Charge density wave order parameter revealed by scanning tunnelling microscopy

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Abstract
The charge density wave (CDW) phase in bulk and exfoliated crystals of transition metal dichalcogenides was studied by scanning tunneling microscopy (STM). In exfoliated flakes of VSe₂ we found a striking non-monotonic evolution of the CDW transition temperature as function of thickness derived from the analysis of the real space charge modulation amplitude imaged by STM. This finding lifts the contradiction of previous measurements. In bulk crystals of VSe₂, CuₓTiSe₂ and NbSe₂ we examined the CDW phase by our original method to extract the local amplitude, wavelength and phase of the CDW. This high resolution spatial mapping of the full complex order parameter provided unprecedented insight into fundamental aspects of CDWs. It experimentally proved that the CDW in these materials consist of three individual charge modulations. Furthermore, it explained the different contrasts often observed in STM images and revealed a rich variety of features like phase domains and topological defects.

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Charge Density Wave Order Parameter Revealed by Scanning Tunnelling Microscopy

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To Anna Dalma and Zsófi
Résumé

Les matériaux à dimension réduite, notamment les matériaux bidimensionnels, offrent beaucoup d’opportunités pour la recherche fondamentale et appliquée. L’exfoliation, soit le détachement du matériau en couches jusqu’à l’épaisseur d’une seule cellule unité, permet de concevoir et d’examiner en détail ces nouveaux matériaux aux propriétés extraordinaires.

Les dichalcogénures de métaux de transition (TMD) sont extrêmement attractifs dans ce contexte. C’est une famille de matériaux en couches avec une grande variété de propriétés chimiques qui peuvent être facilement exfoliés jusqu’à isoler une seule monocouche. Ces nanoflocons présentent des propriétés uniques et leur empilement dans des hétérostructures synthétiques offre des possibilités infinies pour concevoir de nouveaux matériaux fonctionnels.

Une compréhension approfondie de leurs propriétés massiques et en fonction de l’épaisseur est essentielle pour les appliquer dans de nouveaux dispositifs fonctionnels. L’épaisseur s’avère être un paramètre efficace pour contrôler les propriétés des phases électroniques corrélées, telles que les ondes de densité de charge (charge density wave - CDW) ou la supraconductivité. Ces phases électroniques quantiques peuvent jouer un rôle clé dans de futurs appareils aux fonctionnalités inédites et aux performances sans précédents.

Dans cette thèse, nous étudions la phase CDW dans des cristaux de TMD massiques et exfoliés par microscopie et spectroscopie à effet tunnel (STM/STS).

Dans un premier temps, nous avons développé une nouvelle technique d’exfoliation in-situ qui permet de préparer des nanoflocons de matériaux en couches dans un environnement sous ultra-haut vide (UHV). Nous avons conçu un outil pour exfolier des nanoflocons dans des conditions très contrôlées avec une large gamme d’épaisseurs et une couverture de substrat dense. Il est facilement adaptable à tout système UHV et permet d’étudier à différentes épaisseurs des nanostructures sensibles à une exposition à l’atmosphère par des sondes de surface. Cette approche nous a permis de réaliser une étude originale et détaillée de l’évolution de la CDW dans les échantillons de VSe$_2$ massifs et exfoliés en fonction de la température et de l’épaisseur.

Nous avons développé une méthode numérique pour extraire le paramètre d’ordre de la CDW en fonction de la température basé uniquement sur la modulation spatiale de la charge mesurée par STM. En appliquant cette analyse aux images STM obtenues sur des monocristaux (massifs) de VSe$_2$, nous avons établi une correspondance entre le paramètre
d’ordre mesuré à une température spécifique et la température de transition en utilisant une forme approximative de l’équation BCS du gap.

L’analyse du paramètre d’ordre obtenu à partir des images STM révèle une surprenante dépendance non monotone du paramètre d’ordre de la CDW et de la température critique en fonction de l’épaisseur dans les flocons exfoliés de VSe₂. C’est le premier résultat original obtenu dans le cadre de cette thèse. Lorsque l’épaisseur du nanoflocon décroît, la température de transition vers la phase CDW ($T_{CDW}$) diminue graduellement à partir de sa valeur massique jusqu’à environ 20 nm, puis elle augmente rapidement pour finalement dépasser la valeur massique de 30% dans l’échantillon le plus mince (2.2 nm). Les températures de transition que nous calculons sont en excellent accord quantitatif avec les valeurs obtenues dans des mesures de transport indépendantes. Nos expériences expliquent des mesures de transport apparentement contradictoires, qui trouvaient des dépendances opposées de $T_{CDW}$ en fonction de l’épaisseur. Nos données STM montrent que les deux expériences sont correctes. Les contradictions rapportées dans différentes publications sont la conséquence de mesures de gammes d’épaisseur différentes et ne se recouvrent pas. Elles n’ont en particulier aucun lien avec la qualité des échantillons ou les méthodes de préparation comme postulé dans la littérature.

Un autre résultat remarquable de notre analyse de la CDW en fonction de l’épaisseur du VSe₂ est que l’accroissement de la température de transition pour les échantillons les plus minces n’est pas dû au changement du régime de couplage, mais est probablement la conséquence directe du confinement dimensionnel. Notre analyse suggère en effet que la dépendance non monotone de $T_{CDW}$ en fonction de l’épaisseur est la conséquence d’un changement de la dimensionnalité et d’un confinement quantique entre le cristal massif et la monocouche.

Dans ce travail de thèse, nous avons aussi développé une méthode numérique originale pour obtenir des images du paramètre d’ordre complexe local de la CDW dans des cristaux de VSe₂, Cu₀.₀₂TiSe₂ et NbSe₂. Notre analyse permet d’obtenir des cartes de l’amplitude, de la longueur d’onde et de la phase du paramètre d’ordre CDW. Comme la méthode donne accès à la phase et à l’amplitude, nous l’appelons imagerie holographique. La capacité de cartographier le paramètre d’ordre CDW complexe complet avec une résolution spatiale de l’ordre de la longueur d’onde CDW offre un aperçu sans précédent des aspects fondamentaux des CDWs. En particulier, elle nous permet de démontrer de manière indiscutable que l’état fondamental de la CDW dans ces TMDs consiste en trois CDW individuelles liées par la symétrie cristalline dans le plan ab, où chaque composante développe sa propre configuration du...
paramètre d’ordre qui ont chacun ses caractéristiques propres.

L’imagerie holographique du paramètre d’ordre de la CDW fournit une explication originale aux différents contrastes observés dans les images STM de la CDW dans les TMDs. Ils ne sont pas le résultat de changements de pointes comme fréquemment proposé dans la littérature, mais s’expliquent naturellement par une variation de la configuration de la phase locale des trois CDWs.

L’imagerie holographique du paramètre d’ordre CDW complexe nous a permis d’identifier différents défauts, tels que des domaines de phase, des parois de domaines et des défauts topologiques. Dans Cu$_{0.02}$TiSe$_2$, nous avons trouvé que les parois de domaines de phase associées dans la littérature avec un changement de phase de $\pi$ ne correspondent en fait pas nécessairement à un déphasage $\pi$ du paramètre d’ordre de la CDW. Dans VSe$_2$ et NbSe$_2$, les images de la phase de la CDW révèlent des vortex et des anti-vortex, c’est-à-dire des défauts topologiques autour desquels la phase du paramètre d’ordre s’enroule par multiples de $2\pi$. Les images montrent des paires vortex-antivortex étroitement liées ou bien séparées. Une caractéristique remarquable de ces images est de voir que la nature et la distribution des défauts sont distinctes pour chaque CDW. Par ailleurs, dans NbSe$_2$, notre imagerie holographique a fourni la première image à haute résolution de $\ll$discommensurations$\gg$ individuelles, un défaut particulier dans la phase des CDWs dites $\ll$quasi-commensurées$\gg$ prédit dans les années 1970.

La cartographie du paramètre d’ordre complexe des CDWs, c’est-à-dire des images de la phase, de l’amplitude et de la période de la CDW dans l’espace réel avec haute résolution spatiale, offre de nouvelles possibilités d’études des CDWs. Elles ont le potentiel de contribuer à une meilleure compréhension des CDWs qui sont loin d’être compris et font toujours l’objet de recherches soutenues. Le(s) mécanisme(s) à l’origine de la transition de phase CDW, la bande interdite associée dans la densité d’état électronique et leurs interactions avec d’autres phases électroniques corrélées à l’échelle nanométrique sont quelques-uns des thèmes que l’imagerie holographique va contribuer à mieux comprendre.
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<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>1D</td>
<td>one dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>two dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>three dimensional</td>
</tr>
<tr>
<td>ARPES</td>
<td>angle-resolved photoemission spectroscopy</td>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>BCS</td>
<td>Bardeen-Cooper-Schrieffer</td>
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<tr>
<td>CDW</td>
<td>charge density wave</td>
</tr>
<tr>
<td>DCs</td>
<td>discommensurations</td>
</tr>
<tr>
<td>LDOS</td>
<td>local density of states</td>
</tr>
<tr>
<td>MBE</td>
<td>molecular beam epitaxy</td>
</tr>
<tr>
<td>NC-CDW</td>
<td>nearly commensurate charge density wave</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>πDW</td>
<td>$\pi$-phase shift CDW domain walls</td>
</tr>
<tr>
<td>PLD</td>
<td>periodic lattice distortion</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunnelling microscopy</td>
</tr>
<tr>
<td>STS</td>
<td>scanning tunnelling spectroscopy</td>
</tr>
<tr>
<td>TDs</td>
<td>topological defects</td>
</tr>
<tr>
<td>TMD</td>
<td>transition metal dichalcogenide</td>
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<tr>
<td>UHV</td>
<td>ultra high vacuum</td>
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Chapter 1

Introduction

The 20th century brought us the fastest and probably greatest technological development in the history of mankind. The widespread of electricity brought light to millions of homes, and initiated the invention of a vast amount of household appliances. Transportation became faster than ever, myriads of flights crossing the skies daily and fast automobiles running on endless highways. Information spreads even faster and reaches people all over the world through the radio, the television and the internet. Meanwhile computers became an integral part of our everyday life. Electronics is at the forefront of this development and electronic devices changed our lifestyle, our society and the way we think about the world.

In the 21st century we have to face new challenges such as the global climate change, the overpopulation, the environmental pollution and the sustainability of the exponentially fast development started in the last century. According to Moore’s law [1] the number of transistors in an integrated circuit doubles about every two years, a trend which is fuelled by a huge social and economical demand.

Novel advanced materials will play a crucial role in finding solutions to these problems. In particular, materials with reduced dimensionality, so called two-dimensional materials, offer tremendous opportunities. Exfoliation, namely the peeling of layered materials down to a single unit-cell thin foil, enables the design and fundamental investigation of these new materials with potentially unprecedented properties.

Transition metal dichalcogenides are extremely appealing in this context. This is a chemically versatile family of layered materials which can be easily exfoliated down to the monolayer. While these nanoflakes already show unique properties, their stacking into synthetic heterostructures provides literally infinite possibilities to design novel functional
However, a comprehensive understanding of their properties in the bulk form, and as a function of thickness is essential to apply them in functional devices. Thickness can be an effective tuning parameter of properties of correlated electronic phases such as charge density waves or superconductivity. These phases may play a key role in future devices with novel functionalities and optimal performances.

The charge density wave phase is of great interest also from a fundamental physics point of view. Its formation mechanism and interplay – competition, coexistence or promotion – with other ordered electronic phases, like superconductivity, are still under debate and intense scrutiny.

The focus of my PhD thesis is on characterizing the charge density wave phase in bulk and exfoliated transition metal dichalcogenides by means of scanning tunnelling microscopy. My original contributions are a novel scheme to map the full complex charge density wave order parameter in real space and a complete study of the thickness dependence of the charge density wave in exfoliated VSe$_2$. These studies are described in details in Chapter 6 and 7. I also had the opportunity to contribute to several other topics during the course of my PhD studies. They are briefly introduced in the appendices to this thesis. Some of the work discussed in the present thesis has been published [2, 3, 4, 5] or is currently under review [6]. Therefore, part of the text is largely inspired from those manuscripts, but the experiments and data are discussed in more details.

The thesis is organized as follows. In Chapter 2 we summarize selected aspects of the charge density wave state. Chapter 3 is dedicated to the introduction of the materials studied in this thesis, as well as to give a brief outlook in terms of emerging materials and open questions. Chapter 4 is about scanning tunnelling microscopy and the in-situ preparation of exfoliated flakes, which are the main experimental methods that we applied and developed in this project. In Chapter 5 we describe the quantitative methods that we used to analyse the experimental data. The study of the spatially averaged charge density wave order parameter in bulk and exfoliated VSe$_2$ is presented in Chapter 6 which is followed by the holographic imaging of the local complex charge density wave order parameter in Chapter 7. Chapter 8 presents a summary of the accomplished studies and a brief outlook on future possible investigations. In the appendices, we discuss an unpublished work (A) and briefly present two published studies I have contributed to (B [4] and C [5]) also including their first pages.

Atomic force microscopy and scanning tunnelling microscopy images
are presented – if it is not stated or marked otherwise – with color mapping where the dark and bright colors correspond to low and high values, respectively. Numerical values are marked only when they carry relevant information. Equations and references are numbered in the order of appearance and are parenthesized in (round) and [square] brackets. Chapter numbers are referenced as a plain number, e.g Chapter 1.
Chapter 2

Charge density waves

Electronic phases with broken symmetry are of central interest in solid state physics research. Spontaneous symmetry breaking occurs when the physically realized state does not have all the symmetry of the Hamiltonian describing the system. It is a common phenomenon with the probably best known examples of ferromagnetic and superconducting ground states where the continuous spin-rotational and gauge invariance symmetries are broken, respectively. An inhomogeneous charge distribution in the electronic subsystem with a periodicity different from the underlying atomic lattice breaks the discrete translational symmetry of the crystal. Such a symmetry breaking electronic phase is called charge density wave (CDW). In this chapter we review selected aspects of this ordered electronic phase. A more comprehensive overview is given by a number of great reviews and books [7, 8, 9, 10, 11] which also served as a point of reference in writing this chapter.

2.1 Peierls transition and Kohn anomaly

The CDW ground state is a coherent superposition of electron-hole pairs driven by electron-phonon or electron-electron interaction. Peierls [12] showed that a one dimensional (1D) metal coupled to the underlying atomic chain is unstable against the simultaneous formation of a charge density wave and a periodic lattice distortion (PLD). In the PLD the ions have a periodically modulated displacement with respect to their original equilibrium position, while in the CDW phase the charge density has a periodic spatial modulation. It is described by an amplitude ($\rho_1$), wave- or ordering vector ($\mathbf{q}_0$) and phase ($\varphi$) [11]:
\( \rho(r) = \rho_0 + \rho_1 \cdot \cos(q_0 \cdot r + \varphi), \) \hspace{1cm} (2.1)

where \( \rho_0 \) is the electron density in the normal state. As we will see, within the mean-field approximation the \( \rho_1 \) amplitude is proportional to the gap in the single particle spectrum opening due to the formation of the CDW. The wavevector connects the electron-hole pairs in momentum space that form the CDW condensate, while the phase describes the relative position of the CDW with respect to the atomic lattice.

The displacement of the ions is modulated by the same wavevector with a \( u_0 \) amplitude which is typically much smaller than the atomic lattice constant\(^1 \): \( u_0/a \ll 1 \)

The formation of such a modulation of the charge density and the atomic displacements clearly has a Coulomb and an elastic energy cost. In the Peierls model this energy cost is compensated by the opening of a gap in the single particle spectrum at the Fermi energy. The energy of empty and occupied states are pushed up and down respectively resulting in a net band energy gain which compensates for the Coulomb and the elastic energy cost.

The **Peierls transition** is the consequence of a strong electron-phonon coupling and a quantitative mean-field description can be developed starting from the Fröhlich Hamiltonian of electron-phonon interactions (neglecting the spin):

\[
H_F = \sum_k \varepsilon_k c_k^\dagger c_k + \sum_q \hbar \omega_q b_q^\dagger b_q + \frac{1}{\sqrt{L}} \sum_{k,q} g_q c_{k+q}^\dagger c_k (b_{-q}^\dagger + b_q), \quad (2.2)
\]

where \( c_k^\dagger (c_k), b_q^\dagger (b_q) \) are the electron and phonon creation (annihilation) operators with momenta \( k \) and \( q \), \( \varepsilon_k \) and \( \omega_q \) are the electron and phonon dispersions, and \( g_q \) is the electron-phonon coupling (assumed to be independent of \( k \)).

In this model, by comparing the elastic energy of the lattice distortion and the band energy change of the system one finds the instability condition for the formation of a CDW:

\[
\frac{4g_q^2}{\hbar \omega_q} > \frac{1}{\chi_0(q)}, \quad (2.3)
\]

where

\[
\chi_0(q) = \frac{1}{L} \sum_k \frac{f_{k+q} - f_k}{\varepsilon_k - \varepsilon_{k+q}} > 0 \quad (2.4)
\]

\(^1\)This is the condition in the so-called _weak coupling_ limit described in this chapter.
is the non-interacting electron susceptibility, $f_{\mathbf{k}}$ represents the $f(\varepsilon_{\mathbf{k}})$ Fermi function and $L$ is the length of the 1D atomic chain.

As a result of the electron-phonon interaction, the phonon energies are also modified and the renormalized phonon frequencies ($\tilde{\omega}_{\mathbf{q}}$) depend on the electron-phonon coupling and on the electron susceptibility:

$$\tilde{\omega}_{\mathbf{q}}^2 = \omega_{\mathbf{q}}^2 \left( 1 - \frac{4g_{\mathbf{q}}^2}{\hbar \omega_{\mathbf{q}}} \chi_0(\mathbf{q}) \right). \quad (2.5)$$

The softening of the phonon modes due to the electron-phonon interaction is called the Kohn anomaly (see Figure 2.2) [10, 13, 14].

![Figure 2.1: Susceptibility of the 1D electron gas as a function of wavevector.](image)

At $T=0$ K the susceptibility $\chi_0(\mathbf{q})$ is divergent (Figure 2.1) at the double of the Fermi wavevector $k_F$, the corresponding phonon mode $\mathbf{q}_0 = 2k_F$ is entirely softened: $\tilde{\omega}_{2k_F} = 0$ and the condition (2.3) is satisfied: the system forms a CDW/PLD phase.

The divergence of the susceptibility is due to the particular topology of the Fermi surface of the 1D free electron gas: it is composed of parallel planes at $\pm k_F$ [8]. This property is called perfect nesting of the Fermi surface. Although, the two (2D) and the three dimensional (3D) free electron gas do not have this property the notion of Fermi surface nesting can be transferred to higher dimensions: a Fermi surface with extended parallel sections. Such topology can be found in several models. For instance, the tight-biding model of the 2D square lattice with a nearest-neighbour interaction at half-filling shows a perfectly nested square Fermi surface [15].
Chan and Heine [16] extended the above model by including the Coulomb and exchange interactions and found the following CDW formation criteria:

\[
\frac{4g_q^2}{\hbar \omega_q} - 2\tilde{U}_q + \tilde{V}_q \geq \frac{1}{\chi_0(q)}, \tag{2.6}
\]

where \(\tilde{U}_q\) and \(\tilde{V}_q\) are the average Coulomb and exchange energies, respectively, with \(2\tilde{U}_q > \tilde{V}_q\). In spite of the simplifications (e.g. k independence), condition (2.6) is a good intuitive starting point for the interpretation of experiments. It shows that the CDW formation is favoured by

- a strong electron-phonon coupling (large \(g_q\)),
- a softening of phonon modes (small \(\omega_q\)),
- a weak Coulomb interaction (small \(\tilde{U}_q\)),
- a strong electron-electron exchange (large \(\tilde{V}_q\)) and
- a large non-interacting susceptibility (large \(\chi_0(q)\)) determined by the Fermi surface topology.

### 2.2 Transition temperature and energy gap

As symmetry cannot change continuously, it is either absent or present, the ordering and symmetry breaking must happen at a defined temperature. This temperature is the transition temperature \((T_P)\) of the CDW phase. Within the Peierls model the CDW condensate forms at the temperature where (2.6) is first satisfied. At finite temperature \(\chi_0(q_0)\) is also finite, though it is peaked around \(q_0 = 2k_F\) with an increasing peak height with decreasing temperature [8]. Upon lowering the temperature one eventually reaches the giant Kohn anomaly with a renormalized phonon frequency of \(\tilde{\omega}_{q_0} = 0\) (see Figure 2.2). The complete softening of the phonon mode, which now can be macroscopically populated, signals a phase transition to a phase with a static lattice deformation. The inequality (2.6) is satisfied\(^2\) and a CDW/PLD phase develops.

In a tight-binding model with a full bandwidth of \(2D\) the mean field transition temperature [10] is

\[
k_B T_P = \frac{2e^\gamma}{\pi} D e^{-1/\lambda}, \tag{2.7}
\]

\(^2\)Conditions (2.3) and (2.6) can be obtained from the \(\tilde{\omega}_{q_0} = 0\) equation in the different approximations. For instance, (2.3) is obtained from the condition that (2.5) vanishes.
2.2 Transition temperature and energy gap

Figure 2.2: Kohn anomaly [13] as function of temperature ($T_3 > T_2 > T_1 > T_P$): the softening of the phonon mode is strongest at $q = 2k_F$ and upon approaching the transition temperature. Reproduced from [10].

where $\gamma$ is the Euler-Mascheroni constant ($0.577$), $k_B$ is the Boltzmann constant and

$$\lambda = \frac{2g_{q_0}^2 N(\varepsilon_F)}{\hbar \omega_{q_0}},$$

(2.8)

is called the dimensionless electron-phonon coupling constant with $N(\varepsilon_F)$ being the density of states at the Fermi energy.

Figure 2.3: Normalized order parameter amplitude ($\Delta/\Delta(T = 0)$) as a function of the reduced temperature ($T/T_P$). The temperature dependence of the order parameter follows the BCS form.

