire is held with support, and a portion below the film is connected to a voltage source by a very thin copper wire. The thickness of the wire is 0.25 mm. Etching occurs at the meniscus formed by the electrolyte film at W wire when a positive bias is applied to the wire. The detailed chemical reactions [208] are below



W oxidizes to form soluble anion  $WO_4^{2-}$  at the anode, water reduces into hydrogen gas and  $OH^-$  ions at the cathode.  $E_0$  is the sum of the standard reduction potential (SRP) and standard oxidation potential (SOP) for tungsten. Etching starts when potential exceeds  $E_0$  value of 1.43 V. Voltage applied for etching is 4 V. Circuit breaks as wire falls down after etching completion due to the wire weight below the film. The tip is then cleaned with distilled water. Tips formed by this method are sharp and hyperboloidal in shape. Parameters that affect the sharpness of the tip are

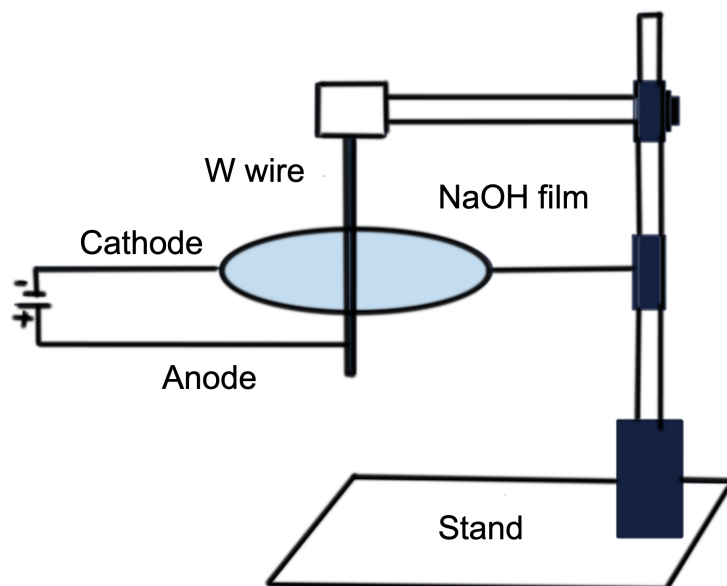


Figure A.1: Schematics of the tip preparation set-up

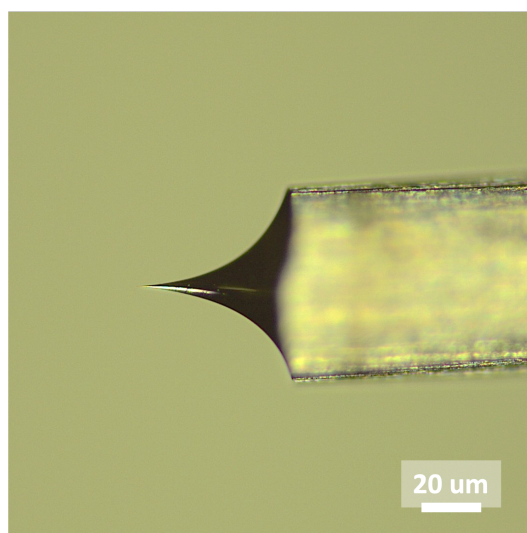


Figure A.2: Optical microscope image of *W*-tip after etching.

the length of the wire in the film; the voltage applied, and the cleaning procedure. An optical microscope is used to check the quality of the tip quickly. Figure [A.2](#) shows the tip etching setup and optical microscope image of a good tip below.

## *Appendix B*

### LAWLER-FUJITA CORRECTION ALGORITHM

#### B.1 Introduction

In essence, data acquired from Scanning Tunneling Microscopy (STM) or other Scanned Probe Microscopy (SPM) systems can all be condensed into 2D matrices, or stacks of such matrices in the case of  $dI/dV$  maps. These datasets, mathematically represented as  $\tau(\mathbf{r}, E)$ , encapsulate the recorded values (such as topographic height, tunneling current, or  $dI/dV$ ) corresponding to the tip's position  $\mathbf{r} = (x, y)$  and the tunneling energy  $E = eV_b$ , where  $V_b$  is the tunneling bias voltage. We'll omit the explicit energy dependence for brevity. However, within  $\tau(\mathbf{r})$  lies a wealth of valuable information, extending far beyond a visually appealing color-scale representation of the 2D matrix. This appendix will explore geometric phase analysis (GPA) [209–211]—a straightforward yet potent method for extracting the local amplitude and phase of spatial modulations in STM images. Beginning with the foundational mathematical concepts behind GPA, we'll conclude by highlighting one of its most practical applications in STM analysis: the Lawler-Fujita algorithm, designed to rectify images affected by temporal drift and piezo creep.

