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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Master of Science

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ABSTRACT

Effects of synthesis conditions on the transition metal dichalcogenide TiSe₂

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TiSe₂ is part of a family of materials known as the transition metal dichalcogenides. Their quasi-two dimensional crystal structure sometimes gives rise to interesting phenomena, spanning a vast array of physical and electronic properties including charge order or superconductivity when various intercalants or dopants are added. TiSe₂ was shown to have charge ordering at a temperature of 200 K almost 45 years ago. Despite the time that has elapsed between this discovery and now, TiSe₂ continues to be an intensely studied material because the nature of its charge ordering is still under debate. Some of the conflicting results are fueled by sample dependency related to growth method and conditions.

Due to the small band gap or band overlap in TiSe₂, it is not surprising that dilute impurities and growth conditions can affect drastically the transport properties of TiSe₂. In this work I systematically study the effect of variable growth conditions including post synthesis cooling rate, anneal time, and temperature, on the electrical resistivity of TiSe₂. I find that slow cooling polycrystalline TiSe₂ post synthesis drastically increases the low temperature resistivity, which is in stark contrast to the metallic low temperature resistivity observed in single crystalline TiSe₂ grown by iodine vapor transport, where the iodine charge dopes the sample. Together, the logarithmic divergence of the resistivity and signatures in low temperature magnetoresistance point to signatures of the weak-localization effect. Annealing samples at low temperatures post synthesis also increases the low temperature resistivity, but with a less profound effect. Finally, quenching samples from high temperature freezes in disorder and decreases the low temperature resistivity.

Acknowledgments

I would like to thank my adviser Emilia Morosan for her guidance during this work as well as everyone in our group, both past and present, and all collaborators that have helped me along the way. I also would like to thank my committee members for their time in serving on my committee. Furthermore I would like to thank my entire family for their continued love and support.

This work was funded by NSF DMREF Grant No. 1629374.

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List of Acronyms

TMDC: transiton metal dichalcogenide CDW: charge-density wave CCDW: commensurate charge-density wave ICDW: incommensurate charge-density wave FS: Fermi Surface ARPES: Angle resolved photomemission spectroscopy EPMA: electron probe microanalysis

Chapter 1

Outline

This thesis is focused on my work on the transition metal dichalcogenide TiSe₂. TiSe₂ continues to be actively studied in the condensed matter physics community due to the rich physics involved in the formation of its charge order as well as the interplay of the charge order with superconductivity. In this work I focus and document how TiSe₂ electrical transport properties systematically vary based on synthesis conditions.

In Chap. 2 I give a brief introduction to TiSe_2 and show how sample variation has led to different conclusions about the nature of the charge order in TiSe_2 . In Chap. 3 I review the physics relevant to the charge ordering in TiSe_2 , namely the Peierls instability, the band-Jahn Teller mechanism, and the excitonic mechanism. Furthermore, I review some concepts involved in weak localization for which I found evidence for in TiSe_2 . Finally Chap. 4 is largely reproduced from my publication [1] where I detail the effects of synthesis conditions on the electrical resistivity of TiSe_2 .

Chapter 2

Introduction to $TiSe_2$

2.1 Overview

TiSe₂ is part of a family of materials called the transition metal dichalcogenides (TMDCs). Such materials have attracted considerable interest in the condensed matter community in part due to their quasi-two dimensional crystal structure which can sometimes lead exotic to ground states. Furthermore their layered crystal structure allows for easy intercalation or doping, which births an experimental playground for tuning their electronic and physical properties.

While some TMDCs exist in many polytypes, $TiSe_2$ only exists in the 1*T* polytype with trigonal symmetry in which the Ti atoms are octahedrally coordinated to Se atoms, forming layers, Fig. 2.1a. These Ti-Se layers are bonded to each other by van der Waals forces.

Di Salvo *et al.* first reported a commensurate $2 \times 2 \times 2$ charge modulation or charge density wave (CDW) in TiSe₂ at $T_{CDW} = 200$ K accompanied by a periodic lattice distortion [2]. The CDW transition was marked also by an anomaly in resistivity at T_{CDW} , Fig. 2.1b. While the first band structure calculation, Fig. 2.1c shows that TiSe₂ should be a semimetal [3], the Fermi surface (FS) is not nested as shown in Fig. 2.1d [4]. As explained in Chap. 3, often CDWs can be explained by heavily nested FSs, but clearly this is not the case in TiSe₂. Hence, proposed mechanisms include the band Jahn-Teller mechanism [5], and an excitonic insulator scenario [6]



Figure 2.1 : (a) The crystal structure of TiSe_2 with Ti (blue) atoms are octahedrally coordinated with Se (green) atoms. (b) Temperature dependent resistivity of TiSe_2 from Ref. [2], with the anomaly being marked as a minima in the first derivative (inset). (c) First published band structure of TiSe_2 from Ref. [3] showing TiSe_2 is likely a semimetal. The Fermi surface plot of TiSe_2 from Ref. [4] shows an unnested Fermi surface.