Below the transition temperature, a gap ($\Delta$) opens in the single particle spectrum at the Fermi energy. It is determined by the Bardeen-Cooper-Schrieffer (BCS) [17, 18, 19] gap equation and its temperature
dependence follows the characteristic BCS form [11] shown in Figure 2.3. The minimization of the total (lattice and band) energy with the tight-binding band leads to the zero-temperature energy gap [9, 10] of

\[ \Delta(0) = 2De^{-1/\lambda}. \] (2.9)

Combining this with equation (2.7), we find the well-known BCS relation between the zero-temperature energy gap and the mean-field transition temperature:

\[ 2\Delta(0) = 3.52k_B T_P. \] (2.10)

### 2.3 Geometrical characteristics

In a general three-dimensional (3D) case, the ordering vector can be given in terms of the \( a^*, b^* \) and \( c^* \) reciprocal lattice vectors: \( q_0 = \alpha a^* + \beta b^* + \gamma c^* \). If any of the real numbers \( \alpha, \beta \) and \( \gamma \) are irrational, we talk about an incommensurate ordering. On the other hand, if they are all rational numbers we talk about a commensurate ordering [20]. In case of layered materials, ordering along and perpendicular to the layers are often distinguished and \( q \) is decomposed as \( q_0 = q_\parallel + q_\perp \), where \( q_\parallel = \alpha a^* + \beta b^* + 0c^* \), \( q_\perp = 0a^* + 0b^* + \gamma c^* \). The layers define the ab-plane direction and the c-axis defined along the direction perpendicular to the layers. In the literature, the real space periodicity of the CDW modulation is often given in terms of the lattice vectors, for example for a triangular lattice the \( 2a \times 2a \times 2c \) notation means that the CDW lattice constants are two times longer than the atomic lattice constants both in the in- and out-of-plane directions. The rotation of the atomic and CDW modulations are not included in this notation and is usually given separately. For the compounds considered in this thesis, the atomic and CDW modulations are aligned (e.g. along \( a^* \)) and the question of commensuration reduces to the relative length of the atomic reciprocal lattice constant and the CDW ordering vector.\(^3\) In that case a CDW is called commensurate if there exist relative prime numbers \( n \) and \( m \) such that

\[ |a^*| = \frac{n}{m} |q_\parallel|. \] (2.11)

\(^3\)In textbooks and reviews they usually discuss the most simple 1D case. In this case the atomic lattice modulation wavelength and the lattice constant numerically coincide. However, this is not necessarily the case in 2D, for example for the triangular lattices discussed in this thesis. In the description here, we would like to give general definitions that hold true in two and three dimensions.
If $|q|/|a^*|$ is irrational the CDW is called incommensurate. In this case, the CDW and atomic modulations do not have a common periodicity.

While the above definitions are rather precise from a crystallography point of view, very often another interpretation of commensuration is used in practice, motivated by the fact that $n$ is very often equal to 1. For instance, for all the materials we study in this thesis $n = 1$ and $m = 2, 3 + \delta$ or 4, where $\delta$ is not an integer. In such a case, the community call a CDW commensurate if $m$ is an integer number: "the CDW modulation length is an integer multiple of the atomic one". CDWs that are close to being commensurate are often called nearly-commensurate meaning that their wavelength is close (e.g within a few percent) to being an integer multiple of the atomic modulation length. In the next section we will see that such CDWs can have very interesting properties.

### 2.4 Order parameter, collective and topological excitations

Besides the above formal similarity between BCS superconductors and CDWs in terms of the energy gap, they are both described by a complex order parameter. In case of the CDW it is defined as

$$\Psi = \Delta e^{i\varphi} = g_{q_0} \left\langle b_{q_0} + b_{-q_0}^\dagger \right\rangle.$$  \hspace{1cm} (2.12)

The absolute value of $\Psi$ gives the temperature dependent energy gap and $\Psi$ determines the periodic displacement of the ions:

$$\langle u(R_n) \rangle \propto \Delta \cos(q_0 \cdot R_n + \varphi),$$  \hspace{1cm} (2.13)

where $R_n$ is the n-th atomic position in the chain. Similarly the modulation of the charge density is

$$\delta \rho(r) = \rho(r) - \rho_0 = \rho_1 \cdot \cos(q_0 \cdot r + \varphi) \propto \Re \left( \Psi e^{i q_0 r} \right).$$  \hspace{1cm} (2.14)

In general the order parameter can have both spatial and time dependences $\Psi = \Psi(r, t)$ leading to collective and topological excitations [10]. The collective modes are related to oscillations of the amplitude and the phase of the order parameter. They are called *amplitudons*.

---

\(^4\)In practice, due to the finite precision of digits, we always measure a rational number for such a ratio. Thus the above convention may fail in practice. A better definition is given by the temperature dependence of the ratio. If it is independent of temperature the CDW is commensurate otherwise incommensurate.
and *phasons*. The oscillations of the amplitude of the CDW lead to periodic charge accumulations or depletions. Thus, the energy of the amplitudons is finite even in the long-wavelength limit. The phasons are the low-energy collective excitations of an incommensurate CDW as its phase is not pinned to the lattice. The dispersion relation of amplitudons and phasons in an incommensurate CDW near \( q=0 \) is shown in Figure 2.4. In a commensurate CDW the maxima and the minima of the charge density are arranged relative to the atomic lattice in a way that it minimizes the energy. Any fluctuations of the phase has a finite energy cost which lifts the long-wavelength softening of phasons.

![Dispersion relation of amplitudons and phasons in an incommensurate CDW near \( q=0 \).](image)

In case of the above collective excitations the deformation of the order parameter was small. However, there exist other types of excitations with a strong variation of the order parameter. In a commensurate CDW with \( n = 1 \) there are \( m \) degenerate ground states with phase difference of \( 2\pi/m \). Such ground states can be realized in different parts of the sample at distinct pinning centres (e.g at the end of the chain, at contacts, at impurities and defects which are discussed in the next section). Transition between these energetically equivalent deformation patterns happens in domain walls where the CDW is either compressed or stretched. This can be described by the sine-Gordon equation [10] leading to solitary wave solution. These *solitons* are topological excitations of the CDW state which can propagate along the chain carrying a net charge and spin. Not only the phase of the CDW can have a strong spatial variation, but also the amplitude: *amplitude solitons* can exist in incommensurate CDWs [10].
Figure 2.5: A schematic representation of the spatial evolution of the phase of the 1D CDW. In a commensurate CDW (yellow line) the charge modulation is locked to the atomic lattice and the phase remains constant with position. In case of an incommensurate CDW (green line) the phase depends linearly on position. In systems with nearly-commensurate CDW (red line) phase-locked and rapidly varying phase regions (discommensurations) form.

McMillan [21] proposed that a nearly-commensurate CDW can gain energy by forming locally phase-locked areas that are separated by regions with rapidly changing phase. These regions -with a typical core size of the order of a few nanometer for TaSe$_2$- are called discommensurations (DC). In spite of a different formation mechanism, they are analogous to the phase solitons of the commensurate CDW described above. Thus, a sequence of DCs is often called a soliton lattice. The spatial evolution of the phase of a 1D CDW is summarized in Figure 2.5.

### 2.5 Fukuyama-Lee-Rice model of impurity pinning

Incommensurate charge density waves have an energetically degenerate position with respect to the atomic lattice. Such a CDW could in principle slide over a perfect atomic lattice and carry an electric current without dissipation. This is the fundamental idea behind Fröhlich’s theory of superconductivity [22]. While his theory may explain zero-resistivity in a perfect lattice, it fails to account for the Meissner-effect, and it cannot be applied to realistic systems due to the presence of de-
Defects and impurities play an important role in determining the local order parameter of the CDW phase. A good starting point in the theoretical description of this problem is given by the model of Fukuyama, Lee and Rice (FLR model) [23, 24, 25]. They study the interaction of a 1D CDW with impurities at low temperature where amplitude fluctuations are negligible. The impurity potential may distort the CDW to minimize Coulomb energy, while this distortion costs an elastic deformation energy to the CDW. These two competing energy terms are compared in the FLR model.

The impurity potential is modelled by a local short ranged potential in the form of
\[ v(r) = \sum_i v_0 \delta(r - R_i) \]
where \( R_i \) is the location of the \( i \)-th impurity. Hence, the interaction energy of the CDW with the impurities is given by:

\[ E_{imp} = \int d\mathbf{r} \rho(\mathbf{r}) \cdot \sum_i V_0 \delta(\mathbf{r} - \mathbf{R}_i), \] (2.15)
where \( \rho(\mathbf{r}) \) is the charge density given in (2.1). Assuming that \( \varphi = \varphi(\mathbf{r}) \) in (2.1) we get:

\[ E_{imp} = V_0 \rho_1 \sum_i \cos(q_0 R_i + \varphi(R_i)). \] (2.16)

The deformation energy [10, 23, 26, 27] is given by

\[ E_{el} = \frac{\hbar v_F}{4\pi} \int d\mathbf{r} (\nabla \varphi(\mathbf{r}))^2, \] (2.17)
where \( v_F \) is the Fermi velocity.

The system can gain energy by pinning at the impurity sites by adjusting its phase to \( q\mathbf{R}_i + \varphi(\mathbf{R}_i) = -\pi \). In this case the impurity energy gain is \( V_0 \rho_0 \). However, this has an elastic energy cost of \( \hbar v_F \) per impurity. The \( \epsilon = V_0 \rho_0 / n_i v_F \) dimensionless parameter characterizes the pinning strength and separates two extreme cases.

The \( \epsilon >> 1 \) limit corresponds to strong pinning which is realized either by having a strong impurity potential or a dilute impurity concentration. In this case the CDW is pinned at every impurity site to the \( q\mathbf{R}_i + \varphi(\mathbf{R}_i) = -\pi \) value by distorting the CDW.

The opposite limit \( \epsilon \ll 1 \) is the weak pinning regime where the phase smoothly varies over the randomly distributed impurities with the total phase \( q_0 \mathbf{R}_i + \varphi(\mathbf{R}_i) \) having almost random values. In fact,

\footnote{we will refer to both simply as impurity}
2.5 Fukuyama-Lee-Rice model of impurity pinning

Figure 2.6: Impurity pinning of a CDW in the Fukuyama-Lee-Rice model: the phase of the CDW as function on position. Dots are denoting atomic positions while the letter "i" marks the impurity sites. (a) In a defect-free crystal the phase (green) of a commensurate CDW is constant. (b) In case of strong pinning the phase (blue) has abrupt variation at each impurity site. (c) While in the weak pinning limit a smooth variation of the phase (red) expected over a interval larger than the average impurity distance. Figure is based on Figure 3 of ref [26].

it is not totally random as the system can gain energy by properly distorting the equilibrium phase to exploit fluctuations of the impurity distribution [24, 28]. In the weak pinning limit of the FLR model, the system forms distinct domains within which the phase smoothly varies over a length scale which is much longer than the average impurity distance [24, 26]. The impurity concentration determines the domain size whose characteristic length $L_0$ is calculated as $L_0 = A_0 \cdot n_i^{-1/3}$, where $A_0 = (3 \cdot V_0 \rho_0 / \pi v_F)^{-2/3}$. The spatial variation of the phase of the CDW in the different pinning regimes is visualized in Figure 2.6 for a 1D CDW. While the original discussion is focused on the one dimensional case the general consideration can also be applied to higher dimensions. For instance, the domain size in 2D is predicted to be $L_0 \propto n_i^{-1/2}$ [24].
### 2.6 Symmetry and order parameter

In Section 2.4 we have seen that the order parameter of the CDW state is a complex quantity with an amplitude and a phase which is closely related to the spatial modulation of the charge density (see (2.14)). In this thesis we study layered materials (see Chapter 3) that all have a crystal structure with a three-fold symmetry in the ab-plane (along the layers, see in Figure 3.1). This crystal symmetry implies that if there exists an ordering vector $\mathbf{q}_1$ for which the formation of a CDW is favourable in the ab-plane, there are two other momentum vectors $\mathbf{q}_2$ and $\mathbf{q}_3$ for which the CDW formation is equally favourable. These three $\mathbf{q}$-vectors are connected by a three-fold $2\pi/3$ rotation symmetry and are often referred to as the three components of the tri-directional CDW. The total spatial modulation of the charge density can be expressed as the sum of these three charge density modulations:

$$
\delta \rho(r) = \sum_{n=1}^{3} A_n \cos(q_n \cdot r + \varphi_n) 
$$

(2.18)

where $A_n$, $q_n$ and $\varphi_n$ are the corresponding amplitude, ordering vectors and phase shifts in the three directions. This form of the total charge modulation strongly suggests to define a $\Psi_n$ order parameter direction by direction:

$$
\Psi_n = A_n e^{i\varphi_n}.
$$

(2.19)

The total charge density modulations is given by:

$$
\delta \rho(r) = \sum_{n=1}^{3} \Re \left( \Psi_n e^{i\mathbf{q}_n \cdot r} \right).
$$

(2.20)

The formulation of the total charge density modulation derived from the sum of the order parameters for each direction will be exploited in Chapter 5, while its physical meaning and consequence will be discussed in Chapter 7.
Chapter 3

Materials

In the wake of the systematic exfoliation of graphite into one atom thin carbon sheets, an increasing number of layered compounds can now be isolated from their bulk matrix in the form of one to few unit-cell thin layers [29]. These sheets often feature unique [30, 31, 32] or enhanced [33, 34] properties in comparison to their parent bulk compounds. They depend on material thickness and can be further tuned through doping, electrostatic gating [35] and assembly of distinct layers into complex heterostructures [29, 36]. Transition metal dichalcogenides (TMDs) are of particular interest in this context.

3.1 Transition metal dichalcogenides

Transition metal dichalcogenides (MX$_2$) are layered materials where each slab is composed of a triangular metal layer M (e.g. Mo, Nb or V) sandwiched between two triangular chalcogen X (S, Se, Te) sheets. While the intra-layer M-X bonds are predominantly covalent in nature, the slab stacking is maintained by weak van der Waals (vdW) forces [37]. Different polytypes of the same compound vary in stacking order of the slabs and in the metal atom coordination within the chalcogen matrix. In this thesis we study materials which belong either to the 1T or to the 2H polytype. In the 1T polytype the unit cell is composed of a single slab and the metal atom sits in the center of a chalcogen octahedron. In the 2H polytype the metal atom has a trigonal prismatic coordination and two slabs are involved in the unit cell. One may further distinguish different stacking (a,b or c type) of the layers in the unit cell of the 2H type compounds [38]. In the 2Ha polytype the stacking is AbA CbC: the transition metal atoms are aligned along the c-axis.
(perpendicular to the layers). This configuration is found for example in 2H-NbSe₂ and 2H-TaSe₂ [39]. In the 2Hc stacking the transition metal atoms sit on top of two calcogen atoms of the adjacent layers along the c-axis. Such a CaC AcA stacking is accommodated in the famous 2H-MoS₂ [39]. The 2Hb polytype is found in non-stoichiometric compounds where the excess metal atoms intercalated between the layers, for example in Nb₁₊ₓSe₂ [38]. Note that all three compounds studied in this thesis (1T-VSe₂, 1T-Cu₀.₀₂TiSe₂, 2H-NbSe₂) have a crystal structure with a three-fold symmetry in the ab-plane, regardless of their specific polytype (1T or 2H). In Figure 3.1 we show the 1T ((a) and (b)) and the 2Hc ((c) and (d)) in top ((a) and (c)) and side ((b) and (d)) views. During this thesis we often use a shorthand notation for the compounds name by omitting the prefix of the polytype (e.g VSe₂ instead of 1T-VSe₂).

Figure 3.1: Crystal structures of transition metal dichalcogenides in the 1T (a,b) and in the 2Hc (c,d) polytype. Note the three-fold rotational symmetry around the c-axis. Figure has been produced using VESTA [40].

The large number of possible combinations of the transition metal and chalcogen atoms and the different possible polytypes of the same compound make TMDs a chemically extremely versatile family of materials. They span the entire range of electronic structures, from insulator
to metal, and due to the weak bonding of the adjacent layers they can be readily exfoliated into thin flakes down to the single unit-cell limit [41]. This offers a unique playground for studying the thickness dependence of their electronic properties. For example, in MoS$_2$, photoactive transitions become available in the single layer limit due to the appearance of a direct gap in the band structure [42].

Metallic TMDs host a variety of electronic phases like superconductivity and charge density waves (CDW) [43, 44, 45, 46, 47, 48]. A deep understanding of these ordered electronic phase and the ability of tuning them is essential to exploit them in actual device configurations. The main scope of this thesis is to study the CDW state of VSe$_2$ in bulk single crystals and exfoliated flakes.

3.2 Vanadium diselenide

Vanadium diselenide is a metallic TMD that grows in the 1T polymorph. Each unit-cell layer consists of covalently bonded V atoms sandwiched between two layers of Se atoms in an octahedral configuration. These slabs are stacked by weak van der Waals forces and can be easily cleaved, exposing a triangular Se lattice to the surface. The in-plane and out-of-plane lattice constants are $a=3.356$ Å and $c=6.104$ Å, respectively [49]. The lattice constants are altered by excess of vanadium atoms [50] (see Figure 3.2) whose amount can be controlled by the growth temperature of the crystals [50, 51]. The excess vanadium atoms intercalate between the layers and possess a magnetic moment of $2.5\mu_B/atom$ [50]. They give rise to a strong Curie-tail in low temperature susceptibility measurements [46, 50, 52, 53] which do not show any sign of magnetic ordering.

A characteristic kink in the temperature dependence of the resistivity, a suppression of the Pauli magnetic susceptibility and the appearance of superlattice peaks in diffraction patterns in the vicinity of $T_{c,\text{bulk}}^\text{bulk}=105$ K [54, 53, 49, 55] are the signature of the formation of the charge density wave phase in VSe$_2$. Early studies showed a variation in the CDW transition temperature, probably due to its high sensitivity to different growth condition. For instance, the transition temperature can be decreased at a rate of $13 K/\text{at}\%$ by increasing V self-doping (i.e by increasing the growth temperature) [52] and it also depends on crystal quality quantified by the residual resistivity ratio (RRR) [56]. Interestingly, crystals with larger residual resistivity ratio (RRR) showed lower $T_{c,\text{bulk}}^\text{bulk}$ [56]. The transition temperature also increases when applying pressure which is explained in terms of the broadening of the V d-band resulting in an enhanced electron-phonon matrix element [54].
Figure 3.2: Lattice parameters of V$_{1+x}$Se$_2$ as function of the amount of intercalated vanadium $x$. Figure from [50].

While resistivity and magnetic susceptibility experiments identify the CDW transition temperature, scattering techniques measure the symmetry and wavelength of the emerging superstructure. The CDW in bulk VSe$_2$ is a commensurate $4a \times 4a$ modulation within the layers (ab-plane) and an incommensurate $\approx 3.2c$ modulation along the c-axis [49, 55]. The ordering vector is often given in terms of the reciprocal lattice vectors, $a^*$ and $c^*$, with $q_{CDW} = 0.250a^* + 0.314c^*$ [49].

X-ray diffraction measurements [49] show that this ordering vector does not change down to 90-80 K where the out-of-plane component of the wavevector shifts to 0.307 $c^*$. The temperature dependence of the in- and out-of-plane components of the ordering vector are reproduced in Figure 3.3.

A weak anomaly was also observed in transport measurements [54] in this temperature range however it was misinterpreted as an in-plane lock-in transition. The electron diffraction experiments of Eaglesham et al. [57] confirmed the shift in the out-of-plane incommensuration and proposed a simultaneous 3q to 2q transition at around 85 K based on satellite dark-field images. In such a transition the CDW modulation is suppressed along one crystalline direction. Above 80 K they observed a time-dependent grainy structure on the scale of 20-200 nm while below 80 K they speculate the formation of 2q CDW domains with a size of 100 nm to few micrometers. While the boundaries among domains appeared smooth in these measurements, they were not aligned with the crystallographic directions. On the other hand, Skripov et al. [58] did not find such a transition in their samples. They measured $^{77}$Se NMR (nuclear magnetic resonance) spectra of VSe$_2$ whose lineshape is
expected to strongly change at a 3q to 2q transition. They did not find any change in the linshape around 80 K that could have been ascribed to such a transition. They attributed the absence of this transition in their crystals to sample to sample variation in the interlayer coupling due to intercalated V atoms.

Scanning tunnelling microscope would in principle be a suitable tool to investigate this 3q to 2q transition. However STM imaging of the CDW in VSe$_2$ [59, 60, 61, 62, 63] yields contradicting results with significant variations in the CDW contrast not only among different publications, but also within the same study (see Figure 3.4). The appearance of the CDW in STM images of VSe$_2$ was reported [59, 63] to be quite variable from scan to scan, in different cool-downs and from different cleaved surfaces. This variation was first attributed to unequal amplitudes of the components of the CDW in three directions, to an intricate competition of 2q and 3q CDW domains and to complex q vector changes resulting from cooling the samples through a series of higher temperature transitions [59, 63]. Later, a rather isotropic CDW pattern, without any 2q CDW, was observed [61]. The discrepancy was explained in terms of differences in sample growth and variable STM tip conditions [61].

Similarly to imaging, low energy tunnelling spectroscopic features of VSe$_2$ are also debated. The amplitude of the gap around the Fermi-energy ($E_F$) due to the formation of the CDW would be an interesting quantity in studying the CDW phase transition. However, there is no consensus on the CDW gap measured by scanning tunnelling spectroscopy in VSe$_2$, with reported amplitudes ranging from 80 meV to
Figure 3.4: A gallery of published STM images of VSe$_2$ surface at 4.2 K (a)-(c) and (f) and (g), at 60 K (d) and (h), at 77 K (e). Images (a)-(c) and (e)-(f) from [59], (d) is from [60], (g) is from [61], (h) is from [62], (i) is from [63].
40 meV and to no visible gap feature [59, 62, 64]. A conductance peak ≈100 meV below the Fermi energy associated with the vanadium derived d-band was reported by Ekvall et al. [62]. Indeed, clear identification of the CDW gap by tunnelling spectroscopy is not a straightforward task in VSe₂. The CDW gap develops only on a small portion of the Fermi surface [65], thus a strong reduction of the local density of states (LDOS) at the Fermi energy is not expected. Moreover, the nearby vanadium d-band peak may further obscure the spectral signature of the CDW gap.

The origin of the CDW remains an open and debated issue in many TMDs. In VSe₂, Fermi surface nesting was proposed as the driving mechanism of the CDW transition following band structure calculations [66]. Photoelectron spectroscopy measurements showed the presence of a nesting vector with components in both parallel and perpendicular to the layers [67, 68]. This nesting vector is in good agreement with the CDW ordering vector measured in diffraction studies [49, 57]: a 4×4 modulation within the ab-plane and ≈ 3.2 incommensurate along the c-direction.