The perfect topographic STM image following the references [207, 209–213] would be expressed by

$$\tau(\mathbf{r}) = \sum_{\pm, q} A_q e^{-i\mathbf{g}_q \cdot \mathbf{r}} \quad (\text{B.1})$$

In this context,  $\mathbf{g}_q$  represents the  $q$  th Bragg vector and  $A_q$  stands for the corresponding Fourier amplitude of that mode. However, despite its visual appeal, scientifically, analyzing this dataset alone would be quite uninteresting. Fortunately, nature presents a much more intriguing scenario, where spatial irregularities within a crystal can disrupt this pristine picture. One of the initial deviations from this ideal scenario that we'll explore relates to variations in the amplitude of a specific periodicity. This exploration prompts us to reconsider the aforementioned equation, leading to a new formulation.



$$\tau(\mathbf{r}) = \sum_{\pm, q} A_q(\mathbf{r}) e^{-i\mathbf{g}_q \cdot \mathbf{r}} \quad (\text{B.2})$$

To extract the spatial amplitudes,  $A_q(\mathbf{r})$ , we adopt a strategy similar to an electronic lock-in amplifier. Our objective is to determine the intensity of a spatial oscillation characterized by a frequency or wavevector,  $\mathbf{g}_q$ . Analogous to the electronic scenario, we multiply our data signal, which may contain noise, by this designated input signal. Subsequently, we perform spatial averaging over a characteristic length,  $L$ . This process can be expressed mathematically as follows:

$$\sum_{\mathbf{r}'} \tau(\mathbf{r}) e^{-i\mathbf{g}_q \cdot \mathbf{r}'} \frac{1}{2\pi L} e^{\frac{-(\mathbf{r}-\mathbf{r}')^2}{2l^2}} = \sum_{\pm, q} \sum_{\mathbf{r}'} A_q(\mathbf{r}) e^{-i\mathbf{g}_q \cdot (\mathbf{r}-\mathbf{r}')} e^{\frac{-(\mathbf{r}-\mathbf{r}')^2}{2l^2}} \quad (\text{B.3})$$

The terms multiplying  $\tau(\mathbf{r})$  represent 2D Gaussian convolutions facilitating spatial averaging. The outcome on the right-hand side of the equation is to isolate solely the  $q$ th Fourier amplitude. This can be conveniently expressed as:

$$A_q(\mathbf{r}) = \sum_{\mathbf{r}'} \tau(\mathbf{r}) e^{-i\mathbf{g}_q \cdot \mathbf{r}'} \frac{1}{2\pi L} e^{\frac{-(\mathbf{r}-\mathbf{r}')^2}{2l^2}} \quad (\text{B.4})$$

Note that  $A_q(\mathbf{r})$  is a complex quantity, so it also contains the local phase information,  $\theta_q(\mathbf{r})$ . We can make this explicit by writing,

$$A_q(\mathbf{r}) = M_q(\mathbf{r}) e^{i\theta_q(\mathbf{r})} \quad (\text{B.5})$$

where  $M_q(\mathbf{r}) = |A_q(\mathbf{r})|$  is the magnitude of  $q$  th spatial mode. In practice, the magnitude is the more useful value.

While often focusing on the amplitude of a spatial modulation, the local phase information provides insights into the spatial variation of the associated wavevector. This relationship becomes apparent when combining equations:

$$\tau(\mathbf{r}) = \sum_q M_q(\mathbf{r}) e^{-i(\mathbf{g}_q \cdot \mathbf{r} + \theta_q(\mathbf{r}))} \quad (\text{B.6})$$

$$\tau(\mathbf{r}) = \sum_k M_q(\mathbf{r}) e^{-i(\mathbf{g}_q \cdot \mathbf{r} + \mathbf{g}_q \cdot \mathbf{u}(\mathbf{r}))} \quad (\text{B.7})$$

$$\tau(\mathbf{r}) = \sum_q M_q(\mathbf{r}) e^{-i\mathbf{g}_q \cdot (\mathbf{r} + \mathbf{u}(\mathbf{r}))} \quad (\text{B.8})$$