Figure 2.2 : ARPES data from Ref (a) [7] leads Watson *et al.* to conclude that TiSe₂ is a semiconductor at (a) T = 300 K with a band gap of about 74 meV, while at (b) T =10 K TiSe₂ is still a semiconductor, but with a smaller band gap. (c) ARPES data from Ref. [8] is consistent with a semimetal above T_{CDW} (top), and a semiconductor below T_{CDW} (bottom).

for the CDW formation, both reviewed in Chap. 3. A much needed starting point to understanding the evolution of the CDW phase is to know both the high temperature 'normal phase,' and the low temperature ground state. However, due to sample to sample inconsistency, semimetal to semiconductor and small band gap to larger band gap semiconductor, have all been reported as the normal state and ground state, across the CDW phase transition respectively. Hence, the mechanism for the CDW phase transition in $TiSe_2$ is still an active and debated topic. The experimental discrepancies will be reviewed next in Sec. 2.1.1.

2.1.1 Sample dependence of the electronic properties

Normally, angle resolved photoemission spectroscopy (ARPES) is the definitive tool for studying the band structure of easily cleavable materials. However, due to the high transition temperature of the CDW phase transition, small band gap/overlap,



Figure 2.3 : (a) The dependence of growth temperature on the resistivity of the single crystals of TiSe₂ from Ref. [2]. The temperature dependence of the resistivity as a function of Se deficiency, δ , which was induced by annealing on TiSe₂ from Ref. [17]. (c) Temperature dependence of the resistivity of TiSe₂ single crystals grown by three different methods: (red) a pressure method, (blue) Se flux, and (black) chemical vapor transport with I₂ as the transport agent from Ref. [18].

as well as sample variability, the size and nature (semiconductor or semimetal) of the normal state is still under debate [7–15]. For example, recent ARPES data show that above T_{CDW} , Fig. 2.2(a), the normal state of TiSe₂ is semiconductor with an indirect band gap of about 75 meV, while below T_{CDW} , Fig. 2.2(b), a direct gap of around 15 meV emerges in the folded Brillouin Zone [7]. Preceding this measurement, Cercellier *et al.*'s data is consistent with a small band overlap in the normal state Fig. 2.2(c, top), and a band gap in the CDW state Fig. 2.2(c, bottom) [8]. Furthering the problem, optical studies are consistent with a semimetal to semimetal transition across the CDW phase transition [16].

There also has been a recent resurgence of interest in the electrical resistivity in TiSe₂ [1, 17, 18]. Dating back to DiSalvo *et al.*'s original paper, the authors already understood that synthesis conditions greatly affect the resistivity, as the hump centered around T = 150 K systematically decreases with increasing growth temperature of their single crystals Fig. 2.3a [2]. The authors proposed that this may be due to self intercalation of Ti and iodine inclusions. Later Huang *et al.* showed that by annealing polycrystalline samples at different temperatures, the resistivity of their polycrystalline samples go from a semiconductor - like behavior, to a metallic - like behavior at low temperature [17]. The authors attributed this to increase Se deficiency with increased annealing temperature, and their results are shown in Fig. 2.3b. Finally, Campbell *et al.* synthesized TiSe₂ single crystals via a pressure method, Se flux method, and by I₂ vapor transport [18]. It is seen in Fig. 2.3c (red curve) that the sample grown by the pressure method shows an insulating behavior at low temperatures with thermal hysteresis, in contrast to the low temperature metallic resistivity of the crystals grown by Se flux and chemical vapor transport (blue and black curve, respectively). Furthermore, the authors tried growing crystals at several different pressures, however there was no systematic correlation between the low temperature resistivity and growth pressure. Such discrepancies motivated my study, in which I systematically vary growth conditions in an attempt to understand the temperature dependent resistivity intrinsic to TiSe₂ as described in Chap. 4.

Chapter 3

Background

This chapter is split into two parts: in Sec. 3.1 I review some concepts of charge density wave physics, while in Sec. 3.2 I outline a phenomological understanding of the weak localization effect.

3.1 Introduction to Charge Density Waves

3.1.1 Peierls instability

In metals it turns out that many of their properties are a result of their FS topology. For example magnetism can arise not just from localized unpaired electrons as in the case for insulators, but also from band effects in metals [19]. Furthermore BCS superconductors remove a FS instability via an electron-phonon interaction which leads to electron pairs, called Cooper pairs [20]. Another phenomena that can occur due to a FS instability is a CDW, which is the focus of this introduction.

A CDW is simply a periodic modulation of conduction electrons with respect to a lattice. Rudolph Peierls in the 1930s showed how such a modulation may occur in one dimension [21]. Following Grüner [22], the charge density (in d dimensions) in response to a time independent potential is given by

$$\rho_{ind}(\vec{q}) = \chi(\vec{q})\phi(\vec{q}), \qquad (3.1)$$

where $\chi(\vec{q})$ is the Lindard response function given by

$$\chi(\vec{q}) = \int \frac{d\vec{k}}{(2\pi)^d} \frac{f_{\vec{k}} - f_{\vec{k}+\vec{q}}}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}}.$$
(3.2)