![Figure 3.5: Thickness dependence of the CDW transition temperature measured by Yang et al. [69]. Their empirical formula predicts the disappearance of the CDW in flakes with less than 1.73 nm thickness. It contradicts the result of Xu et al. [70] who measured a T_c=135 K in thin flakes which well exceeds the bulk value. The contradiction was blamed on the different sample preparation.](image)

We have seen that the CDW transition temperature in bulk crystals
of VSe$_2$ can be modified in several ways e.g by intercalation of V, by applying pressure and through crystal quality. In the age of 2D materials, thickness appears as a natural tuning parameter of correlated electronic phases, like CDWs. The CDW transition temperature in thin flakes ($T_c$) has been found to deviate up to 30% from the $T_{c\text{bulk}}=105$ K bulk value, with contradicting findings where $T_c$ is either reduced [69] or increased [70], seemingly dependent on sample preparation [71]. Both studies identify the transition temperature by resistivity measurements. Xu et al. [70] prepared 2.28-4.65 nm thick flakes by liquid phase exfoliation (showing $T_c=135$ K) while Yang et al. [69] studied mechanically exfoliated flakes down to $\approx 11$ nm. They found that the CDW transition temperature decreases with decreasing thickness, a trend that is well described by the following empirical formula [69] (as shown in Figure 3.5)

$$T_\rho = T_{\rho 0} (1 - d/d_0) - \Delta T,$$

where $T_{\rho 0} = 105$ K and $\Delta T = 5.6$ K. In this formula $d_0 = 1.73$ nm is a critical thickness below which there would no longer be any CDW amplitude. They attribute the discrepancy with the work of Xu to possible residues from the liquid phase exfoliation process. They explain the decrease of $T_c$ with reducing thickness in analogy with pressure: in their explanation reducing the thickness acts the same way as releasing pressure from the material that is known to reduce the transition temperature in the bulk crystals [54].

Another interesting result of Yang et al. [69] is related to impurities and disorder. Contrary to previous measurements in bulk VSe$_2$ where the transition temperature increased with decreasing RRR [56] in exfoliated flakes decreasing RRR, with decreasing flake thickness, resulted in decreasing transition temperature. This suggests that thickness dependent variation of $T_c$ is not the result of the variation in RRR, and a possible increase in $T_c$ in thinner flakes could not be imputed to increasing disorder or impurities.

At the end of this brief overview of the literature related to VSe$_2$ we summarize some of the questions that are still unresolved as far as we know. First in bulk crystals, the details of the transition at around $\sim 85$ K remain unclear. While the existence of the shift in the perpendicular component of the ordering vector is supported by solid evidence, the proposed 3q to 2q transition is rather unambiguous. The origin and the consequence of the change in the out-of-plane component of the ordering vector as well as the possible relation of these transitions are hardly discussed. Although STM imaging could provide valuable insight in this question, published STM data show a big variation of the CDW real space pattern impeding the drawing of a solid conclusion.

Investigating such a 3q to 2q symmetry breaking transition would be interesting not only in the bulk, but also in thin exfoliated samples. For
instance, the possible interplay with the transition of the out-of-plane component may be tuned with thickness. On the other hand, apart from rather contradicting resistivity characterizations, the CDW phase in thin flakes of VSe$_2$ is totally unexplored. The thickness dependence of the transition temperature and of the real space CDW structure are open questions that we have successfully addressed in this project and will be discussed in Chapter 6 and 7.

3.3 Titanium and niobium diselenides

Although the main focus of the thesis is on VSe$_2$, we also present in Chapter 7 the analysis of STM images obtained by other group members on different compounds using the tools developed during the present PhD.

Titanium diselenide grows in the same 1T crystal structure as VSe$_2$, with in- and out-of-plane lattice constants of $a=3.537$ Å and $c=6.00$ Å[72], respectively. Below $T_{\text{c bulk}}^{\text{bulk}}=202$ K a $2a\times2a$ commensurate CDW develops [73]. This transition temperature can be modified in several ways. While an excess of Ti (controlled by the growth temperature) acts only on the CDW state, decreasing its transition temperature [73], the application of pressure not only decreases the $T_{\text{c bulk}}^{\text{bulk}}$, but drives the system into a superconductor [74] in the 2-4 GPa pressure range [75]. This compound also becomes a superconductor upon intercalating Cu above 4% [76]. In 1T-Cu$_{0.02}$TiSe$_2$, copper atoms intercalate on the octahedral site in the vdW gap between the TiSe$_2$ slabs [77]. It has been shown that the intercalation of Cu [77] or large amount of Ti [78] can break the long range $2\times2$ CDW order and trigger the formation of phase shifted CDW domains with a phase difference of $\pi$ ($\pi$DWs). These domain walls were proposed to promote superconductivity [79, 80] in Cu$_{0.02}$TiSe$_2$. The maximal superconducting transition temperature induced by optimal pressure and optimal Cu intercalation are 1.8 K [75] and 4.1 K [76] respectively.

Pristine niobium diselenide is a superconducting TMD at ambient pressure with a superconducting transition temperature $T_{\text{sc}}=7$ K [43]. Although it can be found in different polytypes, it is most commonly studied in the 2H phase in which the lattice constants are $a=3.45$ Å and $c=12.54$ Å. Apart from superconductivity it also hosts a coexisting CDW phase. 2H-NbSe$_2$ has been shown to develop a slightly incommensurate $(3+\delta)a\times(3+\delta)a$ CDW modulation below $T_{\text{c bulk}}^{\text{bulk}}=33.5$ K [44], with $\delta=0.03-0.08$ depending on temperature. The CDW ordering can be suppressed by pressure which in turn enhances $T_{\text{sc}}$ [81]. Controlled voltage pulses with an STM tip can trigger transition from the 2H to 1T
polytype as well as reversible switching between triangular 3q to stripy 1q CDW [82]. This rotational symmetry breaking quantum phase transition was attributed to local strain [83]. Indeed, intentional straining of NbSe$_2$ allowed to engineer the ordering geometry including trigonal 2a and stripy 4a CDW modulation [84].

Cu$_{0.02}$TiSe$_2$ and NbSe$_2$ are of great interest due to their rich physics. They would merit a much more comprehensive overview which is certainly out of the scope of this thesis. The analysis that we present in Chapter 7 contributes to advancing our description and understanding of the CDW states of these materials.

### 3.4 Thickness dependence and outlook

Thickness dependence of electronic properties of TMDs are usually studied by transport and optical techniques focusing on macroscopic properties, like transition temperature of ordered electronic phases (CDW, SC) or spatial averaged band gap of semiconductors. However, these studies lack important real space information to reveal the nature of these electronic phases. While local probe studies could provide such details, they are mainly limited to in-situ grown (e.g. by molecular beam epitaxy, MBE) samples in a narrow thickness range sometimes showing remarkably different behaviour from exfoliated flakes.

NbSe$_2$ is a great example where theory [85], optical [34] and local probe [86] studies confront. Density functional theory based calculations predict a thickness dependent CDW ordering vector [85] that was not found by STM on MBE grown samples [86], nor the enhanced transition temperature previously observed in exfoliated flakes by Raman spectroscopy [34].

Bulk 1T-TaS$_2$ undergoes several phase transitions while arriving from the high temperature normal state to the famous "David-star" commensurate CDW (CCDW) at low temperature. Although different studies addressed the thickness dependence of the CCDW phase, it is still under debate [87, 88]. Interestingly, Yu et al. [87] measured that the transition to the CCDW phase is suppressed already below 10 nm thickness which would be a suitable experiment to verify in our in-situ exfoliation scheme (see section 4.2).

Our study (see Chapter 6) of the thickness dependence of the CDW transition temperature in VSe$_2$ [2] has lifted the seemingly contradicting result of previous transport studies [69, 70]. However, several questions remain open in the ultrathin (monolayer) limit. Beside the exact transition temperature, the microscopic structure (symmetry, periodicity) of the CDW are still under debate [89, 90]. As well as the interplay of the
recently proposed ferromagnetic order [90] with the charge order. Furthermore, monolayer (ML) 1T-VSe$_2$ is potentially interesting for exotic spin orders (like spin density wave) [89] while ML-2H-VSe$_2$ is predicted to show a biaxial strain tunable strong valley splitting [91] as well as a metal to semiconductor transition upon reducing thickness from bilayer to monolayer [92].

Transition metal dichalcogenides with heavier transition metals (e.g Ir, Pt) are newly emerging compounds which are not only interesting for the possible topological physics due to the strong spin-orbit coupling, but also for their potential thickness tunable electronic properties. For instance, PtSe$_2$ shows a metal to semiconductor transition as the thickness is reduced below 2.5 nm [93]. Monolayer films can be grown by direct selenization of a Pt(111) substrate [94]. Controlling the annealing temperature and the amount of Se deposited on the Pt(111) crystal one can obtain either a homogeneous single layer film of 1T-PtSe$_2$ or a monolayer of PtSe$_2$ with a periodic triangular structure of alternating 1H and 1T phases [95]. This patterned monolayer is interesting e.g for selective adsorption of molecules and nanoclusters [95].

IrTe$_2$ is another very promising material to explore both in bulk and in exfoliated form. Compared to other TMDs it has a much more three dimensional (3D) character with interlayer Te-Te bonds and strong electronic dispersion along the out-of-plane direction. In spite of its enhanced 3D nature, it is still easily cleavable along the ab-plane revealing a suitable surface for surface sensitive techniques such as STM [96, 97, 98]. It has a high temperature (around 260 K) transition to a 3D stripe order along the (1,0,1) crystalline direction which is followed by other transitions to coexisting phases in the intermediate temperature range. Although a great number of studies addressed the exact nature and origin of these transitions they are still debated. Explanations [96, 97, 99, 100, 101] are ranging from CDW formation driven by Fermi surface nesting, orbital ordering, Ir-Ir dimerization, structural transition etc...

Superconductivity can be induced by suppressing the 3D charge order by intercalation or doping of Pt or Pd [99, 102]. While superconductivity was not found in the pure material, samples that were cooled very fast (quenched) developed areas where the 3D stripe charge order was exchanged by a honeycomb charge order with superconductivity below 3 K [98]. Superconductivity emerges when the 3D stripe order is suppressed. We propose that reducing the thickness may be another way to suppress the 3D charge order and obtain superconductivity while combined non-contact AFM and STM measurement could shine new light on the origin of the ordering in bulk crystals.
Chapter 4

Methods

4.1 Scanning tunnelling microscopy

The tunnelling\(^1\) effect is one of the fundamental predictions of quantum mechanics that led to a paradigm shift in physical science. It predicts a finite probability for a particle to enter and eventually traverse a classically forbidden potential barrier, i.e a barrier whose height \(V_0\) is higher than the energy \(E\) of the particle. It was first applied by Gamow [103] in 1928 to quantitatively explain the \(\alpha\)-decay of heavy nuclei. It has since proved itself an essential component in the explanation of many physical phenomena such as in the main energy producing process of proton-proton nuclear fusion [104] in the core of the Sun. The chemical and biological importance of quantum tunnelling is very well highlighted in the review of Trixler [105]. Besides the core of the Sun, quantum tunnelling is also present in the heart of our modern technology like in the tunnel diodes or flash memories and set the physical limits of how far we can push the miniaturization of electronic devices such as transistors.

Scanning Tunnelling Microscopy (STM)[106] which is the main experimental technique used in this thesis is also based on the quantum-mechanical effect of tunnelling. The principle of a STM experiment can be easily summarized, a schematic view is presented in Figure 4.1. A bias voltage is applied between two metal electrodes: an ideally atomically sharp wire –the tip– and the sample. Then, the tip is approached toward the sample until a previously determined (setpoint) current of tunnelling electrons is observed. At this moment the distance of the tip

\(^1\) Depending on whether American or British English spelling is used both tunneling and tunnelling is correct. Here we use the British spelling.
and sample is of the order of a few Å and depends on the current set-point and the bias. The tunnelling current at a given bias is extremely sensitive to the tip-sample distance\(^2\) which we exploit to obtain a topographic image of the sample surface. The tip is moved along a raster scanning pattern above the surface while a feedback loop is adjusting the height of the tip to maintain the tunnelling current constant. By continuously recording the position of the tip we obtain a \textit{constant current} STM image of the surface. Unless stated otherwise, all the STM micrographs presented in this thesis were obtained in that mode. Alternatively, one can move tip above the surface with the feedback loop open to obtain a \textit{constant height} image by mapping the tunnelling current as function of tip position.

Figure 4.1: Schematic view of a STM.

The tunnelling current is so sensitive to tip-sample distance that atomic corrugations of the surface may be resolved if one manages to move the tip at the scale of the fraction of the size of an atom. Besides extreme mechanical stability it requires the use of piezoelectric crystals whose elongation or contraction can be controlled in the pico-meter scale by applying a voltage. Piezoelectric scanners provide the necessary ultra fine positioning technology that enabled the rapid and diverse development of scanning probe techniques.

In addition to topographic imaging of a sample surface, various

\(^2\)Typically one order of magnitude change in current for every Angstrom change in tip-sample separation.
other experiments may be performed by an STM. Scanning Tunnelling Spectroscopy (STS) is probably the most well-known as it provides extremely valuable atomic scale information about the local electronic properties of the sample. In such an experiment the tip is held at a constant height (open feedback) while the tunnelling current is measured as function of the bias voltage. The differential conductance, the derivative of the I-V curves (dI/dV), can be obtained by numerical derivation or measured directly using the standard lock-in technique. This quantity—in certain conditions (see section 4.1.2)—is proportional to the local density of states (LDOS) of the sample, which makes STS an extremely valuable tool for studying electronic properties of solids with high spatial resolution.

There are a number of great reviews and textbooks (see e.g [107, 108, 109]) that discuss STM both from a theoretical and a practical point of view. In the following subsections we do not intend to immerse in such deep details, but give a brief overview of some of the critical aspects of quantum tunnelling and STM based on the above literature. First of all, we discuss the problem of electrons in a one-dimensional square potential barrier which gives us a rough idea about the quantum mechanical description of the tunnelling effect and the sensitivity of the tunnelling current on the barrier thickness and height. Then, we turn toward a more sophisticated model, the tunnelling Hamiltonian model, to obtain the tunnelling current within a many-body linear response theory description. The last two subsections of this section are devoted to the description of some technical aspects of the STM experiments presented in this thesis.

### 4.1.1 One-dimensional square potential barrier

The tunnelling effect is most commonly demonstrated on the example of the one-dimensional square potential barrier in which electrons travel from left to right. The potential is given by

\[ V(z) = \begin{cases} V_0 & \text{if } 0 \leq z \leq d \\ 0 & \text{otherwise} \end{cases} \]  

(4.1)

As the potential \( V(z) \) is time-independent the solution of the \( i\hbar\partial_t \Psi(z,t) = H\Psi(z,t) \) Schrödinger-equation can be searched in the form of a product \( \Psi(z,t) = E\Phi(t)\psi(z) \). Inserting this function in the above equation, the time and spatial dependences can be separated:

\[ i\hbar \frac{\partial \Phi(t)}{\partial t} = E\Phi(t) \quad \text{and} \quad H\psi(z) = E\psi(z). \]  

(4.2)
The solution of the first equation of (4.2) is $\Phi(t) = e^{-\frac{i}{\hbar}Et}$ while the second must be solved considering the exact form of the Hamiltonian $(H)$:

$$H\psi(z) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(z)}{\partial z^2} + V(z)\psi(z) = E\psi(z),$$

where $m$ is the electron mass.

We search the solution of the differential equation (4.3) in the form of a left to right travelling plane wave $\psi(z) = C \cdot e^{ikz}$, where $C$ is a non-zero constant which we will discuss later. Inserting this function into (4.3) we find that

$$k = \sqrt{\frac{2m}{\hbar^2} (E - V(z))}.$$ (4.4)

Figure 4.2: Quantum tunnelling through a one-dimensional potential barrier. The barrier has a height $V_0$ and a width $d$. In green we plot the real part (see footnote 3) of the wave-function. In the quantum mechanical description an electron has a finite probability to enter and cross a classically forbidden potential barrier. This phenomenon is called (quantum) tunnelling.

Outside the potential barrier ($z < 0$ and $d < z$) we get an oscillatory solution$^3$ with $k = \sqrt{\frac{2m}{\hbar^2} E}$. Inside the barrier ($0 \leq z \leq d$) for $E < V_0$ we can write $k = i\kappa$ and obtain:

$$\psi_{\text{barrier}}(z) = \psi(0 < z < d) = C \cdot e^{-\kappa z}$$

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

---

$^3$Note that the probability $|\psi(z)|^2$ for the incoming wave is still spatial independent.
which describes an exponentially decaying wave-function inside the barrier. As anticipated in the previous section, the probability of finding the particle inside the barrier ($|\psi_{\text{barrier}}(z)|^2$) is finite: electrons enter and even pass through the barrier. This process is called (quantum) tunnelling. Classical particles with energy lower than the barrier height would not penetrate it, but would simply be reflected from it. Indeed, such process is also included in the quantum mechanical description by the fact that $\psi(z) = C' \cdot e^{-ikz}$ is also a solution of (4.3). Thus, including the reflection of the incident plane wave (coming from the left) on both edges ($z = 0$ and $z = d$) of the potential barrier the total solution reads [108]:

$$
\psi(z) = \begin{cases} 
A \cdot e^{ikz} + B \cdot e^{-ikz} & \text{if } 0 < z \\
C \cdot e^{-\kappa z} + D \cdot e^{\kappa z} & \text{if } 0 \leq z \leq d \\
F \cdot e^{ikz} & \text{if } z < d
\end{cases}
$$

(4.6)

where $k$ and $\kappa$ are previously defined and $A, B, C, D, E$ are constants replacing $C$ in the specific regions. These constants are determined by the boundary conditions of the differential equation (4.3): both the wave-function ($\psi(z)$) and its derivative ($\frac{\partial \psi(z)}{\partial z}$) are continuous at the edges of the potential barrier.

The probability of finding an electron at the end of the barrier is $|\psi(d)|^2 = |F|^2 = T$ which is often called transmission factor as it corresponds to the flux (electric current) through the barrier. In the limit of $\kappa d \gg 1$ it reads

$$
T = \frac{16E(V_0 - E)}{V_0^2} e^{-2\kappa d},
$$

(4.7)

which demonstrates the strong (exponential) dependence of the tunnelling current on the tip-sample distance (barrier width $d$) in an STM experiment.

For a metal one can approximate $E$ with the Fermi-energy and the barrier height $V_0$ by the vacuum energy. The work function $\Phi$ is defined as the difference between the vacuum energy and Fermi-energy: $\Phi = E_{\text{vacuum}} - E_F = V_0 - E$ which gives

$$\kappa = \sqrt{\frac{2m}{\hbar^2} \Phi}.$$  

Although this simple model of the one-dimensional square potential barrier allows us to capture the principle of tunnelling it lacks some important ingredients\(^5\) to model a STM experiment. Moreover, the electronic structure of the tip and sample as well as the bias voltage applied between them are not involved in that model.

\(^4\)Numerically, it is at the order of $\approx 10^{10}$ m$^{-1}$ for a typical metal surface with $\Phi = 5$ eV.

\(^5\)Besides that the wave-function is not normalized.
4.1.2 The tunnelling current

A realistic model of the tunnelling current flowing under an applied voltage between two solids separated by a thin insulating layer must involve the electronic properties of the electrodes and account for the non-linear current-bias characteristic of the junction. Indeed, this is a challenging task and a great number of works [110, 111, 112, 113, 114, 115, 116] have been dedicated to this problem leading to a better understanding of tunnelling experiments. In this subsection we recall some of the main results of these efforts. First we present the tunnelling Hamiltonian model based on ref. [15, 109], then we summarize some of the works on the calculation of the tunnelling matrix element.

The tunnelling Hamiltonian model assumes that two independent systems (say left (L) and right (R) corresponding to tip and sample) separated by a thin insulator layer form the tunnel junction. They are characterized by their own Hamiltonian ($H_L$ and $H_R$), chemical potential ($\mu_L$ and $\mu_R$), set of single-particle wave-functions ($\varphi_\lambda(l)$ and $\varphi_\rho(r)$) to describe a many-body state in these systems and their corresponding electron creation ($c^\dagger_\lambda/\rho$) and annihilation ($c_\lambda/\rho$) operators. The tunnelling of electrons between the sub-systems is modelled by summing the phenomenological tunnelling Hamiltonian over all electron states:

$$H_T = \sum_{\lambda\rho} T_{\lambda\rho} c^\dagger_\rho c_\lambda + h.c., \quad (4.8)$$

where $T_{\lambda\rho}$ is tunnelling matrix element and describes the amplitude for an electron to jump from state $|\varphi_\lambda\rangle$ to $|\varphi_\rho\rangle$.

We want to calculate the tunnelling current as a function of the applied bias voltage ($eV = \mu_R - \mu_L$)$^6$ between the electrodes. We define the tunnelling current as the rate of change in the number of electrons in one of the systems$^7$ multiplied by the electron charge$^8$

$$I = |e| \left\langle \dot{N}_R \right\rangle. \quad (4.9)$$

Applying linear response theory with $H_T$ as perturbation we find that there are two contributions to the tunnelling current. One describes a current of single particles while the other the coherent tunnelling of electron pairs. This term, the Josephson current, vanishes unless both materials are superconductors. The single particle current is given by

---

$^6$One may assume that in the absence of voltage the sub-systems are equilibrated, their chemical potentials are aligned.

$^7$We call the current positive if electrons flow from the left system to the right system.

$^8$We use the convention of $e = -|e|$. 
where \( f(\omega) \) is the Fermi function and \( A_{\lambda/\rho}(\omega) \) are the spectral functions of the single-particle Matsubara Green’s functions in the left and right systems.

We get a very enlightening illustration of the content of (4.10) by moving to real-space representation and calculating the current in a simple situation \cite{15} where we consider tunnelling only between two particular points of the left (\( l_0 \)) and right (\( r_0 \)) systems. In this case the tunnelling matrix element in real-space representation can be expressed as

\[
T(l, r) = t \delta(l - l_0) \delta(r - r_0).
\]

Using that the diagonal part of the spectral function in real-space representation is just the local density of state and assuming that the left system is a probe (tip) with a featureless LDOS \( (N_L(l_0, \omega) \approx N_L(l_0, 0)) \) the tunnelling current is:

\[
I_s = \frac{2\pi |e|}{\hbar} \sum_{\lambda\rho} |T_{\lambda\rho}|^2 \int_{-\infty}^{\infty} d\omega [f(\omega - |e| V) - f(\omega)] A_{\lambda}(\omega - |e| V) A_{\rho}(\omega),
\]

(4.10)

The derivative of this tunnelling current with respect to the bias voltage, the differential tunnelling conductance, is given by

\[
\sigma(V) \equiv \frac{dI_s}{dV} \propto \int_{-\infty}^{\infty} d\omega [-f'(\omega - |e| V)] N_R(r_0, \omega).
\]

(4.12)

In the zero temperature limit, (4.12) shows that the differential tunnelling conductance is proportional to the sample LDOS: \( \sigma(V) \propto N_R(r_0, |e| V) \). This is the foundation of tunnelling spectroscopy that we mentioned at the beginning of this section. Note that at finite temperature the tunnelling spectrum is broadened (thermally smeared) by the Fermi function.