Here, we have expressed the local phase as

$$\theta_q(\mathbf{r}) = \mathbf{g}_q \cdot \mathbf{u}(\mathbf{r}) \quad (\text{B.9})$$

The vector  $\mathbf{u}(\mathbf{r})$  represents a local displacement field, essentially shifting atomic lattice positions at  $\mathbf{r}$  away from perfect periodicity by the displacement vector  $\mathbf{u}(\mathbf{r})$ . This property of the local phase information is particularly potent in identifying shifts or discontinuities within atomic lattices, a capability immensely valuable in analyzing crystal dislocations [210, 211]. In local phase maps, a solitary dislocation manifests as a vortex, where a discontinuous phase jump of  $\pm 2\pi n$  ( $n$  being an integer) occurs around the dislocation site. Beyond identifying atomic dislocations, these vector fields  $\mathbf{u}(\mathbf{r})$  prove beneficial in detecting physical strain within a crystal. Assuming the absence of temporal drift or systematic experimental errors in the scanning probe, the strain fields unveil the physical strain inherent in the system.

## B.2 Correction Algorithm

Depending on the image's pixel count and the scanning speed of the STM tip, acquiring a typical STM topographic image can take minutes to even an hour. More notably, conducting  $dI/dV$  spectroscopy maps can extend over several hours or days. Throughout this duration, the sample might drift concerning the scanning probe. One of the highly beneficial applications of geometric phase analysis in STM data involves extracting the displacement fields, denoted as  $\mathbf{u}(\mathbf{r})$ . These fields prove instrumental in isolating the pristine atomic lattice obscured within the drifted experimental data. Initially proposed by Lawler and Fujita [207], this algorithm found utility in detecting spatial symmetry disruptions within a single unit cell of BSCCO.

In a measured STM topograph or  $dI/dV$  map, the atomic lattice is distorted by  $\mathbf{u}(\mathbf{r})$ . The measured topography can be expressed using,

$$\tau(\mathbf{r}) = M_0 \sum_{\pm, q} e^{-i\mathbf{g}_q \cdot (\mathbf{r} + \mathbf{u}(\mathbf{r}))} \quad (\text{B.10})$$

Here, we've assumed a constant spatial amplitude, denoted as  $M_0$ , for simplicity. As explained earlier, in an ideally periodic lattice devoid of distortions, the