 $f_{\vec{k}}$, the Fermi function is a function of $\epsilon_{\vec{k}}$. The topology of the FS greatly affects $\chi(\vec{q})$. The FS of a one dimensional metal consists of two sheets located at $\pm k_f$, Fig. 3.1a (top). This is an example of the so called "perfect nesting" condition which occurs for FSs that have large parallel sheets that can be connected by the same wavevector \vec{q} . In such a scenario $\chi(\vec{q})$, diverges at \vec{q} due to the two states at $\pm k_f$ which have the same energy. In Fig. 3.1b I have plotted the $\chi(\vec{q})$ for one, two, and three dimensions. While $\chi(\vec{q})$ diverges in one dimension due to this FS nesting, the divergence is reduced to a kink due to the lack of FS nesting in two dimensions (the FS is a circle Fig. 3.1a (middle)), and a smooth curve in three dimensions (the FS is a sphere). The divergence in one dimension suggests that the charge distribution is unstable to any external perturbation. Though the example of the divergence is most apparent in one dimension, FS nesting can lead to an instability in low dimensional systems so long as large portions of the FS are nested, as seen for example in Fig. 3.1a (bottom).

When coupling the one dimensional free-electron-gas to a lattice, through electronphonon coupling, the renormalized phonon dispersion can be written as

$$\omega_{ren,\vec{q}}^2 = \omega_{\vec{q}}^2 + \frac{2g^2\omega_{\vec{q}}}{\hbar}\chi(\vec{q},T), \qquad (3.3)$$

where $g_{\vec{q}}$ is the electron-phonon coupling constant given as

$$g_{\vec{q}} = i\left(\frac{\hbar}{2M\omega_{\vec{q}}}\right)^{1/2} |\vec{q}| V_{\vec{q}}.$$
(3.4)

Hence, at the wave vector where $\chi(\vec{q}, T)$ diverges ($\vec{q} = 2k_f$ in one dimension), the phonon dampens and the frequency goes to zero. I have plotted this in Fig. 3.1c (blue



Figure 3.1 : (a) (top) A one-dimensional Fermi surface displaying perfect nesting at wavevector $|\vec{q}| = 2k_F$. (middle) A two-dimensional Fermi surface which displays no nesting. (bottom) A schematic of a two-dimensional Fermi surface that displays partial nesting. (b) Lindhard response function in one dimension (blue), two-dimensions (yellow), and three dimensions (blue). (c) Renormalized phonon-dispersion when accounting for electron-phonon interaction in one dimension. Above T_{CDW} , the phonon dispersion remains largely unchanged (grey), while below the T_{CDW} the phonon mode softens (blue). (d) (top) A one-dimensional lattice with lattice constant *a* (blue circles) and the electron density (black line) that results from the half-filled band structure above T_{CDW} bottom. (e) Below T_{CDW} a periodic lattice distortion occurs with a new lattice constant 2*a*, and periodic charge distribution (top), resulting in an energy gap (bottom).

curve). This is sometimes termed "phonon freezing," and the temperature at which the phonon freezes is the definition of the CDW transition temperature T_{CDW} . The "frozen" lattice results, in a new lattice and charge distribution from $\rho(x) = constant$ (Fig. 3.1d, top) above T_{CDW} to

$$\rho(x) \propto \cos(2k_f x + \phi), \tag{3.5}$$

shown in Fig. 3.1e, top, where ϕ is a phase constant, below T_{CDW} . This new periodicity opens an energy gap, at $\pm k_f$, shown in Fig. 3.1e bottom. Hence in one dimension, the CDW phase transition is associated with a metal to insulator transition when considering a half-filled band. If the CDW has a period proportional to integer numbers of lattice spacings, the CDW is termed a commensurate CDW (CCDW), whereas for non-integer periods it is called an incommensurate CDW (ICDW).

While Peierls explained how CDWs, accompanied by a periodic lattice distortion, form, it was expected that such a transition could occur only in one dimension. However, it was experimentally discovered that CDWs can exist in two dimensions, for example, the transition metal dichalcogenides [23], and also in three dimensions, reviewed in [24]. Furthermore, it has been experimentally shown that a CDW can arise without a periodic lattice distortion, as is the case in $K_{0.9}Mo_6O_7$ [25], showing the electron-electron interactions can also play an important role in the formation of CDWs.

3.1.2 Jahn-Teller mechanism

The band type Jahn-Teller mechanism was first proposed to explain the CDW in $TiSe_2$ by Hughes [5]. This mechanism requires the normal state of $TiSe_2$ to be a semimetal. In the 1*T* polytype the chalcogenide atoms are octohedrally coordinated around the transition metal, whereas in the 2H compounds the chalcogenide atoms are trigonally coordinated around the transition metal atom. Band structure calculations show that the *d*-bands of 1T and 2H polytypes of the TMDCs have slightly different energies with the 1T type having slightly higher energies. Thus, a structural phase transition from 1T to 2H was predicted, where a local increase in the density of states of negative charge at the unit cell corners from the rotation of the chalcogenide atoms results in an attractive potential for the transition metal ion. In this scenario, the CDW is driven by the real space coordination of the transition metal and chalcogenide atoms, and is not a FS effect.

