Role of Incommensuration in the charge density wave and superconducting states of 1T-$TiSe_2$

Astha Sethi

May 10, 2017

Abstract

A brief review of some of the most recent experiments on the charge density wave (CDW) transition in 1T-$TiSe_2$ is presented. With increasing pressure or intercalation, the CDW can be suppressed and a superconducting (SC) phase emerges. In the pristine 1T-$TiSe_2$, a commensurate CDW develops around 202 K. These experiments show that by tuning these external parameters like pressure, or doping, the commensurate CDW melts into an incommensurate CDW phase through the formation of domain walls. The incipient incommensurate CDW phase coincides with the onset of superconductivity, thus providing insight into the importance of incommensurability in formation of SC phase.

1 Introduction

There has been a great deal of interest in materials exhibiting a universal phase diagram in which charge- and/or magnetically ordered phases exist in close proximity to a superconducting (SC) phases. Low-dimensional materials like tranistion metal dichalcogenides (TMDs), denoted by MX_2, where M is a transition metal and X denotes a chalcogen atom are one such class of materials in which a charge ordered phase called the charge density wave (CDW) exists which can be suppressed by external parameters like pressure, doping, or electrostatic gating eventually leading to the emergence of superconductivity. The relation between CDW and SC phases is not very well understood and a lot of work is ongoing

in this area to understand the microscopic mechanism behind the origin of these two phases and the connection between them. 1T-$TiSe_2$ is one such TMD material which has a charge density wave transition at around 200 K. It is unique in a sense that it undergoes a transition to a commensurate CDW state (CCDW) [1] directly without going through an intermediate incommensurate CDW (ICDW) phase, which is unusual in TMDs.

We organize the term paper in the following manner, first in Sec. 2 we discuss the basic mechanisms of CDW in 1D or 2D, especially focusing on Peierls instability. Next, in Sec. 3 and Sec. 4, we present highlights of the recent experimental studies on the CDW in 1T-$TiSe_2$ under the effects of pressure and intercalation, respectively. Finally, we summarize with conclusions in Sec. 5.

2 Charge Density Wave

Let us begin by considering a simple picture to understand the basics of charge density wave. Consider a chain of N atoms (with one electron each), separated by distance a. The spectrum of the electrons, loosely bound to these atoms has a gap at the (Brillouin) zone boundary, $k = \pm\pi/a$. This will be a metal if there is enough number of energy states available well below the gap, in other words the Fermi momentum k_F should be in the valence band. Now imagine every second atom has been displaced by a small distance δ. Approximately (adiabatically), this causes the lattice spacing to go to $2a$. So instead of having gap at $\pm\pi/a$, it's at $\pm\pi/2a$. So it could happen that some of the electrons now have to occupy energy states which are above the gap. Hence now this is an insulator, a transition that was driven by lattice distortion. This is known as Peierls transition [1]. This is also known as the Peierls instability, because what we just found is *a 1D equally spaced chain with one electron per ion is unstable.* This instability produces fluctuations in the electron density, which collectively transport charge, hence called charge density wave (CDW).

Now we briefly discuss how the energy of the system changes, and under what conditions the CDW becomes a preferable ground state instead of a metallic state. Firstly, for an average distortion δ, it can be shown that the CDW is a periodic

[1] Consider the ratio, λ/a. When this ratio is rational ($pa = q\lambda$, for integer p, q), it's called a commensurate CDW phase, meaning q number of CDW waves fit in p number of lattice points. An irrational p/q is called an incommensurate CDW phase.

function of x with periodicity, $\lambda = \pi/k_F$,

$$\psi(x) = \delta \cos(Qx), \quad Q = \frac{2\pi}{\lambda} = 2k_F \,. \tag{1}$$

The average elastic energy associated with the lattice deformation is, $\Delta E_{lat} = \frac{1}{2}C\langle\psi^2\rangle = C\delta^2/4$, where C is the force constant of the lattice. Since the effective centers of the atomic potentials have moved, the electrons also rearrange themselves, costing some energy, denoted by $\Delta E_{el} \propto -\delta^2 \ln \frac{E_F}{\delta}$ [1, 7]. Thus, when the net change in energy (for small distortion)

$$\Delta E_{el} + \Delta E_{lat} = \Delta E, \tag{2}$$

is negative, the system favors to distort the lattice, hence exhibit CDW phase. In the CDW state, the order parameter is the energy gap. In the mean field approximation, this gap is equal to zero at $T = T_{CDW}$ and increases with decreasing temperature (see Fig. 1a), $\Delta(T)/\Delta_0 = (1 - T/T_{CDW})^{1/2}$. Since this order parameter continuously changes with T and reduces to zero, the phase transition is of the second order with the critical exponent $\beta = 1/2$.