So far we have used a simple model of the tunnelling matrix element to evaluate the tunnelling current obtained in a many-body description of the tunnelling process. To find a more realistic expression for the tunnelling matrix element one may start with Bardeen’s theory \cite{111} for elastic tunnelling which gives the

\[
T_{\lambda\rho} = -\frac{\hbar^2}{2m} \int_S \left[ \varphi^*_\rho(x) \nabla \varphi_\lambda(x) - \varphi_\lambda(x) \nabla \varphi^*_\rho(x) \right] \cdot dS
\]

(4.13)

\( ^9 \)It is the amplitude for an electron to tunnel from point \( l \) to point \( r \).
Table 4.1: Some of the tunnelling matrix elements obtained in the model of Chen [116] for different tip states using the derivative rule.

<table>
<thead>
<tr>
<th>State (λ)</th>
<th>$T_{λρ}$ (value at $x_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>$ψ_ρ$</td>
</tr>
<tr>
<td>$p_x$</td>
<td>$\frac{∂ψ_ρ}{∂x}$</td>
</tr>
<tr>
<td>$p_y$</td>
<td>$\frac{∂ψ_ρ}{∂y}$</td>
</tr>
<tr>
<td>$p_z$</td>
<td>$\frac{∂ψ_ρ}{∂z}$</td>
</tr>
<tr>
<td>$d_{zx}$</td>
<td>$\frac{∂^2ψ_ρ}{∂z∂x}$</td>
</tr>
<tr>
<td>$d_{zy}$</td>
<td>$\frac{∂^2ψ_ρ}{∂z∂y}$</td>
</tr>
<tr>
<td>$d_{xy}$</td>
<td>$\frac{∂^2ψ_ρ}{∂x∂y}$</td>
</tr>
</tbody>
</table>

Assuming a s state tip and substituting $T_{sρ} \propto ϕ_ρ(x_0)$ into (4.10) we find that the current is

$$I_s \propto \int_{-∞}^{∞} dω [f(ω - |e|V) - f(ω)] N_L(ω - |e|V) N_R(x_0, ω), \quad (4.14)$$
where we used that
\[
\sum_{\lambda} A_{\lambda}(\omega - |e|V) = N_L(\omega - |e|V) \\
\sum_{\rho} |\varphi_{\rho}(x_0)|^2 A_{\rho}(\omega) = N_R(x_0, \omega). \tag{4.15}
\]

\(N_L(\omega)\) is DOS in the tip and \(N_R(x_0, \omega)\) is LDOS of the sample at the position of the tip apex atom. Again, assuming a featureless tip DOS \((N_L(\omega) \approx N_L(0))\) and taking the derivative we find that the bias dependence of the differential tunnelling conductance measures the thermally broadened LDOS of the sample at the position of the tip (outside the sample):

\[
I_s \propto \int_{-\infty}^{\infty} d\omega [f(\omega - |e|V) - f(\omega)] N_R(x_0, \omega) \tag{4.16}
\]

\[
\sigma(V) \equiv \frac{dI_s}{dV}(V) \propto \int d\omega [-f'(\omega - |e|V)] N_R(x_0, \omega). \tag{4.17}
\]

All in all, we have demonstrated that the tunnelling current depends exponentially on the tip-sample distance as the sample wave-function decays exponentially outside the sample. This is the property that enables the high spatial resolution imaging of conductive surfaces. Combining this ultimate atomic scale spatial resolution\(^{10}\) with the spectroscopic power of measuring the sample LDOS makes STM an extremely powerful experimental tool.

### 4.1.3 Instrumentation

All the STM and STS measurements presented in this thesis were performed using commercial STM heads in ultra high vacuum (UHV). The measurements of NbSe\(_2\) and TiSe\(_2\) bulk single crystals were carried out in a SPECS JT-STM system. The experiments on the bulk single crystals and exfoliated flakes of VSe\(_2\) were carried out either with a Sciencta Omicron LT STM or with a SPECS Tyto system. All the three systems operate in UHV with a base pressure lower than \(2 \cdot 10^{-10}\) mbar. The base temperatures are 1.2 K and 4.2 K for the SPECS and Omicron systems respectively.

The low temperature is achieved by attaching the STM head to a cryostat which is composed of two concentric cryogenic containers (all\(^{10}\) The exponential decay of the tunnelling current is so sensitive that the lateral resolution is basically limited only by the sharpness of the tip.)
in UHV): the outer vessel is surrounding the inner vessel (also called He bath). During low temperature operation the outer vessel is filled with liquid nitrogen to improve thermal isolation of the inner vessel. 4.2 K is achieved by filling the inner vessel of the cryostat with liquid helium while for lower temperatures a Joule-Thompson stage is operated in the SPECS systems. Higher temperatures are available either by counter heating or filling the inner vessel of the cryostat by liquid nitrogen. For temperatures above the boiling point of liquid nitrogen (≈77 K) counter heating is used.

The UHV system is composed of several chambers separated by gate valves. A (fast-entry) load-lock enables easy insertion of tips, samples and other tools to use in UHV. The load-lock is pumped by a roughing and a turbo molecular pump to attain a high vacuum of around $10^{-8}$ mbar. This vacuum is sufficient to safely open the gate to move objects to the preparation chamber. Depending on the specific system, the preparation chamber is equipped with different instruments to perform further sample characterization and preparation of the STM experiments. For example, samples may be heated to high temperature in this chamber that we use during the preparation of substrates described in 4.1.4. The SPECS JT-STM is currently installed in a vacuum system where there is no separate preparation chamber, the load-lock is directly linked to the STM chamber.

The final steps of the sample preparation e.g in-situ (low temperature) cleaving may be performed in the STM chamber before inserting the sample and tip to the STM head to perform the measurements. The ultra high vacuum of the preparation and STM chambers are maintained by titanium sublimation and ion pumps.

The extreme conditions attained in these system are required for optimal high resolution STM/STS experiments. The UHV environment improves the tunnelling barrier between the tip and sample by preventing the deposition of contaminant materials. For instance, tunnelling through a thin layer of water –that is naturally present at ambient conditions– may impede high quality imaging and spectroscopy. Moreover, the inert atmosphere of the UHV system enables to probe not only the bare surface of the samples but to study it in an intact form by preventing the degradation of air-sensitive samples (see in 4.2). Cryogenic temperatures improve the stability of the STM experiments, increase their spatial and energy resolution and, last but not least, allow us to study physical phenomena that only emerge at low temperature.
4.1.4 Tip and substrate preparation

The tip is one of the most important elements of a STM experiment: the morphology and electronic structure of its apex determine the surface imaging and spectroscopy. Thus, it is crucial to prepare and use a suitable tip for a given experiment.

Tips are usually prepared from metallic wires using different sharpening methods: mechanically cutting or electrochemical etching. Cutting and pulling the wire at the same time is the simplest way to prepare a sharp tip. This method is suitable for tips that are prepared out of materials which can be easily stretched and cut, e.g Au and an alloy of Pt and Ir which is commonly used in STM experiments. This method has the advantage that one can very quickly prepare tips, although with very little control on the final result: the overall shape and the apex morphology of such tips are basically random. This can be very disadvantageous during the coarse approach -the first, manual stage of the approach- as the end of the tip and its reflection can be very difficult to identify. It can throw difficulties in the way of high precision positioning of the tip above a specific region of the sample.

Electrochemical etching offers significantly better control over the macroscopic shape of the tip (see e.g [117]) and is commonly used for harder materials like tungsten. During this processes a piece of W wire is immersed into an electrolyte and a meniscus forms around it. We use a 2M aqueous solution of NaOH or KOH as electrolyte. The etching process, which is the strongest along the meniscus, starts when applying a voltage between the wire and the electrode. The wire tapers during the etching and its lower part falls off once it is cut or weakened so much that the weight of the lower part cannot be held anymore. To avoid over-etching we use the electrolyte in the form of a membrane formed inside a metal hook (electrode). This way a meniscus forms also on the lower side of the wire which actually will be the final tip. The etching finishes when the lower part falls. As this part detaches from the membrane when it falls down this piece is no longer etched even if the voltage is still on. To avoid damages of the apex caused by the falling, the tips with their blunt end on the bottom fall into shaving foam which is soft enough to prevent damages of the tip. Then, we wash them in hot water and isopropanol, and dry them in nitrogen flow. This process yields sharp tips with a regular macroscopic shape. Such a tip is shown in Figure 4.3.

Contrary to Pt/Ir or Au, W oxidises at ambient conditions. Thus it is not practical to use W tips for experiments in air. On the other hand, they are absolutely suitable for experiments in UHV. The oxide layer can be easily removed e.g by a few minutes Ar$^+$ ion sputtering
Figure 4.3: Optical microscope image of an electrochemically etched tungsten tip.

(bombardment by Ar ions).

Regardless of the material and the method we choose to prepare our tip, we do not have any control over the microscopic state of the tip. Prior to approaching on a new samples one should always make sure that the tip properly reproduces well established topographic and spectroscopic features of a known sample. The surface states (Figure 4.4(a)) and the herringbone reconstruction (Figure 4.4(b)) of a cleaned and annealed Au(111) single crystal are such characteristics [118]. We routinely used the reconstructed Au(111) surface to characterize and condition the STM tip prior to and during the experiments.

The tip conditioning is the process during which one tries to tune the microscopic state of the tip to reproduce these known features of the sample. It is not a well-defined procedure and usually each person develops their own style over the time. In general, it includes operations like poking of the surface and applying voltage pulses. After such tweaking one checks for these features and keeps conditioning the tip until it properly resolves them. We found that we do not need to aim for atomic resolution, which on Au(111) is typically more difficult than imaging the surface reconstruction, to get a well-prepared tip to scan our samples. Clean and stable imaging of the Au(111) herring-bone reconstruction, step edges and adsorbates are sufficient topographic signatures to start experiments on the TMD samples. Once the tip is ready, one may test its stability by scanning at different scanning and tunnelling conditions (bias voltage, current, speed, etc...). A well-prepared tip greatly helps
Figure 4.4: Characterization of the STM tip on a Au(111) prior to the experiments. (a) Differential tunnelling conductance $dI/dV(V)$ and (inset) $I(V)$ spectra measured at 77.6K on Au(111) surface. The surface state (green arrow) of Au(111) is clearly visible at around $-0.5$ V. (b) STM image ($70 \times 70$ nm$^2$) of a reconstructed Au(111) surface ($V_{bias} = 1$ V, $I_t = 1$ nA) shows the famous herring-bone surface reconstruction with some adsorbates (white dots).
to obtain more easily interpretable results in a shorter time.

During this project the Au(111) single crystal was not only used as a calibration sample, but also as a substrate in the study of in-situ exfoliated nanoflakes of VSe$_2$. Both the tip characterization and the thickness dependent measurements require a clean and reconstructed Au(111) surface. It has been achieved by cleaning the surface by repeated cycles of Ar$^+$ ion sputtering and annealing at temperatures in the range of 400-500 °C in UHV.

During the years of this project a huge effort has been made in our group to implement and optimize methods of tip and Au(111) preparation. Although, the details of these works is far beyond the scope of this thesis let us have a few examples here: annealing of the W wires before etching, implementation of biased sputtering of W tips and a tool for in-situ treatments of tips via e-bombardment or field emission and simultaneous sputtering and annealing of Au(111) for a more effective cleaning.

4.2 In-situ exfoliation

While exfoliated flakes and thin films of semiconducting TMDs are routinely studied and already integrated in practical device configurations, their metallic counterparts have been much less investigated. This is a direct consequence of their greater reactivity under ambient conditions [119, 120], restricting their use to controlled atmosphere, vacuum or encapsulated configurations. The latter makes it difficult to investigate their properties by surface sensitive techniques. One alternative to overcome this difficulty is in-situ growth of van der Waals materials [121, 122]. However, they require sophisticated equipment and do not offer the wide thickness range from bulk to monolayer accessible in a single exfoliation experiment. In this section we present a device that we developed to prepare mechanically exfoliated metallic TMDs in UHV that enables photoemission and scanning probe investigation of their bare surface. This work has been published in Review of Scientific Instruments [3].

4.2.1 Degradation at ambient conditions

First of all, we demonstrate the surface degradation of bulk VSe$_2$ by the means of optical and atomic force microscopy. We do not intend to describe the details (e.g chemistry) of this process, but to show that for successful STM experiments on VSe$_2$ (nanoflakes) the samples must be prepared and studied in an inert atmosphere.
4.2 In-situ exfoliation

Single crystals which have been stored for a long time at ambient conditions typically have a matt, blackish color while freshly cleaved samples have a shiny, metallic color. The dramatic difference between a crystal stored for a long time and a freshly cleaved one is well visible in Figure 4.5 where we show optical microscopy images of the surface of a bulk VSe$_2$ before (Figure 4.5a) and after (Figure 4.5b) cleaving by scotch tape.

![Figure 4.5](image)

Figure 4.5: Optical microscope image of the surface of a VSe$_2$ single crystal before (a) and after cleaving (b) by scotch tape.

To get a better insight on the typical time scale of the degradation process we performed atomic force microscopy (AFM) measurements on a freshly cleaved VSe$_2$ bulk single crystal. We recorded images in tapping mode with the same scanning parameters at regular time intervals. A series of consecutive images is shown in Figure 4.6. During the first few hours there was a significant creep of the scanner resulting in images recorded on different areas. Thus, in Figure 4.6 we show images starting from 10 hours after the cleaving. Progressive formation of bright contrasted islands is clearly visible. After 40 hours the surface is almost totally covered.

At another occasion we focused on few (2-5) layer thick terraces on the surface of freshly cleaved bulk VSe$_2$. While the terraces are clearly visible after cleaving (Figure 4.7 left side) we only see their faint contour after 15 hours of exposure to ambient atmosphere (Figure 4.7 right side).

Last but not least, we have also performed STM experiments on freshly cleaved bulk VSe$_2$ at ambient conditions. The imaging stability was strongly decreasing with time indicating a progressive diminution...
Figure 4.6: Consecutive AFM images (2×2 μm²) of a cleaved bulk VSe₂ surface at ambient conditions. The elapsed time since the cleaving is marked in each figure. The contrast has been adjusted to optimize the visibility of the progressively forming islands on the left side of the images.
of sample surface quality. Shortly after cleaving we could not obtain stable, consistent imaging. These observations were confirmed by several attempts using different tips and newly cleaved samples.

All in all, these observations clearly show that even the surface of a bulk crystal of VSe$_2$ is sensitive to ambient conditions. On the other hand, they also suggest that a few minutes exposure of a freshly cleaved sample to air may not affect the surface quality too dramatically, at least on the micron scale as seen by AFM.

### 4.2.2 The UHV exfoliation tool

The UHV exfoliation tool we present in Figure 4.8(a) is built around a sample storage carousel mounted on a linear shift and a sample holder manipulator. It can in principle be adapted to any UHV system, be it in the load-lock, preparation or STM chamber. The central part is an exfoliation wheel mounted on a standard sample holder. We fix an insulator, low outgassing, residue-free clean-room adhesive tape (UltraTape product) on the circumference of the wheel by means of a double sided adhesive tape, with the adhesive side facing outwards. This sticky surface is then loaded with freshly cleaved flakes in the following way: starting from a bulk single crystal, we perform 1-3 steps of standard exfoliation to achieve a freshly cleaved surface and then transfer the thinned crystals to the wheel. The loaded exfoliation wheel is then transferred to the UHV system load-lock and pumped to below $10^{-6}$ mbar within less than ten minutes.
Figure 4.8: (a) In-situ exfoliation setup: the substrate sits on the storage carousel that can be moved vertically. The exfoliation tool is loosely held on a linear transfer arm. The arrows 1-4 indicate the exfoliation sequence (refer to main text). Typical dimensions are given in mm. (b) Optical microscope image of MoS$_2$ flakes after three exfoliation cycles (scale bar 100 µm). Inset: the red rectangle represents a 4×100 µm$^2$ area that we automatically search for flakes overnight.
The exfoliation process is done manually using standard manipulators. It starts after reaching the base pressure of the load-lock ($< 3 \times 10^{-8} \text{ mbar}$). We grab the exfoliation tool with the transfer arm and align it over a previously prepared substrate on the carousel. The substrate is then carefully raised until gently touching the exfoliation wheel (Figure 4.8(a), step 1). We then move the transfer arm horizontally to roll the cylinder over the substrate surface at an average speed of about 2 mm/s (Figure 4.8(a), step 2). Because the exfoliation tool is only loosely held with the transfer arm, the wheel self-aligns to roll perfectly flush over the substrate surface. When reaching the end of the substrate, we lower the carousel to get out of contact (Figure 4.8(a), step 3) and withdraw the transfer arm (Figure 4.8(a), step 4). The complete cycle can be repeated to deposit more flakes on the substrate and/or further thin the already deposited ones. Occasionally, the already deposited flakes can break into smaller pieces leading to a decreasing average lateral size with increasing number of exfoliation cycles. Ultimately, we distribute and thin the starting material on the surface of the substrate and on the exfoliation wheel resulting in a dense coverage of the substrate with thin flakes (Figure 4.8(b)).

During the exfoliation (Figure 4.8(a), step 2), it is important to maintain a "rolling without slipping” condition by controlling the translation speed and contact force. This is crucial to obtain high quality flakes and to minimize the amount of glue transferred from the adhesive tape to the substrate. Alternative implementations of our in-situ exfoliation scheme include the use of an empty (covered with adhesive tape, but not loaded with crystals) wheel that can be loaded in-situ by first rolling repeatedly over a thick single crystal before starting the exfoliation process. This method may prove critical to prepare single layer flakes of extremely air sensitive materials.

### 4.2.3 Proof of principle

The procedure was first tested by exfoliating MoS$_2$ nanoflakes on a gold coated silicon substrate. MoS$_2$ is stable in air, allowing us to confirm the in-situ deposition of nanoflakes from high magnification optical microscopy outside UHV (Figure 4.8(b)). We observe a suitable coverage after only three exfoliation cycles. Increasing this number will increase the coverage if needed.

As a proof of principle, we demonstrate scanning tunnelling microscopy and spectroscopy of a VSe$_2$ nanoflake exfoliated in-situ ($3 \times 10^{-8} \text{ mbar}$) on a Au(111) substrate using the method and device described in section 4.2.2. Within the same exfoliation process one nat-
urally prepares nanoflakes of different thicknesses\textsuperscript{11}. The thickness dependence of the charge density wave phase of VSe\textsubscript{2} will be presented in Chapter 6. The STM tips and the reconstructed Au(111) substrate was prepared as we described in section 4.1.4. Tunnelling I(V) and differential conductance dI/dV(V) curves were acquired simultaneously using a standard lock-in technique with a 14.1 mV rms bias modulation at 337.7 Hz.

Positioning the STM tip over the exfoliated nanoflakes is challenging. Indeed, they are too small to be seen in the optical setup of our UHV system. Even if we were able to identify a flake on the exfoliation stage, the long working distance and absence of an absolute sample position monitoring would make it impossible to locate it on the STM stage. We therefore relied on a systematic scan and search procedure to locate a suitable flake. We first scan a large surface area (red rectangle in Figure 4.8(b) inset) by recording a sequence of adjacent low resolution and large scale 4×4 µm\textsuperscript{2} micrographs. These images are then analysed to identify morphological characteristics expected for nanoflakes, such as large atomically flat terraces and long straight edges. Once we identify an image with such features (Figure 4.9(a)), the presence of a VSe\textsubscript{2} nanoflake is unambiguously confirmed from high resolution STM micrographs (atomic and CDW lattices) and from tunnelling spectra.

Figure 4.9(b) shows a high resolution atomic-scale STM micrograph of an in-situ exfoliated VSe\textsubscript{2} flake. This image reveals the expected atomic lattice and the 4×4 CDW modulation developing below 105 K [54]. The Fourier transform shows the perfect commensuration of the atomic and CDW lattices and their six-fold symmetry (Figure 4.9(c)). Tunnelling spectroscopy of thick flakes (Figure 4.9(f)), where bulk-like behavior is expected (see Chapter 6), show a metallic I(V) characteristic and the vanadium d-state derived band in the dI/dV(V) spectrum, in agreement with bulk data presented in [62] and Chapter 6. While we find the freshly cleaved bulk surface is degrading within hours in air, we did not observe any sign of surface degradation of thin flakes in-situ, even after several weeks.

The spectroscopic and topographic fingerprints shown in Figure 4.9 demonstrate that we have successfully prepared exfoliated VSe\textsubscript{2} nanoflakes which are stable and can be extensively studied in UHV. We find that a few exfoliation cycles (6-10, this may be material dependent and naturally depends on the wheel loading) are enough to obtain high quality VSe\textsubscript{2} flakes on Au(111) with appropriate coverage to easily locate a suitable flake with the STM tip using the scan and search scheme described

\textsuperscript{11}These may be separated flakes with different thickness or a single piece of crystal with parts (terraces) with varying thickness.
Figure 4.9: (a) Large scale (4×4 µm²) STM micrograph (V_{bias}=1 V, I_t=10 pA) of VSe₂ nanoflakes with different thicknesses. (b) 9×9 nm² high resolution STM micrograph (V_{bias}=-100 meV, I_t=1 nA) of a VSe₂ nanoflake showing the atomic lattice and a strong CDW modulation (T=77.6 K). (c) Fast Fourier transform of the micrograph in (b). Red and green circles indicate the first-order atomic and CDW modulation peaks, respectively. (d) STM micrograph (V_{bias}=0.5 V, I_t=10 pA) of the edge of a VSe₂ nanoflake showing the undisturbed underlying Au(111) herringbone reconstruction (non-linear color scale). (e) Topographic traces marked in (a). (f) Tunnelling spectra of a thick (46 nm) VSe₂ flake at 77.6 K.
above. The thickness of the exfoliated flakes ranges from hundreds of nanometers to few (1-2) layers, enabling thickness dependent studies in a much broader range than in-situ grown thin films. We have perfect control over the exfoliation process as evidenced by the preservation of the herringbone reconstruction of the underlying Au(111) single crystal all the way to the edge of the exfoliated nanoflake (Figure 4.9(d)).