3.1.3 Excitonic mechanism

The excitonic insulator mechanism for a CDW to form was first set forth by Jerome et al. [6]. Such a scenario exists in a low carrier semimetal with a small band overlap or a semiconductor with a small band gap. Due to the low carrier concentrations, interactions between holes and electrons are very weakly screened. Therefore, by a Coulomb interaction, holes and electrons can form bound pairs called excitons, and remove free carriers from the FS if the binding energy of the exciton is larger than the band gap or band overlap of the material. Hence, this transition is often a semimetal to semiconductor transition. The exciton modes can couple to phonon modes, driving a periodic lattic distortion that doubles the unit cell. It is important to note that even though there is an electron-phonon interaction as a result of the exciton formation, the driving force in the excitonic insulator scenario is an electron-electron (hole) interaction. This is in contrast to that of the Peierls instability scenario which is driven by the electron-phonon.

In reality, electron-electron and electron-phonon interaction probably play a role

in the formation of the CDW formation in $TiSe_2$. The question that remains is the relative involvement of each.

3.2 Introduction to weak localization

3.2.1 Feynman's path integral approach to Quantum Mechanics

Feynman created an equivalent approach to the Schrodinger approach to quantum mechanics [26]. I show it because later in Sec. 3.2.3, it is a nice way to phenomonalogically explain the physics of weak localization. Thanks to Professor Jena's online lectures for giving a good synopsis of the physics weak localization [27].

Following is a review the equivalence between Schrodinger's Hamiltonian approach and Feynman's path integral approach, starting with the Schrodinger equation Eq. 3.6.

$$i\hbar \frac{\partial |x_i\rangle}{\partial t} = \left[\frac{\hat{p}^2}{2m} + V(\vec{r}, t)\right] |x_i\rangle, \qquad (3.6)$$

where \hat{H} is the Hamiltonian and $|x_i\rangle$ is a state vector. The initial state $|x_i\rangle$ evolves with time as

$$|\psi(t)\rangle = \hat{U}(t) |x_i\rangle = e^{-i/\hbar \hat{H}t} |x_i\rangle, \qquad (3.7)$$

where \hat{U} is the time evolution operator. Then, the transition amplitude from an initial state $|x_i\rangle$, to the final state $|x_f\rangle$ is given by

$$\left\langle x_f \right| e^{-\frac{i}{\hbar}\hat{H}t} \left| x_i \right\rangle. \tag{3.8}$$

We can imagine a particle traversing some path from $a \rightarrow b$. It is possible to slice the time into equal parts as shown in Fig. 3.2 such that



Figure 3.2 : An example of three different one-dimensional paths that could be traced out starting at point a and ending at point b.

$$\hat{U}(t) = \hat{U}(t/2)\hat{U}(t/2),$$
(3.9)

and Eq. 3.8 becomes

$$\langle x_f | e^{-\frac{i}{\hbar}\hat{H}t/2} e^{-\frac{i}{\hbar}\hat{H}t/2} | x_i \rangle.$$
 (3.10)

Inserting the resolution of identity

$$1 = \int_{-\infty}^{\infty} \mathrm{d}x \left| x \right\rangle \left\langle x \right|, \qquad (3.11)$$

Eq. 3.10 becomes

$$\int_{-\infty}^{\infty} \mathrm{d}x \, \langle x_f | \, e^{-\frac{i}{\hbar} \hat{H} t/2} \, | x \rangle \, \langle x | \, e^{-\frac{i}{\hbar} \hat{H} t/2} \, | x_i \rangle \,. \tag{3.12}$$

We can further imagine slicing time into infinitesimal slices called $\Delta t = t_n - t_{n-1} = t/N$ and space, into the corresponding intervals $x_i \to x_1 \to x_2 \to \dots \to x_j \to x_{j+1} \to \dots \to x_{N-1} \to x_f$ so that we can cover all possible paths. Then, Eq. 3.8 becomes

$$\left\langle x_{f}\right|e^{-\frac{i}{\hbar}\hat{H}\Delta t/2}e^{-\frac{i}{\hbar}\hat{H}\Delta t/2}\dots e^{-\frac{i}{\hbar}\hat{H}\Delta t/2}\left|x_{i}\right\rangle,\tag{3.13}$$

and has N terms. Inserting the appropriate resolutions of identity, Eq. 3.14 becomes

$$\int_{-\infty}^{\infty} \mathrm{d}x_1 \mathrm{d}x_2 \dots \mathrm{d}x_{N-1} \left\langle x_f \right| e^{-\frac{i}{\hbar} \hat{H} \Delta t/2} \left| x_{N-1} \right\rangle \dots \left\langle x_2 \right| e^{-\frac{i}{\hbar} \hat{H} \Delta t/2} \left| x_1 \right\rangle \left\langle x_1 \right| e^{-\frac{i}{\hbar} \hat{H} \Delta t/2} \left| x_i \right\rangle.$$

$$(3.14)$$

Taking $N \to \infty$ so that Δt is very small, we can do a Taylor expansion such that

$$e^{-\frac{i}{\hbar}\hat{H}\Delta t} \approx 1 - \frac{i}{\hbar}\hat{H}\Delta t.$$
 (3.15)

Now looking at only one term in the integral in Eq. 3.14, we have

$$\langle x_{j+1} | e^{-\frac{i}{\hbar}\hat{H}\Delta t} | x_j \rangle \approx \langle x_{j+1} | 1 - \frac{i}{\hbar}\hat{H}\Delta t | x_j \rangle.$$
(3.16)