Now we ask, what causes the lattice to distort, in other words what shifts the ions from their high symmetry points, thereby breaking translational invariance. One of the reasons could be strong electron-phonon coupling (EPC). Especially in 1D, due to this coupling the (acoustic) phonon spectrum is so strongly renormalized that the energy of a phonon branch can go to zero, see Fig. 1b, which means a static distortion in the lattice can appear causing the formation of a superlattice with periodicity $Q = 2k_F$. This is called *Kohn anomaly*. Note that this is present in metals only, since the derivation assumes a homogeneous free electron gas. In higher dimensions the anomaly branch gets smeared but sometimes it can be significant. Note that the Peierls transition was metal to insulator transition (which is the case in 1D only), however, according to the EPC mechanism CDW order can exist in metallic phase (due to ungapped remaining FS) as well. In fact most of the 2D CDW materials are metallic until some other instability such as superconductivity sets in.

Another mechanism responsible for the onset of CDW is electron energy instability caused via electron-hole coupling (EHC), see Fig. 1c. This can be explained by looking at the linear response function (or Lindhard susceptibility) of the electrons, $\rho_{ind}(\vec{q}) = \chi(\vec{q})\phi(\vec{q})$, where a perturbation in the potential $\phi(\vec{q})$ causes an induced charge ρ_{ind}. A plot of $\chi(q)$ is presented in Fig. 1d. At a specific momentum (called nesting momentum) the susceptibility diverges. In 1D the planar