4.2.4 Summary

In summary, we presented a novel method for mechanical exfoliation of van der Waals materials in UHV that yields high quality nanoflakes with dense substrate coverage. Performance of the device is demonstrated by preparing and imaging in-situ exfoliated VSe$_2$ nanoflakes by scanning tunnelling microscopy. Our device can be easily adapted to any UHV system and offers possibilities for further development and fine tuning. Monitoring the force applied between the cylinder and the substrate may increase reproducibility. The diameter of the exfoliation wheel, hence the cleaving angle, is another tunable degree of freedom to obtain flakes of different size and thickness. Our method is applicable to a broad range of layered materials and opens new opportunities to study few layers to monolayer thin air sensitive materials with surface probes like tunnelling and atomic force microscopy and photoemission.
Chapter 5

Quantitative analysis of STM images

We study the CDW state from many aspects in this thesis. In Chapter 6 we examine the temperature and thickness dependence of the CDW state in VSe$_2$ based on topographic STM images. In these cases our quantitative analysis focuses on extracting the spatially averaged CDW order parameter amplitude $\langle |\Psi| \rangle$ as function of thickness and temperature. On the other hand, in Chapter 7 we focus on the spatial variations of the local complex order parameter $\Psi_n(\mathbf{r})$. In spite of that, we will not systematically make an explicit difference between $\langle |\Psi| \rangle$ and $\Psi_n(\mathbf{r})$ calling and denoting both simply the order parameter and $\Psi$, they should be understood in each chapter in the context discussed above. Note also that while in the former case we treat all three directions as a single entity, in the latter case we distinguish the charge modulations along the different directions (hence the ”n” index). We will elaborate these distinctions in more details in sections 5.2 and 5.3.

In all cases we extract quantitative information about the CDW from topographic STM images by performing different numerical analyses. Our main assumption is that the STM signal that we attribute to the CDW modulation well represents the charge density modulation given by (2.1). Namely, the amplitude of the STM signal associated with the CDW modulation is proportional to the amplitude of the charge density modulation and its wave vector and local phase are identical.

In this chapter we briefly discuss the background of these analyses and their technical details. We also provide definitions for later use and a short description and comparison of alternative methods.
5.1 Mathematical background

In this section we introduce some of aforementioned mathematical concepts and image treatment tools that we use in the analysis of STM images. For the sake of readability they are presented in parallel as follows.

First of all, we define the Fourier transform of a function \( f(r) : \mathbb{R}^2 \rightarrow \mathbb{R}^2 \) as

\[
\mathcal{F}\{f(r)\} \equiv f(k) \equiv \mathcal{N}_F \int_{-\infty}^{\infty} f(r) e^{-i k r} dr,
\]

where \( \mathcal{N}_F \) is a normalization constant. The Fourier transform is linear:

\[
\mathcal{F}\{af(r) + bg(r)\} = a\mathcal{F}\{f(r)\} + b\mathcal{F}\{g(r)\}
\]

for any complex numbers \( a \) and \( b \). The Fourier transform of the convolution of two functions is the product of their Fourier transforms and vice versa:

\[
\mathcal{F}\{f(r) \ast g(r)\} = \mathcal{F}\{f(r)\} \mathcal{F}\{g(r)\}
\]

and

\[
\mathcal{F}\{f(r)g(r)\} = \mathcal{F}\{f(r)\} \ast \mathcal{F}\{g(r)\},
\]

where \( \ast \) denotes the convolution

\[
h(r) = f(r) \ast g(r) \equiv \int_{-\infty}^{\infty} f(r')g(r - r')dr'.
\]

We also introduce the Dirac delta distribution \( \delta(k) \) with the following properties:

\[
\mathcal{N}_D \delta(k - k_0) = \int_{-\infty}^{\infty} e^{i(k - k_0) r} dr
\]

and

\[
f(k_0) = \int_{-\infty}^{\infty} f(k) \delta(k - k_0) dk,
\]

where \( -\infty \leq -d < k_0 < d \leq \infty \) and \( \mathcal{N}_D \) is a normalization constant.

As we have seen in Chapter 2, the spatial modulation of the charge density in the CDW state is described by a plane wave in the \( \Delta \rho(r) = \)

\footnote{We assume that the functions we use in this chapter are all well-behaving functions with all the necessary properties that we need to perform the manipulations below.}
A cos(q₀r + φ) form, where A is a positive real number. Now we calculate the Fourier transform of such a function:

\[
\mathcal{F}\{A \cos(q₀r + φ)\} = \mathcal{N}_F \int_{-\infty}^{\infty} \frac{1}{2} \left( A e^{iφ} e^{iq₀r} + A e^{-iφ} e^{-iq₀r} \right) e^{-ikr} dr = 2π\mathcal{N}_F \mathcal{N}_D \left( \frac{1}{2} Ae^{iφ} δ(k - q₀) + \frac{1}{2} Ae^{-iφ} δ(k + q₀) \right),
\]

where we used (5.6) and δ(k) = δ(−k). Hence, we get two Dirac deltas at ±q₀. In practice, when we study the Fourier transform of STM images numerically implemented by the Fast Fourier Transform (FFT) these idealized infinitely sharp Dirac peaks develop a finite width. Note that the Dirac delta can be obtained as the limit lim_{ε→0} 1\sqrt{πε} e^{-x²/4ε}.

Finite size effects and formation of domains\(^2\) can account for such a broadening.

In the TMDs that we study in this thesis such charge modulations develop along three q₀-s which are rotated 2π/3 with respect to each other. Due to the linearity of the Fourier transform (see (5.2)) it means that the Fourier transform of the sum of these plane waves should consist of six peaks forming an equilateral hexagon, see for example Figure 5.1(b).

If the image is large enough these peaks are well separated enabling effective isolation of the real-space modulations by Fourier-filtering the image. This process is composed of the following steps:

1. perform the Fourier transform of the image (we obtain the ”Fourier-map” of the image)
2. mask the peak(s) corresponding to modulations that we want to retain and suppress the rest of the Fourier-map
3. inverse Fourier transform the filtered Fourier-map.

Technically, the second step is performed by multiplying the Fourier-map by a map which is zero everywhere except at the mask location. The mask should be chosen that it well covers the selected peak, but avoids contribution from other peaks.

To be used in the following section, now we define the intensity\(^3\) of the Fourier transform (I_{\mathcal{F}\{f\}}(k)) by taking the absolute value of \mathcal{F}\{f(r)\} at all k. Calculating the integral of I_{\mathcal{F}\{A \cos(q₀r + φ)\}}(k) \equiv I(k) around ±q₀ we obtain:

\(^2\)Or in a wider context: a coherence length that is shorter than the image size.

\(^3\)Also called power spectrum.
\[ \int I(k)dk = 2\pi N_F N_D \int \left\{ \left| \frac{1}{2} A e^{i\varphi} \delta(k - q_0) \right| + \left| \frac{1}{2} A e^{-i\varphi} \delta(k + q_0) \right| \right\} dk = \]

\[ = 2\pi N_F N_D \int \left\{ \frac{1}{2} A \delta(k - q_0) + \frac{1}{2} A \delta(k + q_0) \right\} dk = \]

\[ = 2\pi N_F N_D A. \] (5.9)

### 5.2 The global CDW order parameter

In the previous section we have seen that the integral of the intensity of the Fourier transform of a plane wave is proportional to its amplitude (see (5.9)). This quantity can provide a solid measure of the CDW order parameter amplitude. For a quantitative analysis of the CDW phase transition we thus introduce a quantity, derived from (5.9), which is also called the order parameter:

\[ \Psi = \frac{\int_{S_{\text{CDW}}} I(k_x, k_y)dk_xdk_y}{\int_{S_{\text{lattice}}} I(k_x, k_y)dk_xdk_y}, \] (5.10)

where \( I(k_x, k_y) \) is the intensity map of the Fourier transform and \( S_{\text{CDW}} \) and \( S_{\text{lattice}} \) are the circular shaped integration areas around the CDW and lattice peaks, respectively (see Figure 6.2(b)). \( S_{\text{CDW}} \) and \( S_{\text{lattice}} \) are chosen so that the k-space area is the same for all examined micrographs \( |S_{\text{CDW}}| = |S_{\text{lattice}}| = 0.2 \text{ nm}^{-2} \). We normalize to the atomic lattice components to account for possible differences in tunnelling conditions and in the numerical integration for images with different sizes.

Note that in this case we treat all the directions equally and together: the integral goes around all the peaks. There are several reasons for this choice. Firstly, these directions are indistinguishable in the sense that they are connected by \( 2\pi/3 \) rotation due to the crystalline symmetry. While for bulk single crystals one could attempt to follow the evolution of the CDW direction by direction, for exfoliated flakes it is a more complicated mission. In the exfoliation process (see in section 4.2) flakes are deposited with a random crystalline orientation with respect to the scan axis direction. As we do not have an absolute reference to distinguish these directions one can study the thickness dependence direction-wise only by studying terraces with different thickness of the exact same flake.

Moreover, we do not expect any direction dependence of the averaged, global order parameter as long as the three-fold symmetry is preserved. Symmetry breaking effects, like strain, can induce anisotropy for
example by suppressing the CDW along two ordering vectors within a 3q to 1q transition [82, 83]. As our goal is to study intrinsic properties of the CDW tuned solely by the crystal thickness we treat the three directions together in the definition of \( \Psi \) and in the analysis presented in Chapter 6 we focus only on those STM images which show similar CDW intensity in all three directions.

### 5.3 The local complex CDW order parameter

In the first chapter we have seen that the CDW phase is described by a complex order parameter with an amplitude and a phase. The spatially averaged intensity of the CDW order parameter is usually accessed by scattering techniques sensitive to the local lattice distortions, or electron spectroscopy and transport measurements sensitive to changes in the band structure due to the opening of the CDW gap. Detecting the phase has been traditionally limited to dynamic experiments (for good reviews see e.g. refs [7], [11]). More recently, different strategies have been followed to access phase information from spectroscopic [123, 124] and topographic [125] local probe tunnelling experiments as well as from the periodic distortion of the atomic lattice measured by transmission electron microscopy [126, 127]. However, extracting phase information from reciprocal-space data tends to suffer from the common problem of phase wrapping and fundamental numerical difficulties of finite sampling (see section 5.3.2). Unwrapping the phase in these cases leads to singularities that can easily be mistaken for physical phase variations that actually do not exist and it can also obscure real features, for instance domain walls in 1T-Cu\(_x\)TiSe\(_2\) as we will show later.

In section 2.6 we have discussed that the total charge density modulation within the ab-plane of the TMDs studied in this thesis can be written as the sum of three charge modulations along 2\(\pi/3\) rotated directions (see equation (2.18)). Related to these charge modulations, we introduced three order parameters \( \Psi_n \), one for each direction (see equation (2.20)). Naturally, these order parameters can spatially vary since they are a local complex order parameter \( \Psi_n(\mathbf{r}) \). In this section we describe a new method to extract these local complex order parameters from topographic STM images. This technique combines reciprocal and real space information to map the full complex order parameter giving a complete real space characterization of the CDW with high spatial resolution overcoming the limitations of earlier Fourier space based techniques.
In the case of the local complex order parameter, where we distin-
guish the charge modulations along the different directions (cf. global
order parameter in the previous section), following the proposition of
McMillan [21], we refer to the CDW modulations in the three $q_n$
directions as the three coexisting CDWs. This denomination is fully justified
by our experimental findings presented in Chapter 7.

5.3.1 The fitting procedure

In order to determine the local complex order parameter, phase and
amplitude, we developed a procedure based on a local and direction
specific fitting of the real space CDW modulation measured by STM.
Following the expression (2.18) of the total charge modulation we locally
describe the CDW modulation in each direction ($n=1,2,3$) by a two-
dimensional plane wave function:

$$f_n(r) = A_n(r) \cos \left( \frac{2\pi}{\lambda_n} q_n r + \varphi_n(r) \right),$$

(5.11)

where $\hat{q}_n$ is a unit vector in the direction of the $n$-th ordering vector.
In this model we allow the amplitude ($A_n(r)$) and the phase ($\varphi_n(r)$)
to spatially vary for each direction ($n=1,2,3$), while fitting of the local
wavelength is kept optional and discussed later.

The workflow of the fitting procedure is depicted in Figure 5.1(a).
After importing the STM data into a double precision numeric matrix
in Matlab, we correct for sample tilting by subtracting a linear fit line
by line. We then take its two-dimensional FFT. Both the lattice and the
CDW modulation yield a sharp six-fold symmetric peak structure in the
FFT intensity map (Figure 5.1(b)). We fit these peaks by 2D Gaussian
functions to determine their position, which allow us to define the $\hat{q}_n$
unit vectors in the direction of the CDW ordering vectors. The CDW
modulations are individually Fourier filtered (as described in section
5.1) for each of these three directions by generously masking (Figure
5.1(b)) around the previously identified peaks $q_n$. The local fitting by
$f_n(r)$ functions is performed independently for the three directions on
a subset of the Fourier filtered data by running the fitting procedure
on a dense grid of small and slightly overlapping windows spanning the
entire field of view. Considering the scale at which the smallest physical
features may be expected (order of the CDW wavelength), the size of
the fitting window is set between $0.5 \times 0.5 \text{ nm}^2$ and $1 \times 1 \text{ nm}^2$
and raster scanned with a typical lateral resolution of 0.5-1 nm along the filtered
CDW image.

The amplitude ($A_n(r)$), phase ($\varphi_n(r)$) and wavelength ($\lambda_n(r)$) are
collected and stored during the local fitting for later analysis, processing
Figure 5.1: The fitting procedure. (a) Workflow of the fitting procedure. (b) Intensity map of the main FFT peaks of the STM micrograph shown in Figure 7.1(a). Red and green circles indicate the peaks corresponding to the atomic lattice and CDW modulations, respectively. The circles sizes depict the typical filtering window around the peaks.

and visualization. We also naturally obtain the goodness of fit \( R^2(r) \) at each fitting window during the fitting procedure. The map of these local \( R^2 \) values provide a valuable measure of an eventual coherent model failure and of the effectiveness of the fitting at the local scale. The wavelength \( \lambda_n \) is either fixed to the value measured from the CDW peak position in the FFT or left as a free parameter during the fitting procedure. In the latter case, \( \lambda_n(r) \) is constrained to the range of filtered wavelengths.

The CDW wavelength is mainly featureless (typically constant) in most of the STM micrographs we examined and fixing it to the value measured from the FFT did not affect substantially the outcome of the amplitude and of the phase fitting results. We therefore do not discuss this parameter specifically in all the cases presented in Chapter 7. On the other hand, we have applied our method to other data sets, for example to the 3q-1q transition in 2H-NbSe\(_2\) [83], where fitting the wavelength proved critical to capture essential details of the different CDW phases (see e.g in section 7.5).

We carefully checked the robustness of our fitting procedure by examining the impact of filter range, fitting window size and raster resolution. The main effect of selecting smaller values for these parameters is an increase in the noise levels without affecting the key features discussed in Chapter 7. We further checked that we obtain the same phase, amplitude and \( R^2 \) maps for subsequent images of the same area, as well as for forward, backward, upward or downward scans. This is consistent with the experimental conditions discussed here, where we expect static
CDW phases.

Tip changes can occur while scanning repeatedly the same area. Interestingly, they mostly do not affect the fitting results. We did observe some cases where the fitting output was different after a tip change. This may reflect tip-sample interactions strong enough to modify the CDW as pointed out in a study by Langer et al [128]. The modification of the CDW by a local probe is very important concept in view of the previous understanding that varying CDW contrast is due to varying STM tip condition. Our analysis technique offers novel opportunities to investigate such effects in more details.

5.3.2 Recovering the phase from the FFT

In the method we have introduced previously, we extract the phase of the CDW by fitting the charge modulations in real space. Alternative methods access phase information by means of FFT techniques. They have the advantage that FFT algorithms are very fast, allowing in principle real time\(^4\) processing and visualization of the phase information.

The phase retrieval starts with filtering for the domain of interest in reciprocal space. The filtered FT is then inverse transformed (IFFT) back to real space. The local phase is retrieved by calculating the (four-quadrant) arctangent of the quotient of the imaginary part divided by the real part of the IFFT. However, since the (4-quadrant) arctangent is limited between \(-\pi\) and \(+\pi\), phase jumps occur, and the phase information is said to be wrapped. Phase unwrapping, or the correction of the aforementioned jumps, is a known problem in Fourier transform profilometry [129]. It is a very complicated task in 2D since it requires a complex 2D search strategy to detect possible defects and apply appropriate phase offsets to restore continuity. It is even more complicated in the case we will discuss in Chapter 7, since phase jumps can originate from CDW defects and this information can neither be discarded nor healed.

When dealing with signals with well-defined Fourier components, as is the case with CDW modulations, phase unwrapping can be done in a different way, by shifting the Fourier component of interest to \(q = 0\) before the inverse transformation. Shifting the Fourier component to \(q = 0\) should theoretically entirely suppress the phase wrapping. However, because experimental data have finite resolution, the frequency of interest should be perfectly centred on a pixel, which is impossible to achieve experimentally. For a rectangular lattice, this imperfection can be somewhat minimized by tuning the scan area and resolution, some-
thing that is impossible for the triangular lattices investigated in this thesis. Fourier components that are not precisely centred on a pixel are likely to produce a background in the phase image.

We illustrate the FFT based phase retrieval using the STM micrograph of 1T-Cu$_{0.02}$TiSe$_2$ discussed in Chapter 7 (Figure 7.5). The maps in Figure 5.2(a) were obtained by calculating the (four-quadrant) arctangent of the quotient of the imaginary part divided by the real part of the IFFT for each direction. They show obvious phase oscillations (note the periodic color scale), which reflect the phase wrapping.

In Figure 5.2(b)-(e) we show the working principle of the reciprocal space method, where the phase wrapping problem is addressed by shifting the corresponding CDW FFT peaks toward $q = 0$ . Here, we can see the evolution of the phase maps of each of the three CDWs as their corresponding Fourier peaks $q_1$, $q_2$ and $q_3$ are shifted progressively closer to $q = 0$ by a percentage of the corresponding $q_n$ (0% = no shift; 100% = shift to $q = 0$). Intrinsic features become increasingly visible as the background phase oscillations due to the phase wrapping become less dominant. However, a significant inhomogeneous background remains because of finite resolution, even when shifting the peak to nominally $q = 0$ (panel (e)).

In Figure 5.2(f) we show the results of the analysis of the same STM image with the real space fitting procedure described in this section. It clearly reveals domain walls and extended regions of constant phase which will be discussed in more details in Chapter 7.

In comparison, while the FFT and our real space phase retrieval yield similar domain structures, the FFT method fails to resolve large domains of constant phase. The phase gradient present for the FFT based method (see e.g $q_1$ in panel (e) and compare with panel (f)) prevents to draw conclusion on intrinsic CDW features, e.g on the position dependence of the phase of a commensurate and an incommensurate CDW shown in Figure 2.5. Moreover, the FFT based phase retrieval can also mislead into suggesting domain walls where there are none.
Figure 5.2: Comparison between real space phase fitting and Fourier based techniques. Each panel shows the phase as a function of position of the three CDWs modulations extracted from the STM micrograph of 1T-Cu$_{0.02}$TiSe$_2$ presented in Chapter 7 (Figure 7.5). (a)-(e) reciprocal space method, where the phase wrapping problem is addressed by shifting the corresponding CDW FFT peaks toward $q = 0$ by a percentage of the corresponding $q_n$ ($0\% =$ no shift; $100\% =$ shift to $q = 0$). (f) the same data analysed with the real space fitting method presented in this section. Scale bars = 10 nm.
Chapter 6

Non-monotonic thickness dependence of the charge density wave transition temperature in VSe$_2$

Isolating single unit-cell thin layers from the bulk matrix of layered compounds offers tremendous opportunities to design novel functional electronic materials. However, a comprehensive thickness dependence study is paramount to harness the electronic properties of such atomic foils and their stacking into synthetic heterostructures. In this Chapter we show that a dimensional crossover and quantum confinement with reducing thickness result in a striking non-monotonic evolution of the charge density wave transition temperature in VSe$_2$. We draw our conclusion using the method we developed (see section 5.2) to extract the CDW order parameter based on the real space charge modulation amplitude imaged by STM. We further perform a unique analysis that gives access to the thickness dependent transition temperature based on this order parameter and a calibration of the temperature dependence on bulk crystals. This study lifts the disagreement of previous independent transport measurements. We find that thickness can be a non-trivial tuning parameter and demonstrate the importance of considering a finite thickness range to accurately characterize its influence.
6.1 Bulk single crystals of VSe\(_2\)

Before investigating the thickness dependence of the CDW in VSe\(_2\), we have characterized it in bulk single crystals by transport measurements and scanning tunnelling microscopy.

6.1.1 Crystal growth and transport characterization

Single crystals of VSe\(_2\) were grown in-house\(^1\) by Céline Barreteau and Enrico Giannini. They used the chemical vapour transport technique with I\(_2\) as a transport agent. I\(_2\) was added to a stoichiometric mixture of the pure elements (V and Se) weighed in a glovebox, with a molar ratio of I\(_2\):V=0.05. The mixture was then sealed under vacuum (5\(\times\)10\(^{-6}\) mbar) inside a quartz ampoule with an internal diameter of 8 mm and a length of 120 mm. The sealed quartz reactor was placed in a tube furnace in the presence of a thermal gradient \(dT/dx \approx 5 - 10^\circ\text{C}/\text{cm}\), and heated up to temperatures \(T_{\text{hot}} = 620^\circ\text{C}\) at the hot end and \(T_{\text{cold}} = 590^\circ\text{C}\) at the cold end during one month. Large shiny grey single crystals were obtained at the cold side.

They have also carried out structural and resistive characterization. First of all, the quality of the crystals was characterized by X-ray diffraction in a Philips X’Pert four-circle diffractometer using Cu K\(_{\alpha}\) radiation. Energy dispersive X-Ray spectroscopy (EDX) analyses were performed in a LEO 438VTP electron microscope coupled to a Noran Pioneer X-Ray detector. Both characterizations confirmed the pure stoichiometry and the expected 1T structure (P-3m1 space group). The temperature dependence of the electrical resistivity was measured by a standard four-probe technique in a PPMS (Quantum Design), from room temperature to 4.2 K. The resistivity as a function of temperature (Figure 6.1) shows a characteristic kink at the CDW phase transition \(T_c^{\text{bulk}} = 105\) K, in agreement with previous studies [54].