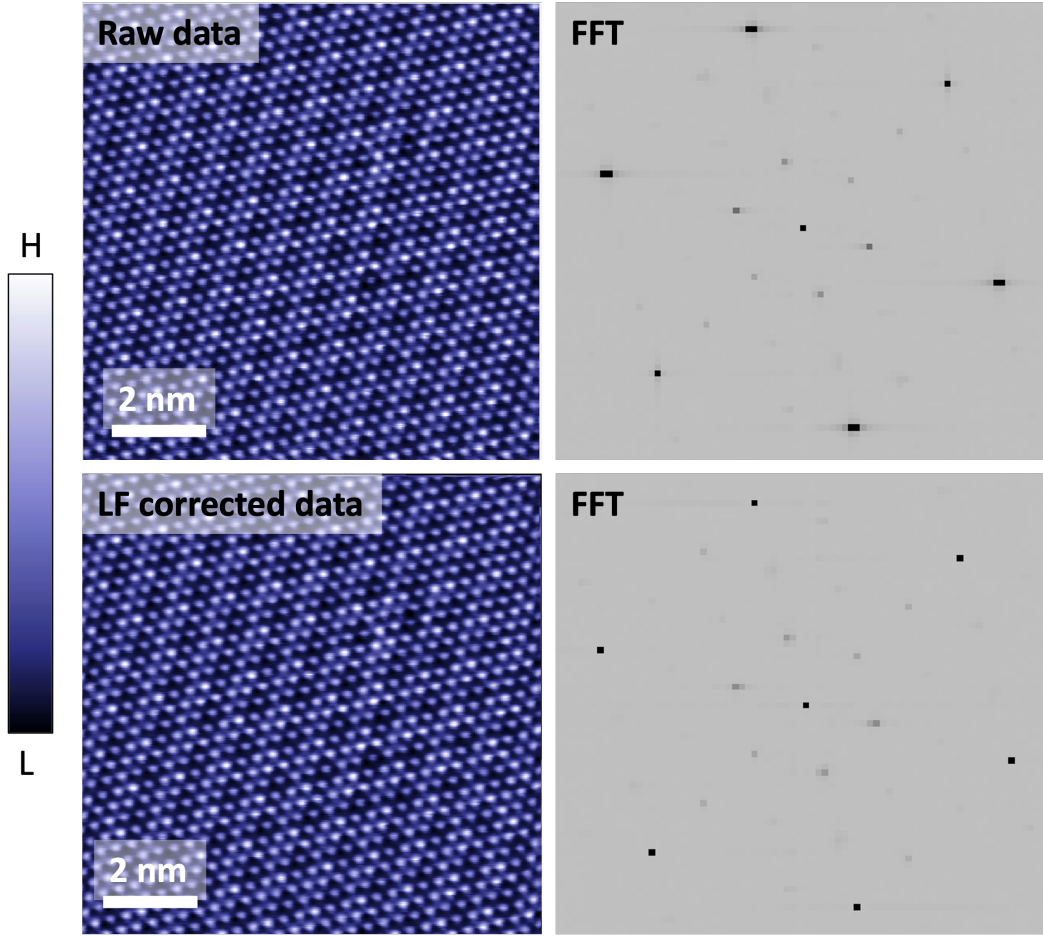


Figure B.1: FFT of raw and LF corrected data

local phase  $\theta_q(\mathbf{r})$  would remain constant across space. Therefore, our objective is to determine the affine transformation that aligns the distorted lattice with the perfect atomic lattice. Essentially, this involves finding the transformation that renders  $\theta_q(\mathbf{r})$  constant throughout space, denoted as  $\tilde{\theta}_q$ . Let  $\mathbf{r}$  represent a point on the distorted image measured and

$$\tilde{\mathbf{r}} = \mathbf{r} - \mathbf{r}(\mathbf{r}) \quad (\text{B.11})$$

the point on the corrected image. The transformation can be expressed by a system of equations:

$$\mathbf{g}_q \cdot \mathbf{r} + \theta_q(\mathbf{r}) = \mathbf{g}_q \cdot \tilde{\mathbf{r}} + \tilde{\theta}_q \quad (\text{B.12})$$

Just to clarify, the left-hand side represents the measured (distorted) spatial phases, while the right-hand side corresponds to the spatial phases in a perfectly periodic (undistorted) scenario after the transformation  $\mathbf{r} \rightarrow \tilde{\mathbf{r}}$ . Solving for  $\tilde{\mathbf{r}}$  and expressing the system of equations in matrix form results in:

$$\mathbf{G} \begin{bmatrix} \tilde{r}_x \\ \tilde{r}_y \end{bmatrix} = \mathbf{G} \begin{bmatrix} r_x \\ r_y \end{bmatrix} + \begin{bmatrix} \theta_1(\mathbf{r}) - \tilde{\theta}_1 \\ \theta_2(\mathbf{r}) - \tilde{\theta}_2 \end{bmatrix} \quad (\text{B.13})$$

$$\begin{bmatrix} \tilde{r}_x \\ \tilde{r}_y \end{bmatrix} = \begin{bmatrix} r_x \\ r_y \end{bmatrix} + \mathbf{G}^{-1} \begin{bmatrix} \theta_1(\mathbf{r}) - \tilde{\theta}_1 \\ \theta_2(\mathbf{r}) - \tilde{\theta}_2 \end{bmatrix} \quad (\text{B.14})$$

we see that the displacement field is given by

$$\mathbf{u}(\mathbf{r}) = \mathbf{G}^{-1} \begin{bmatrix} \theta_1(\mathbf{r}) - \tilde{\theta}_1 \\ \theta_2(\mathbf{r}) - \tilde{\theta}_2 \end{bmatrix} \quad (\text{B.15})$$

As an illustration, we applied LF correction to an STM image of NbSe<sub>2</sub> (as in Figure B.1) . The Fourier transform of the original image revealed dispersed Bragg peaks, a phenomenon stemming from measurement artifacts or intrinsic factors. By fitting Gaussians to locate the centers of these peaks, we used them as references for corrections. Leveraging these peak centers, we generated an accurate lattice by subtracting the calculated displacement field ( $\mathbf{u}(\mathbf{r})$ ). Consequently, the FFT peaks of the resulting image were precisely located at single pixels, indicating perfect periodicity. These displacement fields ( $\mathbf{u}(\mathbf{r})$ ) contain valuable information regarding thermal drift, piezo creep, and intrinsic strain within the sample.

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