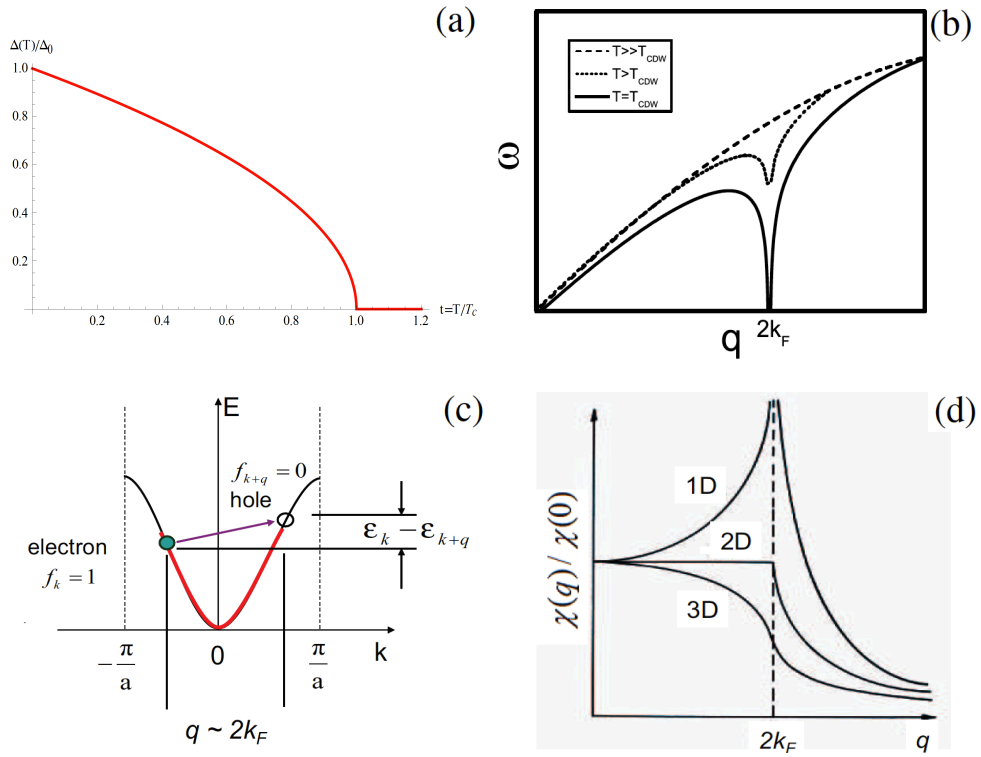

Figure 1: (a) Plot of energy gap (scaled with zero temperature energy gap) as a function of temperature (scaled with critical temperature, (T_C=T_{CDW}); (b) Acoustic phonon mode is softened due to electron-phonon coupling, adapted from [2]; (c) Electron-hole pair formation, energy cost of creating a pair corresponds to $2k_F$ momentum; (d) Lindhard susceptibility for 1-3D. Strong log-divergence occurs in 1D. Figure adapted from [1].

topology of the Fermi surface, causes perfect nesting, hence the divergence is the strongest. However, 2D or 3D topologies don't avail enough number of electron-hole pair states with $2k_F$ momentum, hence nesting is weak.

The material that we discuss here, 1T-$TiSe_2$ is a 'quasi-2D' material, in which chains of identical TiSe2 layers are held together by weak Van der Waals force. The microscopic mechanism behind the origin of CDW in 1T-$TiSe_2$ is not well understood. There have been reports supporting different mechanisms ranging from Fermi-surface nesting (FSN) to excitonic coupling (EHC) to an indirect Jahn Teller effect to the presence of electron-electron and electron-phonon (EPC) inter-

actions, with the relative importance of these still in dispute[3]. However, in the light of recent experiments in the past decade, it is widely accepted that FSN is not a driving force behind the CDW transition in 1T-TiSe2 and both EHC and EPC are present in the CCDW phase, while in ICDW phase only EPC is present[7, 3, 5].

3 Evolution of CDW in 1T-$TiSe_2$ with pressure

A recent x-ray diffraction (XRD) study of 1T-$TiSe_2$ samples performed by Joe *et al.* showed that the CDW phase can be suppressed with pressure [3]. This was the first experimental observation of a Quantum Critical Point (QCP), the point in the phase diagram where the CDW is suppressed all the way to $T = 0$ K with $P_C = 5.1 \pm 0.2$ GPa. Based on the unexpected increase of the CDW coupling strength as P_C is approached, the authors speculated that the suppression of CDW could be related to other effects such as changes in the commensurability or lattice stiffness. To test this further, they developed a novel technique for simultaneous measurement of the Bragg and CDW scattering in momentum space which allowed a precise measurement of the degree of commensurability in the CDW phase. In XRD studies, CDW superstructure ($2a$x$2a$x$2c$) is observed via an additional superlattice reflection at a wave vector of $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, along with the expected Bragg reflection at $(1, 1, 1)$ in momentum space. The CDW peak at half the momentum, $(0.5, 0.5, 0.5)$ and Bragg peak at $(1, 1, 1)$ are coincident at ambient pressure confirming a CCDW phase. As the pressure increases, the CDW peak moves away from the Bragg peak revealing an emerging incommensuration, while going through an intermediate state with 2 peaks, one coincident with Bragg peak (at half the momentum) and other slightly separated indicating the coexistence of commensurate and incommensurate phases. The degree of incommensurability was largest along L direction in the [H K L] momentum space and was attributed to presence of phase slips (domain walls) in CDW stacking order along c axis. The phase diagram developed in this work showing the presence of different phases in $TiSe_2$ is shown in Fig. 2. It can be seen that under the application of external pressure, TiSe2 becomes SC. The SC phase persists for pressures ranging from roughly 2 to 4 GPa attaining an optimal T_C at around 3 GPa.