6.1.2 STM of bulk VSe\(_2\)

STM and STS measurements of bulk single crystals of VSe\(_2\) were carried out on samples freshly cleaved in UHV. Tips were prepared out of an annealed W wire and conditioned on Au(111) as described in section 4.1.4. Constant current STM images and corresponding Fourier transforms at 77.6 K (Figure 6.2(a) and (b)) clearly reveal a triangular atomic lattice (\(a=3.36\) Å) and the in plane 4a\(\times\)4a commensurate CDW modulation [59].

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6.1 Bulk single crystals of VSe$_2$

Figure 6.1: Transport characterization of bulk 1T-VSe$_2$ single crystals. Resistivity as a function of temperature with a kink near 105 K associated with the CDW phase transition (inset: $dR(T)/dT$).

Figure 6.2: STM characterization of bulk VSe$_2$ single crystals. (a) 10×10 nm$^2$ atomic resolution STM image ($V_{bias}$=-100 meV, $I_t$=1 nA) of a cleaved surface at 77.6 K and (b) corresponding Fourier transform. Red and green circles indicate the first-order atomic lattice and CDW modulation peaks, respectively. The circle size depicts the integration area around each peak used to calculate the CDW order parameter $\Psi$. 
While these STM topographic features (wavelength, alignment with the atomic lattice) of the CDW are robust over the whole temperature range (see next section), different crystals measured with different tips and over many different locations of the same crystal we also find a variety of contrasts of the CDW signal. These are reproducible features measured with the same imaging parameters (bias and current setpoint) at the same temperature. The STM images presented in Figure 6.3(a) and (b) were recorded on the same sample surface a few tens of nm apart from each other. Moving back and forward between these regions and recording STM images we reproducibly find the same CDW appearance at each location. In Chapter 7 we also present a larger image (Figure 7.1) where different CDW appearances can be identified on the same scan lines recorded by the same tip probe. All in all, these findings exclude the different tunnelling conditions as the origin of these different contrasts. We will give a thorough explanation of this phenomenon in Chapter 7. An important observation to emphasize here is that while the real space appearance of the CDW can be very different in these cases (e.g Figure 6.3(a) and (b)) the structure and the intensity of the FFT peaks are nearly identical (Figure 6.3(c) and (d)) leading to the same order parameter $\Psi$.

Figure 6.3: Two different appearances of the CDW in VSe$_2$. (a)-(b) $5 \times 5$ nm$^2$ atomic resolution STM image ($V_{bias}=-100$ meV, $I_t=1$ nA) of a cleaved VSe$_2$ surface at 77.6 K and (c)-(d) corresponding Fourier transforms.

Tunnelling spectroscopy (Figure 6.4) is consistent with data reported in the literature [62], including a characteristic conductance peak associated with the vanadium derived d-band below the Fermi level.
6.1 Bulk single crystals of VSe$_2$

(E$_F$) and an asymmetric U-shaped background centred on E$_F$. These prominent spectral features do not change up to room temperature [62], except for thermal broadening. They also remain essentially unchanged on all the exfoliated flakes down to 2.2 nm thickness discussed in this chapter.

Figure 6.4: STS characterization of bulk VSe$_2$ single crystals. Differential tunnelling conductance dI/dV(V) and (inset) I(V) spectra measured at 77.6 K on the surface shown in Figure 6.2.

The vanadium derived d-band obscures the CDW gap and tunnelling spectroscopy does not show any significant reduction in the LDOS at E$_F$ at the phase transition. This observation is consistent with the tiny portion of the Fermi surface that is gapped in the CDW phase of 1T-VSe$_2$ [65], making it impractical to identify the phase transition by the opening of the gap. On the other hand, we show in the following that temperature dependent STM imaging allows us to verify that the quantity $\Psi$, defined by equation (5.2), behaves as a suitable order parameter to study the phase transition, e.g vanishes toward the transition temperature.

6.1.3 Temperature dependence of the CDW phase in bulk VSe$_2$

STM imaging of in-situ cleaved surface of bulk VSe$_2$ as a function of temperature (Figure 6.5) shows a strong CDW modulation at low temperature (4.4 K) whose amplitude is gradually suppressed upon ap-
Figure 6.5: Temperature dependent STM imaging. 10×10 nm² atomic resolution STM images ($V_{bias}=-100$ meV, $I_t=1$ nA) of bulk VSe$_2$ as a function of temperature from 4.4 K to 102.3 K. Note that these images were not recorded at the same physical location, but at different regions of the sample and on different crystals coming from the same growth batch. The CDW signal weakens as approaching the transition temperature, but we do not observe a clear signature of a 3q to 2q transition which is discussed in section 7.5.
proaching the transition temperature \( T_{\text{bulk}} = 105 \text{ K} \) determined from transport measurements (Figure 6.1).

We find that the CDW modulation is aligned with the atomic lattice in the whole temperature range (4.4 K to 102.3 K) examined here. The temperature dependence of the in-plane commensuration (Figure 6.6) is determined from the length of the q-vectors pointing to the first-order atomic lattice and CDW modulation peaks identified in the FFT (Figure 6.2(b)) of the STM images. Analysing a large set of STM data, within experimental uncertainty, we do not find any deviation from the \( 4\alpha \times 4\alpha \) in-plane commensuration as function of temperature.

![Figure 6.6: Temperature dependence of the CDW commensuration in bulk VSe\(_2\) single crystals. The error bars correspond to the standard deviation as determined by analyzing many different STM images for any given temperature.](image)

The visual impression of the weakening of the CDW signal with increasing temperature is very well reproduced by the temperature dependence of the CDW order parameter \( \Psi \) (Figure 6.7) which we have calculated as described in section 5.2. It is gradually vanishing when approaching the transition temperature, as expected for an order parameter.

The temperature dependence of \( \Psi \) (Figure 6.7) can be modelled in a mean field description by a phenomenological BCS gap equation [130]:

\[
\Psi(T) = A \cdot T_c \cdot \tanh \left( 1.74 \cdot \sqrt{\frac{T_c}{T}} - 1 \right),
\]  

(6.1)

where \( A \) is a scaling factor to be determined. The solid line in Figure 6.7 is a fit of equation (6.1) to the experimental data points, where we have
Figure 6.7: Temperature dependence of the CDW order parameter $\Psi$ in a bulk VSe$_2$ single crystal. The solid line is a fit to the BCS approximate form $\Psi(T) = A \cdot T_c \cdot \tanh \left(1.74 \sqrt{T_c/T - 1}\right)$, where $T_c = 105$ K and the only fitting parameter is determined to be $A = 0.0165 \pm 0.0004$. The error bars correspond to the standard deviation of $\Psi$ as determined by analyzing many different STM images for a given temperature.

set $T_c = T_c^{bulk} = 105$ K. The fit has a single adjustable parameter which we find to be $A = 0.0165 \pm 0.0004$. The consistent picture emerging from this analysis confirms that equation (5.2) is an adequate measure of the order parameter enabling a quantitative analysis of the CDW phase transition.

6.2 Exfoliated flakes of VSe$_2$

Now we can focus on the thickness dependence of the CDW phase in VSe$_2$. First we discuss qualitative features based on a visual inspection of STM image then we provide a quantitative analysis of the CDW order parameter and transition temperature.

6.2.1 Thickness and temperature dependent STM imaging

To gain insight into the thickness dependence of the CDW phase we prepared VSe$_2$ nanoflakes using the in-situ exfoliation method described in section 4.2. Besides having a wide range of thicknesses available in the same exfoliation process, we can also take advantage of steps and
terraces naturally present on the exfoliated flakes. The flake thickness is directly determined by STM from a topographic line profile between the reconstructed Au(111) and the top of the investigated exfoliated terrace. Both surfaces are atomically flat, thus enabling the local thickness to be determined in principle with single layer accuracy, especially in the thinnest regions along the edges of the flakes. The uncertainty on the flake thickness is thus less than the symbol size in Figures 6.9 and 6.11.

Figure 6.8: STM images of in-situ exfoliated VSe$_2$ flakes. 5×5 nm$^2$ atomic resolution micrographs (V$_{bias}$=-100 meV, I$_t$=1 nA) measured on different thickness terraces and flakes at 77.6 K and 95.0 K. The atomic lattice is well resolved in all images. The CDW is strongest in the thinnest regions (10 nm) at both temperatures and nearly absent in the 20 nm and 50 nm thin regions at 95.0 K. Here, we concentrate on STM micrographs measured above 77 K, near T$_c^{bulk}$ where thickness dependent CDW features are most prominent. Topographic and CDW features imaged by STM on different exfoliated thin flakes and terraces with distinct thicknesses (Figure 6.8) are very similar to those in bulk crystals. Remarkably, we observe the same 4a×4a charge order down to the thinnest sample studied (2.2 nm). However, a closer inspection of the 77.6 K micrographs reveals a noticeably weaker CDW amplitude in the 20 nm thin region than for all other thicknesses. At 95.0 K, closer to T$_c^{bulk}$, the CDW is almost completely suppressed on the 20 nm and 50 nm thin flakes - similar to what we
observe in bulk crystals - while it remains surprisingly strong on the thinnest 10 nm flake.

6.2.2 Thickness dependence of the order parameter and the transition temperature

A more quantitative analysis of the CDW contrast revealed by STM is required to go beyond the above approximate visual assessment. We have seen that the order parameter Ψ correctly describes the CDW transition in the bulk crystal (Figure 6.7). Thus, we have calculated the thickness dependent order parameter from STM images measured on exfoliated flakes.

Examining a large set of STM images from different terraces and flakes at T=77.6 K, we find a non-monotonic thickness dependence of the CDW order parameter (Figure 6.9). Ψ is gradually decreasing from its bulk value when reducing the thickness in thicker flakes. This thickness dependence is reversed in the thinner flakes below 20 nm, where Ψ is increasing to even significantly exceed the bulk value in the thinnest regions shown here (2.2 nm). Defects have been shown to stabilize a finite CDW amplitude above T_c in their vicinity [131]. However, we can exclude this scenario for the enhanced phase transition in the thinnest flakes because T_c is determined from data measured at 77.8 K and averaged over many different STM images with few defects.

The order parameter Ψ is not suitable for a direct comparison of our STM data with published transport experiments [69, 70]. The latter report T_c as a function of thickness, which is challenging to measure by STM because of thermal drift making it difficult to maintain the tip position over a specific location while changing the temperature above 77 K. As it turns out, we can use equation (6.1) to calculate the local T_c based on Ψ(T) extracted from STM images at a given temperature T<T_c. If we assume that the scaling factor A is the same for all thicknesses, equation (6.1) provides a direct correspondence between T_c and the order parameter Ψ(T). To verify this assumption, we plot (6.1) for the 10 nm, 20 nm, and 50 nm thin terraces, using the transition temperature T_c=122 K, 87 K, and 100 K, respectively, calculated for each thickness from Ψ(T=77.6 K). The agreement with the experimental data points is excellent as shown in Figure 6.10.

The above result demonstrates the validity of our method, providing an unprecedented ability to determine the local CDW transition temperature solely based on the charge modulation amplitude measured by STM. The expected CDW gap amplitudes within this weak coupling model, calculated using equation (2.10) and the thickness dependent
6.2 Exfoliated flakes of VSe$_2$

Figure 6.9: Thickness dependence of the CDW order parameter $\Psi$ in VSe$_2$ at 77.6 K extracted from topographic STM images. The error bars correspond to the standard deviation of $\Psi$ as determined by analysing many different STM images for a given thickness.

transition temperature obtained in our analysis, are in the range of 3.8 meV to 5.7 meV depending on crystal thickness. They are indeed too small to be properly resolved above 77 K by tunnelling spectroscopy. However, recent low temperature STS measurements of the CDW gap [132] give consistent results with these values expected from our analysis.

The CDW transition temperature calculated for different thicknesses using the above method are plotted in Figure 6.11. They are in remarkable quantitative agreement with independent transport studies [69, 70]. The most striking findings of our analysis are a non-monotonic thickness dependence of $T_c$ and a significant increase of $T_c$ above the bulk value in the thinnest terraces. The opposite thickness dependencies of $T_c$ we find in very thin compared to thicker terraces reconcile the contradicting results reported by Xu et al. [70] and Yang et al. [69]. That disagreement has been blamed on the distinct liquid and mechanical exfoliation techniques used in these studies, when it is in fact the result of investigating different thickness ranges. The STM data presented in Figure 6.11 suffers no such ambiguity; they were obtained with the same tip probe on flakes prepared in an identical mechanical exfoliation process.
Figure 6.10: The CDW order parameter as a function of temperature for three different thicknesses. The solid lines are calculated with the \( \Psi(T) = A \cdot T_c \cdot \text{tanh}(1.74\sqrt{T_c/T - 1}) \) BCS interpolation using the bulk scaling factor \( A=0.0165\pm0.0004 \) and the local \( T_c \) calculated from \( \Psi(T=77.6 \text{ K}) \) for each thickness. The error bars correspond to the standard deviation of \( \Psi \) as determined by analysing many different STM images for a given temperature and thickness.
Figure 6.11: Thickness dependence of the CDW transition temperature $T_c$ in VSe$_2$. Solid squares represent $T_c$ calculated from the charge modulation amplitude imaged by STM using equations (5.2) and (6.1). They reveal a clear non-monotonic dependence of $T_c$ on crystal thickness. The vertical error bars correspond to the standard deviation of $T_c$ from many different STM images. The green dashed line symbolizes the transition temperature of a bulk sample. Our data are in quantitative agreement with and reconcile data from previous transport experiments covering separate thickness ranges (represented by the solid red circle [70] and the solid blue line [69]).
6.2.3 Dimensional crossover and quantum confinement

The two distinct and opposite thickness dependencies of the CDW transition temperature illustrated in Figure 6.9 and Figure 6.11 suggest a crossover from a three-dimensional (3D) regime in bulk and thick flakes to a two-dimensional (2D) regime in the thinner flakes. $T_c$ has been found to increase with decreasing thickness also for other very thin TMD compounds [33, 34]. However, these studies lack important real space information to fully assess the nature of the CDW. STM directly and unambiguously shows no alteration in the CDW symmetry and periodicity with thickness and temperature. The only modification we observe is the charge modulation amplitude associated with a modified $T_c$.

We propose that the enhanced $T_c$ in the thinnest samples is a consequence of quantum confinement, in analogy to BCS superconductors governed by a gap equation similar to equation (6.1). For thin films of superconductors oscillations of the transition temperature as function of thickness were predicted [133] when the Fermi level crosses the edge of one of the confinement-induced subbands. In a more advanced modelling [134] these ”shape resonances” are smoothed to a continuous evolution of the transition temperature with film thickness. In that case, for a confinement potential $U$ above a critical value, theory predicts the superconducting transition temperature ($T_{sc}$) to increase with decreasing thickness before vanishing to zero in the zero thickness limit [134]. The characteristic thickness $d_{max}$ for which $T_{sc}$ is maximum in this model depends on $U$, on the coupling strength, and on the carrier density. It is important to note that $d_{max}$ does not necessarily correspond to the single layer limit. It can be larger and it is thus crucial to examine a range of thicknesses to draw definite conclusions about the thickness dependence of $T_c$. In particular, considering only bulk and single layer crystals may lead to inaccurate conclusions about the effect of dimensional confinement, even in the same material if different preparation and substrates result in different $d_{max}$.

The decreasing $T_c$ with decreasing thickness in thick flakes can be understood considering the Fermi surface (FS) topology of VSe$_2$. It has a significant dispersion of a few eV along $k_z$ [65, 68], different from the mostly 2D FS of other layered TMDs. Photoemission [67, 68] reveals large parallel FS portions centered at the M(L) points of the Brillouin zone. They offer good in-plane nesting conditions that persist for all $k_z$. This nesting is strongest at a particular $k_z$, resulting in an effective out of plane nesting vector and a 3D CDW [68] in bulk VSe$_2$. Upon thinning the bulk crystal, the out-of-plane nesting condition eventually becomes
weaker due to the discretization of the FS by the reduced number of available \( k_z \) points. This drives the system into a weaker 2D charge order that is further suppressed by enhanced fluctuations expected in 2D.

We understand the non-monotonic thickness dependence of the transition temperature as a combined effect of these two mechanisms, 3D to 2D crossover and quantum confinement. They act in parallel and dominate in different thickness ranges resulting in a net non-monotonic thickness dependence of \( T_c \).

![Three dimensional representation of the dimensional crossover from 3D to 2D behavior.](image)

**Figure 6.12:** Three dimensional representation of the dimensional crossover from 3D to 2D behavior.

### 6.3 Summary

In summary, we find a striking non-monotonic thickness dependence of the CDW transition temperature in mechanically exfoliated VSe\(_2\) from bulk to 2.2 nm thin flakes. On the other hand, the modulation period and alignment with the atomic lattice are entirely independent on thickness. We propose this behavior is a consequence of a 3D to 2D dimensional crossover in the FS topology around 20 nm thickness combined with quantum confinement in thinner flakes. The dimensional crossover weakens the bulk CDW in the thicker flakes and the confinement enhances it in the thinner ones (Figure 6.12). Unambiguous evidence for
this behavior is provided by the local $T_c$ determined from the CDW order parameter measured by STM over an unprecedented broad range of thicknesses for a single experiment. We demonstrate that the charge modulation amplitude provides a suitable measure of the CDW phase transition order parameter. This allows a robust determination of the local critical temperature based solely on STM topographic images of the CDW at a given temperature below $T_c$. Interestingly, the exact same approximate form of the (weak coupling) BCS equation quantitatively describes the CDW order parameter and critical temperature, independent of sample thickness and temperature. The present study thus strongly suggests that the thickness dependence reported here is not a consequence of a varying coupling regime or the signature of a different CDW phase, but indeed due to the Fermi surface topology, dimensional crossover and quantum confinement.
Chapter 7

Holographic imaging of the complex charge density wave order parameter

The charge density wave in solids is a collective ground state combining lattice distortions and charge ordering. It is defined by a complex order parameter with an amplitude and a phase. The amplitude and wavelength of the charge modulation are readily accessible to experiment. However, accurate measurements of the corresponding phase are significantly more challenging. In Chapter 5 we have introduced a fitting procedure which combines reciprocal and real space information to map the full complex order parameter based on topographic scanning tunneling microscopy images. In this chapter we apply this analysis to a selection of transition metal dichalcogenides: VSe$_2$, Cu$_{0.02}$TiSe$_2$ and NbSe$_2$. Our analysis provides striking evidence that their CDWs consist of three individual charge modulations whose ordering vectors are connected by the fundamental rotational symmetry of the crystalline lattice. Spatial variations in the relative phases of these three modulations account for the different contrasts often observed in STM topographic images. Phase images further reveal topological defects and discommensurations, a singularity predicted by theory for a nearly commensurate CDW.
7.1 The real space CDW pattern

A rapid survey of the literature summarized in Figure 3.4 for VSe$_2$ reveals that the CDW contrast in a given material varies significantly among published STM images, even in the absence of any structural defects. While in several cases this can be explained with changing experimental conditions, either extrinsic, e.g. a change in the tip state, or intrinsic, e.g. bias dependence, we find compelling evidence of contrast variations which are real CDW features and not the consequence of particular tunnelling conditions.

In Figure 6.3 (repeated in Figure 7.2(a) and (c)) we showed two STM images of VSe$_2$ with different CDW appearances. These images were recorded at close-by regions under identical conditions. The observed contrast was reproducible: moving back and forth between these regions we always found the same appearance of the CDW in each region. Even more persuasive is the large scale STM image presented in Figure 7.1(a). In panel (c) and (d) of Figure 7.1 we highlight two adjacent regions with a different contrast in the same STM micrograph. As we show in the following, these two contrasts can be reproduced straightforwardly by tuning the relative phases of the three CDWs discussed above. To quantify the changing configurations, we introduce a dephasing parameter $\Theta$ defined as the sum of the three individual CDW phases $\varphi_n$ modulo $2\pi$:

$$\Theta = \left( \sum_{n=1}^{3} \varphi_n \mod 2\pi \right). \quad (7.1)$$

This dephasing parameter uniquely determines the general appearance of the CDW pattern. Each $\Theta$ value corresponds to a particular CDW imaging contrast, regardless of how individual phase shifts $\varphi_n$ are distributed among the three complex order parameters ($\Psi_n$). A more detailed description of the dephasing parameter is given in the next sections.

In order to determine the phase $\varphi_n$ of each CDW required to compute the dephasing parameter, we developed the fitting procedure described in section 5.3.1. To illustrate this fitting procedure, we apply it to a large scale STM image of an in-situ cleaved VSe$_2$ single crystal measured at 40 K (Figure 7.1). The atomic and the $4a \times 4a$ CDW modulations are clearly resolved in the STM image (Figure 7.1(a)). The red and blue squares, magnified in Figure 7.1(c) and (d), highlight two adjacent regions with different CDW contrasts. This image was acquired from top to bottom, with the fast scan direction running horizontally. The two highlighted regions are thus connected through continuous scan...
Figure 7.1: Real space CDW pattern and the dephasing parameter. (a) High resolution STM micrograph ($V_{\text{bias}}=\text{-100 mV}, I_t=\text{1 nA}$) of an in-situ cleaved VSe$_2$ surface at 40 K. The atomic and CDW modulations are clearly resolved. (b) Spatial variation of the dephasing parameter as determined by the fitting procedure. The areas marked by red and blue squares have distinct dephasing parameters corresponding to the different appearances of the CDW. (c) and (d) are magnified areas corresponding to the red and blue squares in panel (a), respectively. They are connected by single scan lines, the different contrasts can thus not be blamed on different tip state configurations. (e) and (f) are zooms into the large Fourier filtered image of the CDWs at the same location as shown in (c) and (d), respectively. (g) and (h) are reconstructed images from the mosaics of the fitting procedure, in excellent agreement with (e) and (f). All topographic images are plotted with the exact same color scale. The scale bar in (a) and (b) corresponds to 10 nm, while in (c)-(h) to 1 nm.
lines and therefore imaged with exactly the same tip at the same set point. Consequently, the distinct appearances of the CDW in these two regions cannot be imputed to changing tunnelling conditions. Magnifying the same two regions of the Fourier-filtered image of Figure 7.1(a) clearly shows the CDW origin of the changing contrast (Figure 7.1(e) and (f)). Based on the result of the local fitting we can reconstruct the full large scale CDW pattern by assembling the mosaics of the local fit results. The magnified image of the red and blue regions of this reconstructed images are shown in Figure 7.1(g) and (h). Indeed, applying our fitting procedure allows us to perfectly reproduce the experimental CDW contrast (Figure 7.1(g) and (h)) characterized by two distinct dephasing parameters Θ displayed in Figure 7.1(b). Running the local fitting on a dense grid of slightly overlapping small windows spanning the entire field of view of Figure 7.1(a) allows us to map the complete spatial structure of the dephasing parameter (Figure 7.1(b)). We find that the changing contrast over the entire scan area is fully reproduced by a specific local dephasing parameter with a remarkable match between the experimental and the calculated contrasts as exemplified in Figure 7.1(e)-(h).