For simplicity we choose the one dimensional Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x).$$
(3.17)

Plugging the Hamiltonian Eq. 3.17 in Eq. 3.16, and solving by using Eq. 3.18-3.20

$$\langle x_{j+1}|x_j \rangle = \delta(x_j - x_{j-1}) = \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} e^{ik(x_{j+1} - x_j)}$$
 (3.18)

$$\langle x_{j+1} | V(x) | x_j \rangle = \delta(x_j - x_{j-1}) V(x) = \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} e^{ik(x_{j+1} - x_j)} V(x)$$
 (3.19)

$$\langle x_{j+1} | \frac{\hat{p}^2}{2m} | x_j \rangle = \int_{-\infty}^{\infty} \mathrm{d}k \, \langle x_{j+1} | \frac{\hbar^2 \hat{k}^2}{2m} | k \rangle \, \langle k | x_j \rangle \, \langle x | k \rangle = \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} e^{ik(x_{j+1}-x_j)} \frac{\hbar^2 k^2}{2m}, \tag{3.20}$$

where $\delta(x)$ is the Dirac-Delta function, and in Eq. 3.20 I have used the identity $\langle x|k\rangle = e^{\frac{ikx}{\sqrt{2\pi}}}$, we arrive at the transition amplitude

$$\langle x_{j+1} | 1 - \frac{i}{\hbar} \hat{H} \Delta t | x_j \rangle = \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} e^{i(x_{j+1} - x_j)} [1 - \frac{i\Delta t}{\hbar} (V(x_j) + \frac{\hbar^2 k^2}{2m})].$$
(3.21)

Notice, now there are no operators left, and taking advantage of the fact that $1 - u \approx e^{-u}$ for $u \ll 1$, we can write Eq. 3.21 as

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \left[-\frac{i\Delta t}{\hbar} \frac{\hbar^2 k^2}{2m} + ik(x_{j+1} - x_j) - \frac{i\Delta t}{\hbar} V(x_j)\right].$$
(3.22)

Eq. 3.22 has the form of the beloved Gaussian integral $\int_{-\infty}^{\infty} du e^{-au^2+bu+c}$ with a solution $\sqrt{\frac{\pi}{a}}e^{\frac{k^2}{4a}} + c$. Hence,

$$\langle x_{j+1} | 1 - \frac{1}{\hbar} \hat{H} \Delta t | x_j \rangle \to \frac{1}{\sqrt{\frac{2\pi i \hbar \Delta t}{m}}} e^{\frac{i}{\hbar} (\frac{m}{2} (\frac{x_{j+1} - x_j}{\Delta t}) - V(x_j)) \Delta t}.$$
(3.23)

Noticing that the term in parentheses in Eq. 3.23 is the Lagrangian with $\mathcal{L} = \frac{mv^2}{2} - V(x_j)$ where $\frac{x_{j+1}-x_j}{\Delta t}$ is the velocity, v, combining all the terms in Eq. 3.14, and hiding all the differentials with a combined term $\mathcal{D}x(t)$ we come to

$$\langle x_f | \hat{U}(t) | x_i \rangle = \int \mathcal{D}x(t) e^{\frac{i}{\hbar}S_{cl}}, \qquad (3.24)$$

where S_{cl} is the classical action defined as $\int \mathcal{L} dt$. The term on the left is the Schrodinger approach to quantum mechanics while the term on the right is Feynman's approach which he termed the space-time approach to quantum mechanics. I will use it to give some insight later on to the physics of weak-localization.

3.2.2 Diffusion equation for a free particle

Weak localization is a known transport phenomenon that occurs in low dimensional, disordered conductors or semimconductors. It manifests in an anomalous upturn in resistivity at low temperatures that can be suppressed by applying a magnetic field as shown in Fig. 3.33a. It is thus the goal of this section to give a phenomenological understanding of this phenomenon.

The probability distribution P(r, t) for a particle undergoing diffusive transport can be obtained by solving the diffusion equation

$$\frac{\partial}{\partial t}P(r,t) = D\nabla^2 P(r,t), \qquad (3.25)$$



Figure 3.3 : (a) Schematic of the effect of a magnetic field on the temperature dependence of a low dimensional conductor. (b) Comparison of the probability distribution of a wave (dashed line), and a particle (solid line). (c) Two possible real space paths from a point a to a point b. (d) Schematic of the imaginary plane showing how all the phases cancel in the second term of Eq. 3.27 for an object when time reversed paths are not considered.

where $D = \frac{v^2 \tau}{d}$ is the diffusion coefficient, v is the velocity and τ is a time constant. If a particle is placed at the origin r = 0 at time t = 0, such that $P(r = 0, t = 0) = \delta(0)$, the solution is described by a Gaussian in d dimensions.

$$P(r,t) = \frac{1}{(4\pi Dt)^{d/2}} e^{-\frac{|r|^2}{4Dt}}.$$
(3.26)

As time increases, the probability spreads in time such that maximum distance $L \sim \sqrt{Dt}$. Furthermore, the maximum at r = 0 continually decreases as shown in

Fig. 3.33b. However, if one solves the equivalent diffusion equation for a wave, there is an increased probability at r = 0 to find a particle when compared to the case for a particle shown in Fig. 3.33b. Thus, when considering the transport of a particle like an electron, which is a wave, from $a \rightarrow b$, it is reasonable to expect a decrease in the conductivity relative to the situation of a particle, due to the electron spending more time at the origin. In the next section, Sec 3.2.3, Feynman's path integral approach, I show that this is indeed true in some cases in one and two dimensions.

