Charge density waves: the old problem and a new hope

The spherical-chickens-in-a-vacuum joke\(^1\) points out two important aspects in the condensed matter physics: symmetry and interaction. On one hand, different symmetries that are broken in the materials give rise to all kinds of orders and emergent excitations. On the other hand, interactions modify the behaviours of electrons in many-particle systems. These two factors work together to have such a rich condensed matter world.

More specifically, the charge density wave (CDW) phenomenon is a platform where the two factors: symmetry and interaction collaborate or even compete. The CDW state is a typical example of spontaneous symmetry breaking where the electron density loses its translational invariant symmetry and forms periodic wave patterns. The qualitative picture of CDWs can be nicely captured by a weakly coupled 1D model, i.e. the Peierls mechanism, while the real materials, which agree well with the Peierls mechanism, are few. More materials show prominent deviations from the quantitative prediction of the weak-coupling theory. The understanding of diverse CDW phenomena requires the consideration of both symmetry and correlation.

In this thesis, I will focus on the charge density waves in the 1T polytype transition metal dichalcogenides (TMDCs) system, where CDW states are found ubiquitously. The general form of TMDCs can be written as MX\(_2\), where M could be Ta, Ti, Mo, V, Nb and X could be chosen from S, Se, Te.

\(^1\)A chicken farmer asked a theoretician’s help on the infertile issue of his chicken. Eventually, the theoretician came up with the solution which only works for the spherical chicken in the vacuum [5].
The CDW states have been found in any of the combinations of the above elements. There are several advantages of TMDCs as the hosting system of charge density waves. First, as van der Waals materials, most of TMDCs have quasi-2D band structures for their weak interlayer coupling, which is the simplest scenario apart from the 1D toy model. Most of the physics happens in-plane, and their 2D Fermi surface is similar for certain polytypes. Second, this group of materials, though with similar structures and the same symmetry as shown in Fig. 1.1, differ from each other strongly in the sense of the different CDW states can be found. Once again, this suggests the limitations of the nestimg picture in the Peierls mechanism, and the interaction strength, such as electron-electron coupling or electron-lattice coupling seems to become the key. Third, TMDCs have been extensively studied in the past decade due to the 2D fanaticism and many characterisation and manipulation techniques are mature, which allows us to continuously tune the physical properties of them, such as isovalent chemical substituting [6, 7]. Moreover, the dimensionality undoubtedly plays an important role in CDW physics, while the continuous dimensionality crossover can be easily realised in TMDCs with the exfoliation methods [8–11]. In summary, TMDCs are highly tunable systems. With its universal structure, the effect of the electronic correlation and dimensionality on CDW physics can be singled out.

Figure 1.1: The structure of 1T polytype TMDCs. The atoms are in the trigonal lattice on each layer, and the inversion symmetry is preserved within the single layer.
There are several ongoing discussions concerning the charge density waves in TMDCs. The first one is naturally the mechanism of the CDW states in TMDCs. The Peierls mechanism has obvious limitations when applying to the quasi-2D TMDCs. The nesting region is usually small on the Fermi surface \([12, 13]\), so the electronic susceptibility does not diverge but is still enhanced \([14]\). In the best case, we can still obtain the instability by having a relatively strong electron-phonon coupling, which can compensate for the not divergent but enhanced electronic susceptibility. Please be aware that the relatively strong electron-phonon coupling mentioned here should still be within the weak-coupling regime. A typical example of the weakly-coupled system where the nesting and electron-phonon coupling work together is VSe\(_2\), which will be studied in Chap. 4. There are also cases where the nesting is barely found in the materials, such as TiSe\(_2\). As a semimetal, it is suggested to have a strong electron-hole coupling, where the excitons or plasmons are softened to be the driving force of the instability \([15]\). This is the so-called excitonic insulator or Overhauser-type CDW \([16]\). The scenarios mentioned so far, no matter the electron-phonon coupling or the electron-hole coupling, all belongs to the weak-coupling regime\(^2\). For the weakly coupled cases, their theoretical descriptions can be unified in the BCS framework which will be introduced in Chap. 2. As for the materials showing strong electron-electron or electron-phonon coupling, the Peierls picture would be more powerless. We have known many TMDCs that possess strongly coupled CDW states, where the CDW phase usually has stronger lattice distortion, larger CDW gap, small coherence length, and the formation of incoherent electron-hole pairs above \(T_c\) \([15]\). In this case, the electronic energy gain happens not only around the Fermi surface as the weakly coupled materials, but also deep below the Fermi level. Therefore, we could observe the reconstruction of the electronic bands at the high-energy region in accompany by the CDW transition. The electron-electron correlation starts to play a role and no unified quantitative framework can be applied yet. Examples of strongly coupled materials are the Ta family, such as TaS\(_2\) and TaSe\(_2\) \([17, 18]\). In the extremely strong coupling limit, where the main players are the strongly localised electrons, density wave phenomena are described by the Jahn-Teller distortion \([19]\). The degenerate orbitals/bands repel each other to obtain the electronic energy gain. The high symmetry is broken and the structure of the system is distorted as the cost. The Jahn-Teller picture is seldom mentioned in the context of TMDCs except as one of the possible proposals for the CDW phase in TiSe\(_2\) \([20]\). In summary, the formation of CDW order is in general the result of the cooperation or competition among several different driving forces, including the Fermi surface nesting, electron-phonon couplings, and electron-electron correlations. Even though we have acquired some qualitative understanding of the ubiquitous CDW order in TMDCs, the unified theoretical description is still absent if there is any and the instability mechanism for each specific material is usually controversial. In this context,