![Figure 7.2: Illustrative reconstruction of STM images with different dephasing parameters based on the result of real space fitting of the CDW modulation.](image)

Figure 7.2: Illustrative reconstruction of STM images with different dephasing parameters based on the result of real space fitting of the CDW modulation. (a) and (b) are 5×5 nm² atomic resolution STM images (V_{bias}=-100 meV, I_{t}=1 nA) of a cleaved VSe₂ surface at 77.6 K. (c) and (d) are calculated images produced by projecting the CDW pattern which was obtained by running the fitting procedure on (a) and (b), respectively, onto the FFT filtered atomic lattices.

An other example is given in Figure 7.2. Applying our fitting pro-
7.1 The real space CDW pattern

procedure to the STM images with visibly different dephasing parameters shown in Figure 6.3(a)-(b) (repeated in Figure 7.2(a)-(b)) we further demonstrate its capability to reproduce the real space CDW pattern. In order to give a simple visual comparison of the fit result with the experimental data in Figure 7.2(c)-(d) we project onto the FFT filtered atomic lattices the entire field of view CDW pattern, which was reconstructed from the results of the local fitting of the Figure 7.2(a)-(b) STM images, respectively. We get an excellent visual correspondence between the experimental and the calculated appearance of the CDW as displayed in Figure 7.2(a)-(d).

7.1.1 The dephasing parameter

The dephasing parameter $\Theta$ is defined in equation (7.1) of the previous section. It has a very simple graphical interpretation if we represent the CDWs in each direction by their wavefronts. For a 2D plane wave, these amount to periodic arrays of straight lines. First, let us consider only one wavefront for each direction (black lines in the top row of Figure 7.3). We define the reference of the phase for all directions in such a way that the three wavefronts intersect at one point when they all have zero phase. Adding a phase shift $\varphi \in (0, 2\pi)$ to any of the three plane waves with a wavelength $\lambda$ is equivalent to shifting the corresponding wavefront by $\frac{\varphi}{2\pi} \lambda$. As a result, the three waves intersect at three distinct points that form an equilateral triangle of height $h = \frac{\varphi}{2\pi} \lambda$ highlighted in green in the top row of Figure 7.3. By symmetry, the triangle we obtain is independent of which wavefront has been shifted.

We may shift more than one wavefront. In this case, the height of the resulting intersection triangle will be $h = \Theta \frac{\lambda}{2\pi} = \frac{\Theta}{q}$, where $\Theta$ is the dephasing parameter defined by equation (7.1) and $q$ is the length of the wave vector. $\Theta$ uniquely defines the intersection triangle which itself corresponds to one particular appearance of the CDW modulations in an STM micrograph. An extended view including all the wavefronts shows that there is a complementary triangle to each of the green triangles discussed above (red triangles in Figure 7.3). The red and green triangles for a given $\Theta$ are complementary in the sense that $\lambda = h_{\text{green}} + h_{\text{red}}$, where $h_{\text{green}} = \Theta \frac{\lambda}{2\pi}$ and $h_{\text{red}} = (2\pi - \Theta) \frac{\lambda}{2\pi}$. Each set of complementary triangles is associated with a unique appearance of the CDW as shown in the bottom row of Figure 7.3. Note that for every red triangle corresponding to $\Theta$, there is a green one pointing in the opposite direction corresponding to a dephasing parameter of $2\pi - \Theta$. The related CDW appearances differ by a $\pi$ rotation around the $z$-axis which is a manifestation of the above complementarity (bottom row of Figure 7.3).
7.1.2 The choice of fundamental q-vectors

We need to define initial parameters for the fitting procedure. To this end, we read the direction and the length of the starting q-vectors from the Fourier transform of the STM image. For each direction we get two peaks: $\pm q_n$. Hence, in total we have $2^3 = 8$ possibilities to select the three peaks to initialize the fitting (we have to choose one peak for each direction and for each direction we have two options). To follow the symmetry of the lattice we fix the relative position of the three chosen peaks so that they are $2\pi/3$ rotated with respect to each other.

With the above restriction, there are only two possible sets of fundamental q-vectors. These are related by a $\pi$ rotation in k-space and resulting in $\pi$ rotated images in real-space. As noted previously, $\pi$ rotated images correspond to dephasing parameter with $\Theta$ and $2\pi - \Theta$. Thus, choosing either one or the other set of fundamental q-vectors, one can obtain a dephasing parameter $\Theta$ and $2\pi - \Theta$ for the same image. Basically, it is equivalent with the problem of choosing either the red or the green triangles in Figure 7.3 to define the dephasing parameter. Within the same set of measurements and the same single crystal sample one can easily make sure to always select the same set of q-vectors which allows a direct quantitative comparison of such images. On the other hand, as the q-vectors are indistinguishable (connected by sym-
7.2 Coexisting charge density waves

So far, we have established the ability of our model to account for the variety of CDW contrasts observed in STM micrographs of a given material using a single well-defined dephasing parameter. We now advance a step further in the quantitative analysis to discuss the individual amplitudes and phases of each of the three CDWs as a function of position. The spatially resolved amplitudes $A_n(r)$ and the corresponding local phases $\varphi_n(r)$ for each $q_n$, over the same field of view as Figure 7.1(a), are shown in Figure 7.4(a)-(c) and in Figure 7.4(d)-(f), respectively.

Figure 7.4: Coexisting charge density waves. Mapping of the full complex order parameter direction by direction for the same surface as in Figure 7.1(a). (a)-(c) The local amplitude of the CDWs in each direction ($q_1$, $q_2$, $q_3$, respectively) and, (d)-(f) the corresponding local phase referenced to the lower left corner, whose phase is set to zero. Scale bar: 10 nm. Red arrows are indicating tightly bounded phase vortex-antivortex pairs.
A remarkable aspect of this dataset is the absence of any obvious spatial correlation between the amplitude and phase images of the different CDWs. Each map displays its own features, meaning the amplitude and the phase of each CDW can vary at some location, even abruptly, regardless of the other two CDWs whose amplitudes and phases can remain constant and featureless at that same position. This clearly shows that these three CDWs develop their individual local complex order parameters, albeit being indistinguishable in the sense that they are connected by symmetry. We find a very similar behaviour in 1T-Cu$_{0.02}$TiSe$_2$ and 2H-NbSe$_2$ (see Figure 7.7 and Figure 7.9), supporting the idea that the total charge order in these TMDs consists of three coexisting CDWs.

Note that although we find three rather independent $\Psi_n$ in the examples discussed here, interactions mediated by the atomic lattice are possible. For example, pinning by crystalline defects or impurities can distort the charge modulations [23, 24] and introduce correlations between the three CDWs.

The detailed explanation of the complete spatial distribution of the complex order parameter is out of the scope of the present thesis. On the other hand, the Fukuyama-Lee-Rice model of pinning presented in Chapter 2 may account for the main features and may be one of the good starting points of future studies addressing this topic in more detail. Such studies are enabled by the analysis tool-kit we developed and presented here.

7.3 Singularities of the complex order parameter

The ability to determine the local amplitude and phase of each CDW enables a much more thorough characterization of the CDW ground state in real space. Beyond explaining the variety of STM imaging contrasts and demonstrating the individual nature of the three CDWs developing in TMDs, our fitting procedure reveals several intrinsic CDW properties. Of particular interest are singularities in the amplitude and phase, such as domain walls and topological defects. They are important to understand the interplay of ordered electronic phases [123, 135]. For example, the model analysis discussed here provides a unique contrast mechanism to identify and locate domain walls, which have been proposed to promote superconductivity [79, 80].

We now focus on three selected CDW features to illustrate the augmented experimental phase space accessible by fitting the complex order
7.3 Singularities of the complex order parameter

7.3.1 Phase domain walls in Cu$_{0.02}$TiSe$_2$

The first example is a detailed analysis of the $\pi$-phase shift CDW domain walls ($\pi$DWs) developing in TiSe$_2$ when intercalating either Cu [77] or large amounts of Ti [78]. These $\pi$DWs are usually identified by eye in STM images, seeking for one atomic row shifts in the characteristic sequence of bright and dark atoms of the 2$a\times2$a CDW. Such domains can be easily found in Figure 7.5(a). Their topographic structure is magnified in Figure 7.5(b) and (c) corresponding to the red and blue outlined regions in Figure 7.5(a). The real space CDW modulation in these two regions, highlighted in the corresponding filtered images (Figure 7.5(d) and (e)), is perfectly reproduced by our fitting procedure in Figure 7.5(f) and (g). Most instructive are the local phases of the three independent CDWs involved in the above fitting procedure (Figure 7.5(i)-(k)). Each phase is essentially constant within any given domain and changes abruptly at the domain wall.

An original insight of our analysis is that the domain walls do not strictly correspond to a $\pi$-shift as shown by the polar histograms in Figure 7.5(l)-(o). A visual inspection, in the absence of the quantitative phase analysis proposed here, would conclude a $\pi$-shift up to a phase shift close to $\pi/4$, because the same atoms remain the brighter ones within each domain. For a better understanding we give a graphical illustration of the visual perception of a phase shift domain wall of a 2 $\times$ 2 CDW in Figure 7.6.

A simple one-dimensional STM topography model is presented in Figure 7.6(a)-(c)). The blue and red profiles represent the atomic and CDW modulations, respectively. The yellow line is the sum of the atomic and CDW profiles. If the phase shift is zero between the atomic and CDW profiles (Figure 7.6(a)) we find the standard sequence of high-low intensities in the total profile. Shifting the CDW profile with less than 90° (e.g. by 30° in Figure 7.6(b)) affects the total profile, but without changing its high-low atom sequence centred on the same atoms. Shifting the CDW signal more then 90° (e.g by 160° in Figure 7.6(c)) inverts the high-low sequence in the total profile and may be visually interpreted as a $\pi$ phase shift. The same idea applies to the 2D case. A reference model image with the atomic lattice and the 2 $\times$ 2 CDW is shown in Figure 7.6(d). Shifting two of the CDWs by 180° reproduces the changes expected for a $\pi$ domain wall (Figure 7.6(e)). However, the same visual impression is obtained when shifting one CDW by 120° and another by 180° (Figure 7.6(f)), or when shifting one CDW by 150° and another by 210° (Figure 7.6(g)). Although an asymmetry of the total
Figure 7.5: Phase domains of the CDW in Cu$_{0.02}$TiSe$_2$ at 1.2 K. (a) High resolution STM micrograph of an in-situ cleaved surface ($V_{bias} = -200$ mV, $I_t = 100$ pA). (b) and (c) selected magnified areas from panel (a) at locations marked by red and blue squares, respectively. Blue ($q_1$), orange ($q_2$) and yellow ($q_3$) parallel lines highlight the shifted CDW modulations for each direction. (d) and (e) Fourier filtered CDW seen in (b) and (c). (f) and (g) are reconstructed images from the mosaics of the fitting procedure. Note the excellent agreement with (d) and (e). (h) Vectors representing the CDW q-vectors. (i)-(k) Fitted phase images for the three directions ($q_1$, $q_2$, $q_3$). The red and blue squares mark the same areas as in (a). In the red region, $q_2$ and $q_3$ undergo a phase shift (see panel (b)). This is very well reflected in panels (i)-(k): within the red region $q_1$ is homogeneous (no shift) while $q_2$ and $q_3$ undergo an abrupt colour change. Similarly, in the blue region $q_1$ and $q_2$ shift, while $q_3$ does not (see panel (c)). This is very well shown in (i)-(k): $q_1$ and $q_2$ show an abrupt colour change in the blue region, but $q_3$ remains uniform. (l)-(o), polar histograms of the CDW phase (in degrees) corresponding to: (l) blue area in (i); (m) blue area in (j); (n) red area in (j) and (o) red area in (k). Scale bars=10 nm in (a), (i)-(k); Scale bars=1 nm in (b)-(g).
intensity distribution in the unit cell is visible in some cases, signalling a non-$\pi$ phase shift, quantifying the phase shift is impossible without the quantitative analysis provided by our fitting procedure. In conclusion, for a $2 \times 2$ CDW lattice, what looks like a $\pi$ domain wall based on the sequence of bright and dark atoms may in reality correspond to a non-$\pi$ phase shift.

Figure 7.6: Visual perception of a phase shift domain wall in a $2 \times 2$ CDW. It shows that phase shifts different from $\pi$ are likely to be visually misinterpreted as a $\pi$-phase shift because the brighter atoms in the STM topography remain the brighter ones for a finite range of phase values. (a)-(c), One-dimensional STM topography model where the blue and red profiles represent the atomic and CDW modulations, respectively. The yellow line is the sum of the atomic and CDW profiles. (a) $0^\circ$, (b) $30^\circ$, (c) $160^\circ$ phase shift between the atomic and CDW profiles. (d)-(g) Two-dimensional model of a $2 \times 2$ CDW lattice. (d) Reference model micrograph with the atomic lattice and the $2 \times 2$ CDW. (e) Two of the CDWs are shifted by $180^\circ$. (f) One CDW is shifted by $120^\circ$ and another by $180^\circ$. (g) One CDW is shifted by $150^\circ$ and another by $210^\circ$.

Our holographic analysis further reveals these $\pi$DWs to be one-dimensional line-singularities along which the CDW order parameter is suppressed. The complete fitting data set corresponding to the STM micrograph of Figure 7.5 is displayed in Figure 7.7. It indeed shows that the amplitude is vanishing at the domain wall (Figure 7.7(a)-(c)). Further supporting the collapse of the CDW state at the $\pi$DWs are the low values of the $R^2$ maps along the domain walls (Figure 7.7(g)-(i)).
indicating that the fitting procedure fails in those locations because there is actually no periodic CDW modulation.

Figure 7.7: Amplitude, phase and $R^2$ maps in Cu$_{0.02}$TiSe$_2$. Amplitude (a)-(c), phase (d)-(f) and $R^2$ (g)-(i) maps of the Cu$_{0.02}$TiSe$_2$ STM image presented in Figure 7.5. Note that the fitting amplitude and goodness of fit drop along the phase domain walls, indicating the absence of CDW amplitude in these locations. Scale bar=10 nm.

### 7.3.2 Discommensurations

As a second example, we address discommensurations (DCs) that we have already introduced in Chapter 2 and visualized in Figure 2.5. They are a particular type of defects associated with nearly commensurate CDWs (NC-CDW) found for example in NbSe$_2$ or TaSe$_2$. Discommensurations were first proposed in the seminal work of McMillan [21] and
7.3 Singularities of the complex order parameter

Figure 7.8: CDW discommensurations in NbSe$_2$. (a) STM micrograph ($V_{\text{bias}}=100$ mV $I_t=100$ pA) of in-situ cleaved NbSe$_2$ surface at 1.2 K. (b) Phase map of the corresponding $q_2$ CDW. (c) Phase profile extracted from the square to the circle along the red dashed line in panel (b). Scale bars: 10 nm.

searched for, e.g in the NC-CDW phase of 1T-TaS$_2$ [136]. DCs are domain walls where the order parameter phase is changing rapidly between small phase locked regions, which allow the CDW system to lower its energy.

Our holographic analysis reveals precisely such a phase texture in the CDW images acquired on in-situ cleaved surfaces of NbSe$_2$ (Figure 7.8(a)). Figure 7.8(b) is a phase map of one of the three CDWs in the same field of view as Figure 7.8(a). It reveals areas of rather constant phase separated by nanometer-sized regions (domain walls) where the phase is changing rapidly. This staircase structure is best seen in a phase profile (Figure 7.8(c), cf. Figure 2.5) taken along the red dashed line in 7.8(b) which perfectly mimics the prediction by McMillan [21].

The phase-locked region sizes and locations are uncorrelated among the CDW components (Figure 7.9(d)-(f)), which confirms their individual nature. We stress that the DC domain walls observed here for the NC-CDW of NbSe$_2$ are completely different from the $\pi$DWs discussed above for Cu$_{0.02}$TiSe$_2$. The order parameter amplitude remains essentially unchanged along a DC (Figure 7.9(a)-(c)), whereas it is vanishing along the $\pi$DWs (Figure 7.7(a)-(c)), suggesting the different nature and origin of these two CDW defects. While $\pi$DWs can be readily seen in topographic STM images, DCs can only be detected using our holographic fitting scheme. Note that in order to detect DCs, one has to control the phase wrapping in the fitting procedure. Otherwise, cumulative errors introduce an artificial phase gradient in the phase-locked domains delimited by the DCs, making them essentially undetectable (see Figure 5.2).
Figure 7.9: Amplitude (a)-(c), phase (d)-(f) and $R^2$ maps of the STM image of NbSe$_2$ shown in Figure 7.8(a). Red arrows indicate strongly bound vortex-antivortex pairs. White arrows point at single vortices associated with a distant single antivortex; they correspond to weakly bound vortex-antivortex pair. Scale bars: 10 nm.
7.3.3 Topological defects

The final example are topological defects (TDs) which are defined as singularities in the order parameter that cannot be annealed without introducing other singularities outside of an arbitrarily small environment of the TDs [137]. They are characterized by a topological invariant, the winding number, which is conserved under any continuous deformation of the order parameter field. They correspond to points in a 2D landscape around which the total phase of the order parameter winds by an integer multiple of $2\pi$. By analogy to vortices in a superconductor, they are called vortices and antivortices depending on the winding polarity. Such defects appear in the phase images of both VSe$_2$ and NbSe$_2$. We observe tightly bound vortex-antivortex pairs, as pointed out by red arrows in Figure 7.4(e) and (f) measured on VSe$_2$, and well separated vortex-antivortex pairs, as pointed out by white arrows in Figure 7.9(d)-(f) measured on NbSe$_2$. The TD landscape is different for each of the three CDWs in a given STM image, again supporting the conclusion that the CDW consists of three individual charge modulations.

7.4 Structural and CDW defects

![Figure 7.10: Structural and CDW defects in NbSe$_2$. (a) STM micrograph ($V_{bias}=100$ mV $I_t=100$ pA) of a defect free region of in-situ cleaved NbSe$_2$ surface at 1.2 K on the same sample shown in Figure 7.8(a). (b) Phase and (c) amplitude maps of the corresponding $q_2$ CDW. Scale bars: 10 nm.](image)

Crystalline defects and impurities certainly play a role in the amplitude and phase landscape of the CDW phase (see section 2.5) and in the nucleation near the phase transition [131]. The holographic analysis we propose here reveals more subtle aspects of this interplay. A first revealing insight not available prior to the present experiments is that domain walls and TDs can develop independently in any of the three
CDWs as clearly exemplified by the distinct domain patterns of the three CDWs of Cu$_{0.02}$TiSe$_2$ in Figure 7.5(i)-(k). An additional striking manifestation of the coexistence of individual charge orders, highlighted by our holographic analysis, is that a single atom defect can trigger a topological defect in the phase of one CDW, while only producing a smooth phase variation for another one (Figure 7.4, Figure 7.8(a) and 4(b) and Figure 7.9).

While CDW defects are expected in the presence of structural defects, the holographic analysis discussed here reveals that the CDW order parameter landscape (Figure 7.10(b) and (c)) can be remarkably inhomogeneous on a NbSe$_2$ surface with no obvious structural defects (Figure 7.10(a)). This is likely the result of discommensurations not readily detectable in the topographic STM images. It may also reflect 3D CDW correlations with defects below the surface not apparent in the STM micrograph. More generally, Figure 7.10(a)-(c) suggests the ability of the CDW to develop a spatial structure essentially independent of the supporting crystalline lattice.

7.5 Rotational symmetry breaking phases

The CDW phase is a symmetry breaking electronic phase which lowers the discrete translational symmetry of the crystalline lattice. On the other hand, in the TMDs that we have presented above the three-fold rotational symmetry is respected in the sense that three individual CDWs develop along $2\pi/3$ rotated directions (3q). The absence or disappearance of one (2q) or two (1q) of these CDWs at a given temperature may be considered as a further symmetry breaking. Our holographic analysis gives a unique insight in this theme through the mapping of the local CDW amplitude ($A_n(r)$) and wavelength ($\lambda_n(r)$).

A 3q to 2q transition in conjunction with a shift in the c-axis wavelength of the CDW was proposed for VSe$_2$ at around 85 K (see section 3.2). However, there is no consensus neither on the existence nor on the origin of this transition. Our analysis of STM images of VSe$_2$ recorded over a broad temperature range (from around $T_{c bulk}$ down to 4.4 K) clearly shows a finite CDW amplitude for all three CDWs (e.g. see Figure 7.4(a)-(c) at 40 K). We do not observe any extended zero amplitude region in the examined amplitude maps. While we do not find any of the CDWs fully quenched at any temperature we occasionally do find asymmetry in the average of amplitude maps. For instance,

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1Strictly speaking the three fold symmetry is already broken by the fact that the CDWs can develop their own order parameter field, e.g. by having locally different amplitudes of the CDWs in different directions.
in Figure 7.4(a)-(c) the average amplitude of the $q_1$ is higher than the two others. Although, the systematics of this observation is still under investigation it rather seems to be either a sporadic phenomenon with extrinsic origin or an experimental artefact.

A transition to a 1q or a 2q phase should be related to a symmetry breaking renormalization of the band structure due to intrinsic or extrinsic effects. For example, strain could trigger a transition of this kind as it was demonstrated for NbSe$_2$ [82, 83, 84] (see section 3.3). Soumyanarayanan et al. [83] found regions where a 1q CDW with a unique $q_{1q} = \frac{1}{3.5}a^*$ wavevector (corresponding to a commensuration of 3.5) forms a smooth interface with the usual 3q CDW of NbSe$_2$. Now we apply our fitting procedure to this data set to further demonstrate the capabilities of our modelling.