3.2.3 Wave in a diffusive medium

Since we know that an electron is a quantum particle, we know we should treat it as such. In Sec. 3.2.1 I reviewed Feynman's path integral approach to Quantum Mechanics. There we laid out a prescription for finding the amplitude of a particle going from some point $a \rightarrow b$ that does not involve using operators:

- 1. Find the Lagrangian along a single path: $\mathcal{L} = \frac{1}{2}mv^2 V(x)$
- 2. Find the classical action along such a path: $S_{ab} = dt \mathcal{L}(x, v)$
- 3. Sum the quantum phases of all possible paths to get the transition amplitude.

Loosely speaking, to get the probability of such an event we should square the amplitude, A, such that

$$A^{2} = |\langle b|a \rangle|^{2} = |\sum_{i} A_{i}|^{2} = \sum_{i} |A_{i}|^{2} + \sum_{i \neq j} A_{i}A_{j}^{*}.$$
(3.27)

The first term is the particle-like contribution, while the second term, coined the interference term, is due to the wave nature of the electron. It is always zero for a

particle, and even naively expected to be zero for a wave, but under certain conditions which I discuss later, can be non-zero.

First, I talk about the case when the interference term is zero. Consider an electron moving from $a \rightarrow b$ in a flat band such that V = 0. For transport to occur, the Fermi wavelength λ_F must be much less than the mean-free path length l_{el} that a particle goes before scattering inelastically. For weak-localization to manifest itself, $l_{\phi} >> L_i >> l_{el}$. Here, l_{ϕ} , the characteristic length an electron can go without losing its phase due to an inelastic scattering event, hence weak-localization should occur at low temperatures in a disorder medium.

Writing down the Lagrangian for such as system for a path - call it L_i which could be path 1: a-o-c-d in Fig. 3.33c, $\mathcal{L}_i = \int dt \frac{mv^2}{2}$ can be written as

$$\mathcal{L}_i = \int \mathrm{d}t v(mv). \tag{3.28}$$

Since we can expect that only electrons near the Fermi surface will contribute, we let $mv = p_f$ and the integral part, $\int dtv$ gives the length L_i . With $k_F = \frac{2\pi}{\lambda_F}$, the amplitude becomes

$$A_i \sim e^{ik_F L_i} = e^{i\frac{2\pi}{\lambda_F}}.$$
(3.29)

Now including a second path, for example path 2 in Fig. 3.33c, the second term (the interference) in Eq. 3.27 becomes

$$\sum_{i \neq j} A_i A_j^* = \sum_{i \neq j} e^{ik_F(L_i - L_j)} = \cos(k_F(L_i - L_j)) + i\sin(k_F(L_i - L_j)).$$
(3.30)

Still considering only the interference term, but summing over all possible paths from point a to point b which is identical to summing over all possible unit vectors in the imaginary plane (Fig. 3.33d), we find out the interference term is exactly 0.

However, if we consider a closed loop sub-path, L_+ , o-c-d-o in Fig. 3.33c, and its time - reversed path L_- , o-d-c-o, the interference term is 1! This means that there is some enhanced probability for the particle to spend more time at point o, implying that due to self-intersecting paths, the net conductivity must be lower than the classical Drude conductivity, $\sigma_0 = \frac{ne^2 \tau_{el}}{m}$, for some electron traversing from $a \to b$. This is the phenomenological physics of weak localization.

3.2.4 Correction to conductivity

The weak localization correction, $\delta\sigma$ to the conductivity, σ can be calculated as the ratio of the volume swept by self-intersecting paths to the volume spanned due to classical diffusion, given by

$$\frac{\delta\sigma}{\sigma_0} \sim \int_{\tau_{el}}^{\tau_{\phi}} \frac{\lambda_F^{d-1} v_F \mathrm{d}t}{(Dt)^{d/2}},\tag{3.31}$$

so

$$\delta\sigma \sim \frac{e^2}{\hbar} \int_{\tau_{el}}^{\tau_{\phi}} \frac{D \mathrm{d}t}{(Dt)^{d/2}}.$$
(3.32)

The lower limit comes from the condition for conduction to occur, namely $\lambda_F \ll l_{el}$, where τ_{el} is the corresponding time scale, while the upper limit τ_{ϕ} , is the time scale corresponding to the phase coherence length $L_{\phi} = \sqrt{D\tau_{\phi}}$.

Doing the integral for d dimensions gives

$$\delta \sigma \sim \begin{cases} \frac{e^2}{\hbar} L_{\phi} & d = 1\\ \frac{e^2}{\hbar} \ln(\frac{\tau_{\phi}}{\tau_{el}}) & d = 2\\ \frac{e^2}{\hbar} \frac{1}{L_{\phi}} & d = 3, \end{cases}$$
(3.33)

and the total conductivity is written as

$$\sigma = \sigma_0 + \delta\sigma. \tag{3.34}$$

Notice that the integrals in Eq. 3.33 have different limiting behavior as $L_{\phi} \to \infty$ (experimentally $T \to \infty$) in different dimensions. For d = 1, 2 the integrals diverge meaning that as time goes to infinity, it is guaranteed a particle will return to the origin. In 3 dimensions, the integral goes to zero implying a particle on a random walk is guaranteed NOT to return to its origin.