The black dotted line in Fig. 2 shows the suppression of the transition temperature of the CDW phase, and can be fit using $T_{CDW} = T|1 - P/P_C|^{\beta}$, where $\beta = 0.87 \pm 0.08$. This value of β is close to that expected from the quantum critical scaling near a QCP, with $\beta = \nu z$, where ν is the correlation length exponent and z is the dynamical critical exponent. Using Hertz-Millis picture of quantum critical

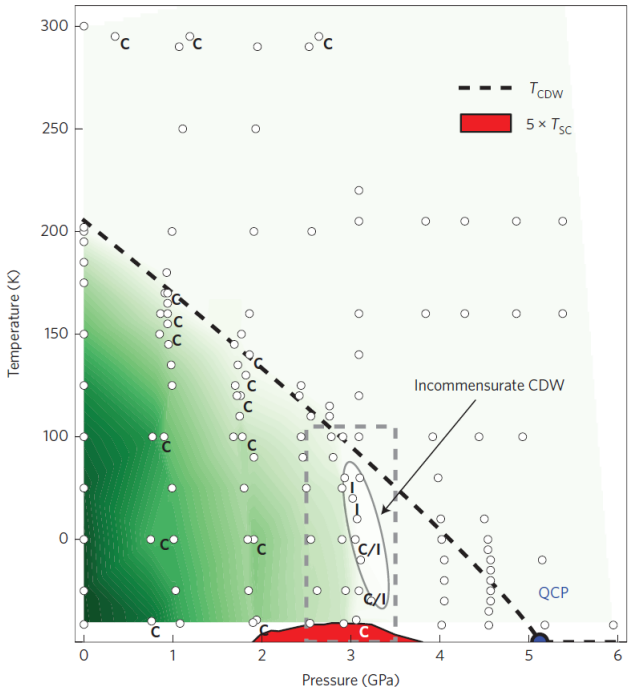

Figure 2: Pressure-Temperature Phase diagram for 1T-$TiSe_2$ showing the CCDW, ICDW and the SC phases (taken from [3])

scaling, correlation length scales with the length exponent ν as $\xi \sim |r|^{-\nu}$ (r is the distance to the QCP which can be tuned by pressure, magnetic field or chemical composition. In this case where pressure is the tuning parameter, $r = \frac{P-P_C}{P_C}$) and the correlation time scales with dynamical exponent z as $\tau \sim \xi^z = |r|^{-\nu z}$ [8]. For a CDW transition within mean field theory, β is predicted to be 1 with $\nu = 1/2$ and $z = 2$. Before this work, the QCP in 1T-$TiSe_2$ was speculated to lie withing the SC dome thus leading to the conclusion that SC emerges from suppression of CDW. However, the present study showed that the QCP was separated from the SC dome by more than 1 GPa. Moreover, the C/I (CDW) transition coincided with the onset of SC (see Fig. 2) thus suggesting that the nucleation of SC could be in the domain walls that develop in the CDW order with pressure.

4 Evolution of CDW in 1T-$TiSe_2$ with *Cu* intercalation

Intercalation offers an alternative to pressure for studying the suppression of CDW order. This possibility was explored in a recent work by Kogar *et al.* where they study the evolution of the phases as a function of copper (Cu) intercalation in the resulting Cu_xTiSe_2 [4]. Using the same technique developed in [3], it was found that with increasing Cu content, incommensurability sets in, as can be seen in Fig. 3, where the CDW peak becomes separated from the Bragg peak.