To perform our analysis we digitalized the STM image presented in Fig. 2.A of ref. [83] (Figure 7.11(a)). The two distinct regions with the 1q and 3q CDWs is clearly visible and further highlighted in the Fourier filtered image of the CDWs (Figure 7.11(b)). This is perfectly reproduced by our CDW pattern which is reconstructed from the mosaics of the local fitting (Figure 7.11(c)). In the amplitude maps (Figure 7.11(d)-(f)) we clearly find two CDWs ($q_1$ (d) and $q_3$ (f)) whose amplitude is suppressed to zero in the upper part of the image. In the third direction ($q_2$ (e)) we find a finite CDW amplitude over the entire field of view.

This time we have left the CDW wavelength $\lambda_n(r)$ as a free parameter during the fitting procedure (see section 5.3.1). The shift of the CDW wavelength in the 3q to 1q crossover direction ($q_2$) is clearly captured by our analysis (Figure 7.11(g)). We can also calculate the local commensuration as the quotient of the length of the corresponding atomic reciprocal lattice vector and the length of the CDW ordering vector quantified by the fitted local wavelength: $|a^*_n|/|q_n(r)|$, where $|q_n(r)| = 2\pi/\lambda_n(r)$. Histograms of these quantities for all three directions are shown in Figure 7.11(j). For $q_1$ (blue) and $q_3$ (yellow) we find one peak centred around 3.05. Note that at those locations where zero amplitude was found for these CDWs (upper part of the image) the fitting brings the wavelength to its upper or lower limit (not shown in the histogram). For $q_2$ (orange) we find two peaks centred around 3.05 and 3.55 reflecting the shift in the wavelength in the 3q to 1q crossover. All these observations are consistent with the conclusions of Soumyanarayanan et al. [83].

A quantitative insight of our analysis is given by Figure 7.11(i) and by Figure 7.11(k). In Figure 7.11(k) we plot the histograms of the amplitude maps (Figure 7.11(d)-(f))). For each direction we find two peaks reflecting the distinct 1q and 3q regions. In the 3q region all the CDWs
Figure 7.11: 3q to 1q transition in NbSe$_2$. (a) STM micrograph of NbSe$_2$ digitalized from Fig. 2A of [83]. (b) Fourier filtered image of the CDWs. (c) Reconstructed image of the CDW pattern from the mosaics of the fitting procedure. (d)-(f) The corresponding amplitude maps ($A_1(r), A_2(r), A_3(r)$) of the $q_1$, $q_2$, $q_3$ CDWs, respectively. (g) Spatial distribution of the fitted wavelength of the $q_2$ CDW. (h) Direction of the $q_1$ (blue), $q_2$ (orange), $q_3$ (yellow) ordering vectors. (i) The average amplitude of the CDWs: $(A_1(r) + A_2(r) + A_3(r)) / 3$. (j) Histogram of the local commensuration. (k) Histogram of the (d)-(f) amplitude maps. Scale bars: 10 nm.
have a similar amplitude corresponding to peaks in the histogram in the 0.08-0.15 (a.u) range. In the 1q region the zero amplitude of the $q_1$ (blue) and the $q_3$ (yellow) CDWs is reproduced in the histogram as a peak close to zero while the $q_3$ CDW has an enhanced amplitude peaked around 0.3 (a.u). This is approximately three times larger than the individual CDW amplitudes in the 3q phase suggesting a rather surprising conservation of the total amplitude in this 3q to 1q crossover. This observation is further confirmed in Figure 7.11(i) where we plot the average of the three amplitude maps: $(A_1(\mathbf{r}) + A_2(\mathbf{r}) + A_3(\mathbf{r}))/3$ yielding a very homogeneous CDW amplitude landscape. Note that all amplitude maps (Figure 7.11(d)-(f) and (i)) were plotted with the exact same color scale.

7.6 Summary

The holographic imaging of the local complex CDW order parameter with a spatial resolution of the order of the CDW wavelength, offers remarkable opportunities to uncover physical details of the CDW state. We find clear evidence for the coexistence of three individual CDWs in transition metal dichalcogenides with a threefold symmetric band structure in the ab-plane, each developing a distinct order parameter landscape and a great variety of features. Unambiguous phase images contribute novel insight on the CDW $\pi$DWs reported in Cu$_{0.02}$TiSe$_2$, where one of the three CDWs does not experience any phase shift, while the phase shift of the remaining two is not necessarily $\pi$. Mastering the phase fitting procedure reveals constant phase domains and provides unprecedented insight into nearly commensurate CDWs, with first real space phase images of individual discommensurations in NbSe$_2$ predicted long ago by theory. We expect significant contributions to the deeper understanding of charge density waves, including their formation mechanism and their interplay with other correlated electron ground states, from the expanded parameter space accessible through the high-resolution real space mapping of the complex CDW order parameter.
Chapter 8

Conclusion and outlook

We developed a novel *in-situ* exfoliation technique which allows to prepare nanoflakes of otherwise air-sensitive layered materials in UHV environment. This method yields nanoflakes which are deposited under identical conditions with a wide range of thicknesses and a dense substrate coverage. Its further development could go in many directions from monitoring the contact force to tuning the physical parameters of the device. This tool is easily adaptable to any UHV system and enables thickness dependent studies by surface sensitive techniques such as tunnelling and atomic force microscopy and photoemission.

Taking advantage of our unique method for sample preparation we have carried out the first STM study of an in-situ mechanically exfoliated transition metal dichalcogenide. Besides the experimental achievement – metallic TMDs are highly reactive and unstable if exposed to atmosphere, unavoidable with standard exfoliation procedures – we explore an unprecedented broad range of thicknesses in a single experiment, from bulk to few layers. We have studied the evolution of the charge density wave phase in bulk and exfoliated VSe$_2$ samples as function of temperature and thickness.

STM imaging of the CDW in bulk VSe$_2$ single crystals as function of temperature allowed us to establish a numerical method to extract the CDW order parameter from the real space charge modulation measured by STM. Also, fitting the temperature dependent order parameter to an approximate BCS gap equation we found the scaling factor to relate the order parameter at a given temperature $\Psi(T)$ to the transition temperature. Applying this analysis to STM images of the CDW in exfoliated VSe$_2$ flakes revealed a non-monotonic thickness dependence of the CDW order parameter and critical temperature.

The CDW transition temperature $T_c$ is first decreasing from the bulk
value with decreasing thickness, down to around 20 nm, then increasing, and ultimately exceeding the bulk value by \( \approx 30\% \) in the thinnest sample (2.2 nm). The \( T_c \) we find is in remarkable quantitative agreement with independent transport measurements. We lift the outstanding and debated contradiction between opposite thickness dependencies of \( T_c \) reported in these experiments [69, 70]. Our STM data show that both experiments are correct. The apparent contradiction is the direct consequence of measuring distinct and too narrow thickness ranges in these two experiments, and has nothing to do with sample quality as currently claimed in the literature.

A remarkable upshot of our analysis is that the increased transition temperature is likely not due to the change in the coupling regime, but is the direct consequence of two-dimensional confinement in the thinnest flakes. Indeed, we can explain the thickness dependence as a consequence of a dimensional crossover and quantum confinement with reducing thickness.

Our study convincingly demonstrates that thickness can be a non-trivial tuning parameter of the macroscopic electronic properties: the CDW transition temperature can be tuned to be higher or lower compared to the bulk value depending on thickness. We also showed the importance of considering a finite thickness range for an accurate assessment of its influence. We introduced and demonstrated a robust method to determine the local transition temperature from the CDW amplitude imaged by STM. It quantitatively matched the transition temperature determined by transport experiments and can be applied to other CDW systems.

Another focus of this thesis was the imaging of the local complex order parameter of the macroscopic electronic properties: the CDW transition temperature can be tuned to be higher or lower compared to the bulk value depending on thickness. We also showed the importance of considering a finite thickness range for an accurate assessment of its influence. We introduced and demonstrated a robust method to determine the local transition temperature from the CDW amplitude imaged by STM. It quantitatively matched the transition temperature determined by transport experiments and can be applied to other CDW systems.

First of all, we found unambiguous evidence that the charge ordered ground state in these TMDs consists of three individual CDWs related through the threefold symmetry in the ab-plane, each developing a distinct order parameter landscape and a great variety of features. To the best of our knowledge, this has not been so unambiguously demonstrated to date. This result brings the observed and reported 3q, 2q and 1q phases and their transitions into an interesting perspective to
be further investigated. Furthermore, we found a straightforward explanation for the different CDW contrasts observed in some STM images for a given compound in terms of locally different phase configurations of the three individual constituent CDWs (and not due to STM tip changes as often claimed in the literature).

Holographic imaging of the complex CDW order parameter revealed a rich variety of features in each compound such as phase domain patterns, domain walls and topological defects. In Cu$_{0.02}$TiSe$_2$, holographic imaging gave a quantitative insight on previously reported $\pi$-phase shift domain walls showing they do not necessarily correspond to a $\pi$-phase shift in the CDW order parameter. The phase images of VSe$_2$ and NbSe$_2$ reveal vortices and antivortices, i.e. topological defects where the order parameter phase winds by multiples of $2\pi$ clockwise or anticlockwise around a point in the ab-plane, respectively. The defect landscapes are different for each individual CDW, with both tightly bound and well separated vortex-antivortex pairs. Moreover, in NbSe$_2$ our holographic imaging provided the first high resolution real space phase image of individual discommensurations, a particular defect of a nearly commensurate CDW predicted in the 1970s.

We shed new light on the real space correlation of crystalline and CDW defects, a topic which deserves further investigations, showing that the CDWs can develop a spatial structure independently of the supporting crystalline lattice.

Last but not least, we further demonstrated the abilities of our analysis to provide quantitative details on the example of the 3q to 1q transition in NbSe$_2$.

The unique real space insight into the amplitude and phase of the complex CDW order parameter delivered by our technique is likely to be applied to many problems in the field of CDWs. They are far from understood and under intense scrutiny. Their formation mechanism, energy gap and interplay with other correlated electron phases at the nanoscale are some of the features holographic imaging will contribute to understand.

Concerning the thickness dependence and materials, we have already given an outlook on open questions in Chapter 3.

We have seen that the thickness is an efficient way to tune macroscopic properties of ordered electronic phases, like their transition temperature. On the other hand, it is a passive control which is complicated to change in an actual device configuration. It would be extremely interesting to explore different routes to obtain an active control over ordered electronic phases. Controlled pinning and sliding of charge density waves by local probe atom manipulation and by application of an elec-
tric field would be one of these routes, along which holographic imaging is the first milestone. Same as in the direction of space charge doping, tuning the ordering vector and amplitude of the charge density wave by controlling the carrier density of the host material is definitely a very exciting topic to investigate.
Appendix A

Nano-scale investigation of exfoliated dichalcogenides

Scanning tunnelling microscopy and spectroscopy studies can make a valuable contribution to the field of 2D materials. However, one has to face with two major experimental challenges in such an experiment. First, to operate the STM one needs to provide a conducting loop connecting the tip and the sample to a voltage source. Two options are available: either deposit the flakes on a conducting substrate or provide some electrical contacts if an insulating substrate is used. Second, one has to locate the STM tip above the sample. In lack of a far-field technique to navigating the tip\(^1\), there are two options also in this case: a large substrate coverage of samples or some kind of markers which guide to the previously selected flakes.

In total four possible experimental schemes can be imagined which are summarized in Figure A.1. During this PhD project we have realized all of them in different experiments with different materials. In some cases these configurations allowed to extend the experimental parameter space, e.g. by electrostatic gating, or simultaneously resolve other difficulties, e.g. degradation at ambient conditions.

High substrate coverage on a conductive and on an insulating substrate was realized in [2, 3] (main text) and [4] (Appendix B), respectively. Flakes on insulating substrate with contacts and markers are presented in [5] (Appendix C).

\(^1\)which is typically the case for UHV systems
Our work about the combination "markers and a conductive substrate" to study a previously selected TMD flake is not yet published. We summarize it here in this Appendix.

For a simple conductive substrate we used a gold covered silicon wafer. Gold is soft and can be easily indented by a sharp atomic force microscope (AFM) tip. Scanning in contact mode AFM using a relatively large force set-point (to be experimented in the specific cases) one can make a series of parallel engravings. These we named "nano bar-codes" (Figure A.2(a)) as one can control the density of the lines by adjusting the scan parameters (size, number of lines) and encode information like the distance to the flake. Such notched regions can be drawn next to each other along any macroscopic (mm size) pattern. These markings can be easily identified in the STM on large scale images (Figure A.2(b)) and followed to the selected flake.

In Figure A.3 we present proof-of-principle optical microscope, AFM and STM images of the exact same few-layer thin MoS$_2$ flake. The flake was exfoliated at ambient conditions and located by optical microscope. Then markers guiding to the flake were drawn by AFM as described above. In the UHV STM setup we could follow the markers to locate the exact same flake as evidenced by the morphological characteristics shown in Figure A.3.

Mastering the AFM nano bar-code lithography method has several advantages. For instance, one can perform targeted STM/STS experiments on specific flakes and then examine the exact same flake with other techniques, e.g in optical measurements.
Figure A.2: Markers drawn by atomic force microscope to locate the STM tip above a previously selected flake. (a) $5 \times 5 \, \text{um}^2$ AFM image of a nano bar-code. (b) $4 \times 4 \, \text{um}^2$ STM image of overlapping bar-codes.

Figure A.3: Proof of principle optical, AFM and STM imaging of the same MoS$_2$ flake exfoliated on gold covered silicon substrate.
Appendix B

Hole Transport in Exfoliated Monolayer MoS$_2$

While exfoliated monolayers of WS$_2$, MoSe$_2$, and WSe$_2$ support high-quality, well-balanced ambipolar transport, exfoliated MoS$_2$ monolayer does not. The hole transport in exfoliated MoS$_2$ monolayers, in an ionic-liquid gated transistor configuration, is systematically anomalous, with a peak in the conductivity at negative gate voltage ($V_G$). A series of experiments, combining ionic-liquid gated transistor transport, gated-dependent optical and STM/STS measurements, were carried out to investigate the origin of this difference.

STM and STS measurements were performed on monolayer films of MoS$_2$ grown by chemical vapor deposition on SiO$_2$/Si substrate. This field effect transistor configuration allowed in-situ transport characterization and electrostatic gating in the STM and STS measurements. STS differential conductance maps revealed atomic scale sized objects producing in-gap states near the valence band. The energy of these states coincide with the energy of those observed in transport measurements.

In the light of all our experimental results and the theoretical calculations from the literature we concluded that the in-gap states are arising from chalcogen vacancies which act as hole traps and are responsible for the anomalous hole transport.
Hole Transport in Exfoliated Monolayer MoS$_2$

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Supporting Information

ABSTRACT: Ideal monolayers of common semiconducting transition-metal dichalcogenides (TMDCs) such as MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$ possess many similar electronic properties. As it is the case for all semiconductors, however, the physical response of these systems is strongly determined by defects in a way specific to each individual compound. Here we investigate the ability of exfoliated monolayers of these TMDCs to support high-quality, well-balanced ambipolar conduction, which has been demonstrated for WS$_2$, MoSe$_2$, and WSe$_2$, but not for MoS$_2$. Using ionic-liquid gated transistors, we show that, contrary to WS$_2$, MoSe$_2$, and WSe$_2$, hole transport in exfoliated MoS$_2$ monolayers is systematically anomalous, exhibiting a maximum in conductivity at negative gate voltage ($V_G$) followed by a suppression of up to 100 times upon further increasing $V_G$. To understand the origin of this difference, we have performed a series of experiments including the comparison of hole transport in MoS$_2$ monolayers and thicker multilayers, in exfoliated and CVD-grown monolayers, as well as gate-dependent optical measurements (Raman and photoluminescence) and scanning tunneling imaging and spectroscopy. In agreement with existing ab initio calculations, the results of all these experiments are consistently explained in terms of defects associated with chalcogen vacancies that only in MoS$_2$ monolayers, but not in thicker MoS$_2$ multilayers nor in monolayers of the other common semiconducting TMDCs, create in-gap states near the top of the valence band that act as strong hole traps. Our results demonstrate the importance of studying systematically how defects determine the properties of 2D semiconducting materials and of developing methods to control them.

KEYWORDS: MoS$_2$, ambipolar transport, scanning tunneling microscopy/spectroscopy, defects, ionic liquid gating

E xtensive studies of monolayers (MLs) of group VI semiconducting transition-metal dichalcogenides (TMDCs) have demonstrated that all these materials share many electronic properties. For example, they all have a direct band gap at the K and K’ points, a finite Berry curvature in the K and K’ valleys responsible for the occurrence of the valley Hall effect, an extremely strong spin–orbit coupling (as large as a few hundreds meV in the valence band), very large exciton binding energies due to the reduced screening characteristic of 2D systems, and more. Differences are also present, such as the relative sign of the spin orientation at the conduction band minimum (CBM) and valence band maximum (VBM), the same for Mo-based compounds and opposite for W-based ones, that lead to a different temperature dependence of the measured photoluminescence (PL). Although important for specific physical phenomena, these differences mostly concern more subtle aspects of the electronic properties.

Having access to a broad class of semiconducting 2D materials with many similar properties is very attractive because, for instance, it facilitates the realization of van der Waals heterostructures obtained by stacking two or more monolayers of different TMDCs on top of each other. It should be realized, however, that these considerations do not take into account that real materials unavoidably contain defects that are specific to each individual compound and that drastically affect their electronic response. This is certainly the case for the systems considered here, since in semiconductors defects generally determine crucial characteristics such as the work function, the position of electrochemical potential, the transport properties (e.g., the carrier mobility), the rate of nonradiative electron–hole recombination, etc. That is why an increasing research effort is currently being devoted to the investigation of defects present in all types of semiconducting 2D materials, whose identification, understanding, and control will be necessary if these systems will eventually be employed in technological applications (not to mention the possibility to exploit new functionalities that are sometimes offered by defects in 2D materials, such as their ability to act as single photon emitters).

One important aspect that is seemingly common to semiconducting TMDC monolayers is their ability to support well-balanced ambipolar transport. Measurements done on
Appendix C

Scanning Tunneling Microscopy of an Air Sensitive Dichalcogenide Through an Encapsulating Layer

We have seen that in-situ exfoliation provides an efficient way to prepare and study flakes in UHV environment. As an alternative, one may prepare samples in the inert atmosphere of a glove box and cover the air-sensitive flakes with a protective capping layer. Such heterostructures were already exploited in transport and optical measurements.

In this study we examined the possibility to study by STM the properties of the capped material in the presence a carefully chosen protective layer. We studied thick flakes of NbSe$_2$ covered by a monolayer of MoS$_2$ and demonstrated that at low energy (within the gap of MoS$_2$) one can access electronic phases, charge density waves and superconductivity, of the underlying material. Coupling of the constituent crystals of the heterostructure was demonstrated to strongly depend on their rotational alignment. The experimental STM images are perfectly reproduced in our detailed modelling of the tunnelling process. We showed that the capping layer adds a non-trivial contribution to the vacuum tunnelling barrier which is modulated on the atomic length scale. This modelling may have implication to other systems where tunnelling happens through a complex non-metallic layer.

In summary, we have demonstrated the possibility to use STM to study air-sensitive samples through a protective MoS$_2$ monolayer.
Scanning Tunneling Microscopy of an Air Sensitive Dichalcogenide Through an Encapsulating Layer

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Supporting Information

ABSTRACT: Many atomically thin exfoliated two-dimensional (2D) materials degrade when exposed to ambient conditions. They can be protected and investigated by means of transport and optical measurements if they are encapsulated between chemically inert single layers in the controlled atmosphere of a glovebox. Here, we demonstrate that the same encapsulation procedure is also compatible with scanning tunneling microscopy (STM) and spectroscopy (STS). To this end, we report a systematic STM/STS investigation of a model system consisting of an exfoliated 2H-NbSe2 crystal capped with a protective 2H-MoS2 monolayer. We observe different electronic coupling between MoS2 and NbSe2 from a strong coupling when their lattices are aligned within a few degrees to essentially no coupling for 30° misaligned layers. We show that STM always probes intrinsic NbSe2 properties such as the superconducting gap and charge density wave at low temperature when setting the tunneling bias inside the MoS2 band gap, irrespective of the relative angle between the NbSe2 and MoS2 lattices. This study demonstrates that encapsulation is fully compatible with STM/STS investigations of 2D materials.

KEYWORDS: 2D materials, heterostructures, charge density wave, superconductivity, encapsulation, scanning tunneling microscopy

Exfoliation of layered van der Waals (vdW) materials has proven to be a remarkably simple technique to produce high-quality crystals of many different compounds that are only one or a few atoms thick.1−3 These atomically thin crystals, or 2D materials, possess new interesting properties that can be very different from those of their parent bulk compounds and can depend very sensitively on the precise number of atomic layers.4,5 As such, 2D materials disclose a vast platform for the investigation of new physical phenomena that were not accessible to experiment until now. Examples include Dirac Fermions in monolayer (ML) graphene,1,10 gate-tuning of the band structure of a 2D material first shown in bilayer graphene,11 phenomena originating from the Berry curvature in the band structure of semiconductor ML transition metal dichalcogenides (TMDs),12−14 and magnetism and superconductivity in the truly 2D limit.4,5,16

Most experimental studies reported so far have been performed on materials that are chemically stable in air because this drastically simplifies their manipulation and device fabrication for a broad variety of experimental techniques. However, many 2D materials tend to degrade when exposed to air and considerable efforts are deployed to protect exfoliated crystals and enable their characterization and use under ambient conditions. An effective strategy is to exfoliate and manipulate the atomic layers in a glovebox and then encapsulate them with another inert single layer crystal,6−8,17,18 for example, graphene, MoS2 or hBN. Even though the procedure is complex, encapsulation is remarkably efficient, enabling air-sensitive 2D materials to be safely exposed to air. Encapsulation has been key to a number of remarkable experiments, for example, the observation of a 2D topological insulating state in ML WTe2,15 the investigation of superconductivity in ML 2H-NbSe2,19 and the observation of 2D ferromagnetism in ML CrI3.7,8

The controlled heterostructure assembly and encapsulation of vdW MLs represents an impressive technical achievement and demonstrates an unprecedented level of control of matter at the atomic scale. While these techniques have been successfully used to prepare samples and devices for transport and optical measurements, their compatibility with surface probes like scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) is yet to be verified. Both are primarily sensitive to the outermost layers of the system under investigation, and covering a 2D material with an encapsulating layer may potentially impede their use altogether. In addition, the encapsulating layer may affect the electronic properties of the underlying 2D material due to their mutual interaction.20−24 If so, even if STM and ARPES
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Bibliography