3.2.5 Application of a magnetic field

Upon the introduction of a magnetic field, the actions along time-reversed paths do NOT accumulate identical phases anymore; the additional phase is the close-loop integral of the vector potential defined as

$$\Phi = \oint \vec{A} \cdot d\vec{r} = \int \nabla \times \vec{A} \cdot d\vec{S} \neq 0.$$
(3.35)

In two-dimensions, the famous Hikami-Larkin-Nagaoka formula [28] shows that the conductivity decreases as

$$\Delta G = \alpha \frac{e^2}{2\pi^2 \hbar} [\psi(\frac{1}{2} + \frac{B_{\phi}}{B}) - \ln(\frac{B_{\phi}}{B})]$$
(3.36)

in a magnetic field *B* perpendicular to the current, where $\Delta G = \frac{1}{\rho(B)} - \frac{1}{\rho(B=0)}$, $B_{\phi} = \frac{\hbar}{4eL_{\phi}^2}$, $\psi(x)$ is the digamma function, and $\alpha = 1$ for weak localization. Hence, I have now explained why the resistivity in Fig. 3.33a decreases upon application of a magnetic field.

Chapter 4

Effect of synthesis conditions on the electrical resistivity of $TiSe_2$

This chapter is reproduced from my work Ref. $[1]^*$, with the exception of Sec. 4.2.1 where I have included additional details on maximizing reproducibility when synthesizing polycrystalline TiSe₂.

4.1 Introduction

Transition metal dichalcogenides (TMDCs) are a class of layered quasi-two dimensional materials. Owing to their low dimensionality, they span a vast area of physical properties. TiSe₂ is one such TMDC that has attracted lots of attention due to its complex electronic properties, including charge ordering [2], superconductivity with intercalation of copper or palladium [29,30], and with the application of pressure [31] or electrostatic gating [32]. On the other extreme, TiSe₂ becomes insulating with platinum doping [33], and displays potential Luttinger liquid states within domain boundaries [34] revealing the versatility of the chemical tuning of this TMDC compound.

The origin of the charge density wave (CDW) transition, occurring in $TiSe_2$ around 202 K [2], has been an ongoing debate for decades, with proposed mechanisms including an excitonic insulator phase [6] and the band-type Jahn-Teller effect [5]. For

^{*}Reproduced from Ref. [1] with permission. ©2019 American Physical Society.



Figure 4.1 : A comparison of the resistivity (normalized to room temperature values) for iodine-grown TiSe₂ single crystals with the current $i \parallel ab$ (dashed line) or $i \parallel c$ (open circles), and polycrystalline (solid line). The full triangle is used to identify samples that are 'As Grown, Air Quenched' throughout the text.

the former, it can arise either in a small band gap semiconductor or a semimetal [6]. Below the CDW transition, angle-resolved photoemission spectroscopy (ARPES) experiments point to a small bandgap. However, the normal state indirect band gap is small, and its absolute value (positive or negative) is still under debate [7–15]. The latter proposed CDW mechanism is independent of the free carrier concentration [5], and this cannot account for the incommensurate diffraction spots seen in TiSe₂ [2]. Recent experimental evidence favors the excitonic insulator scenario [8, 35–39], but theories predict that the exciton condensation can either be a superfluid [40], or an insulator [41]. Most recently, Watson *et al.* presented resistivity simulations, assuming a semiconducting normal state [42]. Even without implementing CDW physics, these simulations reproduced the anomalous peak observed in experiments around 150 K. Huang *et al.* [17] showed insulating behavior for their polycrystalline TiSe₂ samples closest to stoichiometry, with metalicity induced by increasing Se deficiency [17], while Campbell *et al.* recently revealed insulating behavior in iodine-free single crystals [18]. Historically though, single crystal samples grown by iodine vapor transport have shown metallic behavior in resistivity [2, 13, 43]. Bearing all of the above in mind, it is essential to reach experimental resolution of the intrinsic ground state of TiSe₂.

One problem faced in studying TiSe₂ is the inconsistency in the physical properties from sample to sample. The temperature-dependent resistivity $\rho(T)$ shows discrepancy between single-crystalline TiSe₂ grown by I₂ vapor transport [2, 13, 43] and polycrystalline TiSe₂, synthesized by solid state reaction [15, 17, 29]. This is illustrated by the normalized $\rho(T)$ data of TiSe₂ in Fig. 4.1. Even though the $\rho(T)$ behavior is qualitatively similar between single-crystalline and polycrystalline samples with a local maximum between 100 and 200 K, at the lower temperatures $\rho(T)$ varies drastically: metallic behavior ($d\rho/dT > 0$) is registered in the single-crystalline sample (dashed line and open circles), explained by either a doped semiconductor picture [42] or partial gapping of the Fermi surface [2], while semiconductor-like behavior ($d\rho/dT < 0$) is found in the polycrystalline sample (solid line). To our knowledge, no systematic study of this discrepancy exists. It is imperative to understand the intrinsic properties of TiSe₂, and the effect of the synthesis conditions on the observed resistivity measurements, before the more complex effects of chemical doping, intercalation, or pressure can be understood.