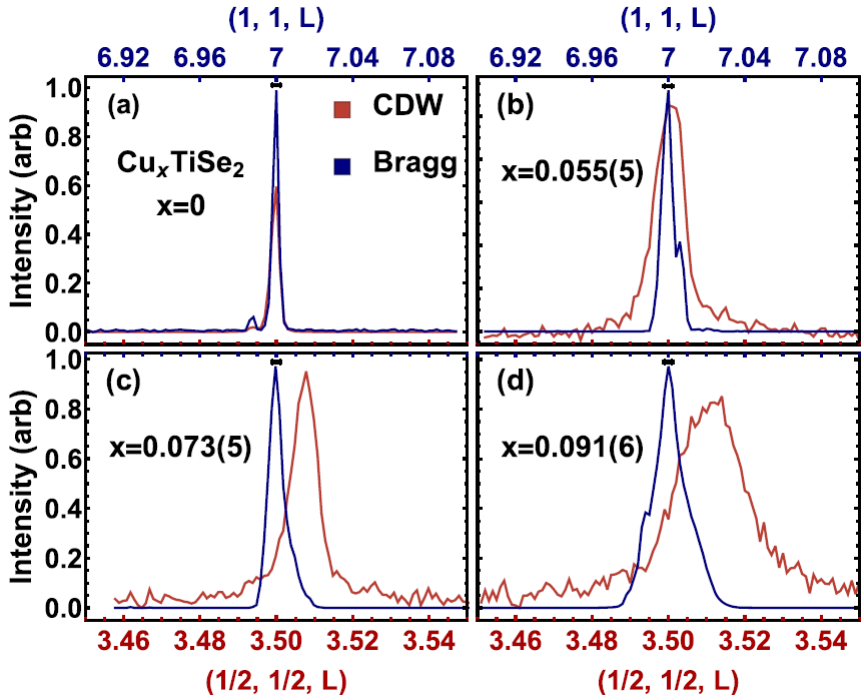

Figure 3: Simultaneous L cuts of the (1,1,7) Bragg Peak and the $(\frac{1}{2}, \frac{1}{2}, \frac{7}{2})$ CDW superlattice peak for different values of x in Cu_xTiSe_2 (taken from [4]).

The resulting phase diagram as a function of Cu content is reproduced in Fig. 4. In contrast to the monotonic T_{CDW} decrease with pressure observed in [3], the T_{CDW} in Cu_xTiSe_2 decreases until $x \approx 0.055$ and then stays approximately constant for higher values of x. This gives some insight into the contribution of different correlations driving the different phases of CDW in $TiSe_2$. Studies

suggest that EHC (excitonic) and EPC both play an important role in the CDW transition in pure $TiSe_2$. Copper intercalation electron dopes the Ti -3d conduction band thereby enhancing screening effects and thus reducing the excitonic contribution to the CDW while leaving the EPC correlations less affected for higher intercalant concentrations.

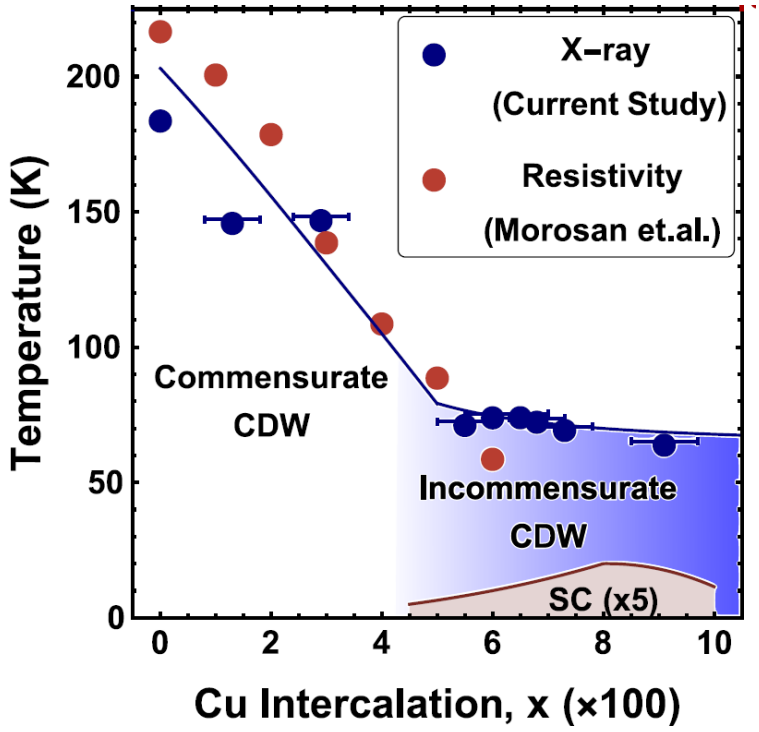

Figure 4: Phase diagram for Cu_xTiSe_2 showing the CCDW, ICDW and the SC phases (taken from [4])