\(^2\)Although, TiSe\(_2\) itself might be an example of the deviation from the weak-coupling regime \([15]\).
far-field optics can be used to study the electronic structure reorganisation over a broad energy range and to shine a light on the possible mechanisms according to the energy scale of the phase transitions.

Another interesting discussion focuses on the non-equilibrium phenomena associated with CDW orders and their potential applications. For example in TaS\textsubscript{2} and its doped variants, a long-lived non-equilibrium hidden state can be excited from the CCDW state using laser or electric pulses [21–24]. The hidden state features the low resistivity, formation of the in-plane domains, and the rearrangement of the inter-layer stacking orders [21, 24–26]. The fast switching between the CCDW state and the hidden state has been achieved in the nanosecond scale, which makes it a promising memristive material with low working temperature [21, 23, 27]. There are also evidence for the glass-like relaxation process and the amorphous packing of the star of David motifs in this system, which is attributed to the quantum jamming transition. As the result, the phase transitions in such a system are sensitive to the cooling rate that is comparable with its relaxation time scale. The super-cooled NCCDW is found in the thin layer TaS\textsubscript{2} and the critical cooling rate strongly depends on the thickness of the samples and the super-cooled phenomena are suppressed in bulk samples [8, 9, 28]. Moreover, the super-cooled state/hidden state in the Se doped samples can be easily reached with the fast cooling process, which will be discussed in detail in Chap. 5. Considering the larger supercell and the strong interlayer coupling, such non-equilibrium phenomena can be understood as the various local interlayer stacking orders create many local minima in the free energy landscape [9, 23, 29, 30]. However, a quantitative model to describe the meta-state state is still needed. The electronic structure of the non-equilibrium is not very clear apart from the STS study on the local regions. We need more information on the non-local, bulk electronic structure over a broader energy range. Therefore, the far field optics becomes an ideal tool for such purpose. In the end, a more detailed understanding of the competing energy scales in the non-equilibrium physics of TaS\textsubscript{2} enables people to utilise its memristive property for applicable purposes.

Scope of this thesis
This thesis consists of five chapters in total. Starting from the second chapter: Chap. 2 introduces the theoretical background of charge density wave physics. It mainly focuses on the primitive Peierls picture of CDW phase transition, in which the Fermi surface nesting and the electron-phonon coupling corporately drive the transition. We shall start from a general theoretical framework: the BCS mean-field theory, which shows the intrinsic instability of the Fermi surface. Then we turn to a more specific case of CDW origin: the electron-phonon coupling. These two paths are used to illustrate the typical CDW phenomena: the divergent of the electronic susceptibility and the phonon softening. Then we shall discuss the typical optical response of the CDW phase and the theoretical model behind it. The similarities between the superconductivity and the charge density wave will be discussed from the microscopical and the
macroscopic perspective.

Chap. 3 introduces the experimental techniques used in this thesis: the Fourier transform infrared spectroscopy (FTIR). We shall discuss the working mechanism of FTIR and its basic setup. Then I will spend the major part of this chapter discussing the common ways that we can use to extract information from the data collected in FTIR experiments. We shall study the classical model and the quantum mechanical linear response theory to understand the optical response functions. The sum rules, as the most important tool to study the optical data, shall be discussed in the end.

Chap. 4 is based on the work [1], in which we will present the optical data of 1T-VSe$_2$ in both the CDW phase and the normal metal phase. By studying the optical functions in these materials, we show that the collective excitation of the CDW phase shows its optical signature in our data.

Chap. 5 is based on the work [2]. We study the optical response of the TaS$_{2-x}$Se$_x$ with two different doping levels. An optical gap is observed at the low-temperature non-equilibrium state of the $x = 0.8$ sample. With the spectral weight analysis, we show that this optical gap has a different origin other than CDW physics. We compare the optical gaps observed in the different CDW phases.