Fig. 4 also shows that the ICDW phase develops at an intercalant value of $x \approx 0.055$ coincident with the onset of SC, which is in qualitative agreement with the results of [3] for pure $TiSe_2$ under pressure. The optimal value of Cu intercalation is around $x \approx 0.08$. An interesting resemblance between the characteristic feature of ICDW and SC phases is discussed in this work for the optimal value of Cu intercalation - incommensurability data in this work gives an estimate of stacking faults at an average of 22 lattice units along c axis, and earlier measurements on the upper critical field give an estimate of the out-of-plane Ginzburg Landau correlation length, $\xi_\perp$, to be approximately 21 lattice units. This excellent agreement between these values along with the coincident onset of ICDW and

SC at the same intercalation value further corroborate the importance of the role incommensuration of the charge ordered phase in the emergence of SC.

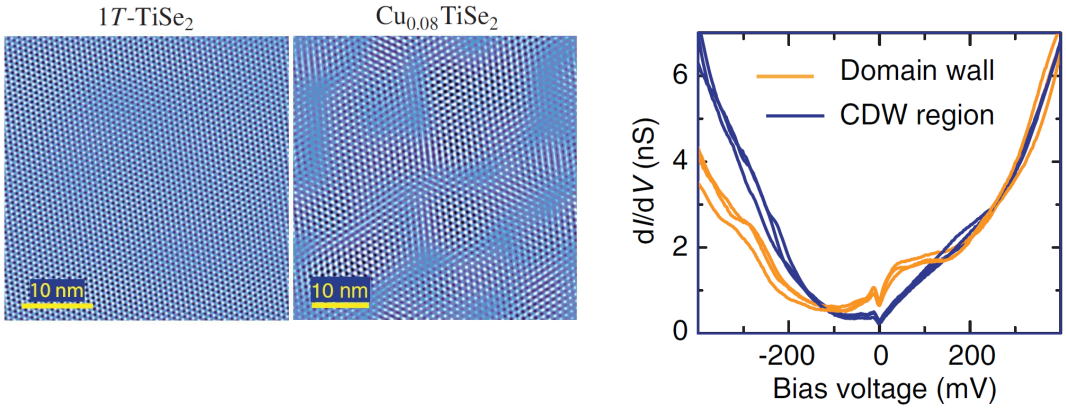

Figure 5: Left: IFT images of the CDW components observed in the STM topography of pure 1T-$TiSe_2$ and $Cu_{.}08TiSe_2$. Right: $\frac{dI}{dV}$ spectra on randomly selected DWs and CDW regions in $Cu_{0.08}TiSe_2$. Figures are taken from [5]

Both the experimental works discussed above [3, 4] suggested development of domain walls or stacking faults as a plausible mechanism for incommensuration. This was verified experimentally by a very recent Scanning Tunneling Microscopy (STM) study of pure $TiSe_2$ and optimally doped $Cu_{0.08}TiSe_2$ by Yan *et al.* [5]. The inverse fourier transform (IFT) images obtained from the STM images for the pure and optimally doped $TiSe_2$ reproduced in Fig. 5 (left) show a clear presence of domain walls (DWs) in the optimally doped sample. The DWs form long stripes which separate the CDW patterns by a phase shift of π. Within a single domain, the CDW is found to be fully commensurate. Because of the supposed relevance of incommensurability (and hence DWs) to the onset of SC, the authors further investigate the effect of DWs on the local density of states (DOS). The results are shown in Fig.5 (right) ; the differential conductance plotted, dI/dV is directly proportional to the DOS. It is evident that DWs (yellow curve) have a higher DOS near fermi energy E_F (corresponding to bias voltage =0) implying a higher population of fermions compared to that in the CDW region confined within a domain (blue curve). Thus the higher DOS within the DWs may be a key factor to the onset of SC in intercalated $TiSe_2$.

5 Conclusion

The recent experimental works reviewed here show that with tuning external factors like pressure [3] and intercalation [4] in 1T-$TiSe_2$, the commensurate CDW phase melts into an incommensurate CDW phase. This emergent incommensurate CDW phase is found in close proximity to the incipient SC in this material suggesting the importance of incommensuration in SC. Incommensuration is explained through the formation of DWs [5], which might also be responsible for SC in 1T-$TiSe_2$.

References

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