It is well known that, for $TiSe_2$ single crystals, the transport agent iodine might partially substitute for Se and dope the system [2,13]. Se deficiency also serves as a method of self-doping [44]. Both dopants presumably contribute additional density of states near the Fermi surface and hence enhance the conductivity on cooling. Here, we report systematic variations in the electrical transport properties of polycrystalline $TiSe_2$ (without doping or Se deficiency), as a function of *cooling rate, annealing time*, and annealing temperature. By decreasing the rate at which samples are cooled postsynthesis, an increase in low temperature resistivity is observed. We surmise that the observed logarithmic temperature dependence is due to weak-localization (WL) effects in low dimensional systems. Annealing polycrystalline samples post-synthesis at low temperatures (200°C) has a similar, but less drastic effect. Our results are consistent with a possible intrinsic semiconducting ground state in TiSe₂.

4.2 Methods

4.2.1 A practical guide to making reproducible TiSe₂ samples

Upon starting this study, polycrystalline samples of TiSe₂ were synthesized by solid state reaction with a Ti:Se ratio of 1:2.02. The excess Se was added to compensate for the partial evaporation inherent during synthesis. The samples were sealed in quartz ampoules under partial Argon atmosphere and heated at 50° C/hr to 650° C, followed by a 48 hour dwell at this temperature. After the 24 hour dwell, samples were quenched to room temperature by pulling the ampoules out of the oven. After quenching, samples were pressed into pellets appropriately sized for resistivity measurements and sintered at 650° C for 24 more hours. Then, the pellets were separated into separate tubes where they were annealed at some predetermined temperature for some predetermined time, and again quenched in the same manner.

Upon growing many sets of samples, I realized that depending on a variety of parameters, the resistivity of 'As Grown' samples varied greatly. This lead me down an extensive path to maximize reproducibility. The first experiments I tried were varying the time and temperature of post synthesis annealing. The effect of time and temperature will be discussed in results and discussion, but for now I will focus on empirical



Figure 4.2 : A comparison of experiments for which the surface of the samples were (a) not polished before putting resistivity leads on and example for which samples were (b) polished before attaching leads.

results that lead to reproducible trends. In one experiment where I annealed samples in one day increments at 200°C, I noticed that in general the resistivity increased, but not always. For example, in Fig. 4.2(a) the lowest temperature resistivity decreased between 3 and 4 days before increasing again. Empirically, I was able to get a more consistent trend if I polished the surface of the samples post annealing and before I attached my leads for resistivity measurements.

Knowing that polishing the samples before attaching resistivity leads affected my measurements, I again set out to investigate the temperature and time dependence of post synthesis annealing, this time polishing all my samples. Along the way, I tested whether the thickness of the samples affected the resistivity. Unsurprisingly, it had no affect on the resistivity. I also tested the dependence of how long I kept a sample on my bench in an uncontrolled environment. It seemed overlong periods of time if I left samples out in air with leads attached, the silver epoxy used for attaching leads would react with the sample, so it is recommended to put the samples in a glove box if wanting to store for long periods of time. I also tested whether the lab policy of curing (sparking) the leads by passing a large current through the sample had an affect on the measured 4-point probe resistivity. No significant difference was observed between sparking and not sparking the leads. However, between 'As Grown' samples, samples that had nominally been synthesized in the same way and had no additional annealing procedure performed on them, there was large sample sample to variation Fig. 4.3a. I found that instead of pelleting the samples, and putting them back in the oven for sintering, I instead let the reaction of the loose powder to continue at 650°C for 24 hours such that the total time in the oven was consistent. I then pressed this reacted powder (I first verified it was fully reacted by x-ray diffraction) into pellets with no additional treatment before attaching resistivity leads. Using this method of sample preparation with out sintering the pellets, seemed to reduce the sample variation between batches as show in Fig. 4.3b.

Along the way, I also found out that how fast I cooled samples post-synthesis had a drastic affect on the transport properties of the polycrystalline samples which are covered in the subsequent sections. The optimal methods I used for preparing TiSe₂ samples are outline in Sec. 4.2.2.

4.2.2 Experimental Methods

Polycrystalline samples of $TiSe_2$ were synthesized by solid state reaction with a Ti:Se ratio of 1:2.02. The excess Se was added to compensate for the partial evaporation inherent during synthesis. The samples were sealed in quartz ampoules under partial Argon atmosphere and heated at 50°C/hr to 650°C, followed by a 48 hour dwell at this temperature. Subsequently, the samples were either cooled at different rates, or annealed at different temperatures or different times under partial Argon atmosphere.



Figure 4.3 : A comparison of experiments for which samples were (a) pelleted then sintered, and samples that were (b) not sintered.

TiSe₂ single crystals were grown by chemical vapor transport with I_2 as the transport agent. Ground elemental Ti and Se were sealed in quartz tubes with a ratio of 1:2.02 and 5 mg/cm³ of iodine. The tubes were then placed in a 550°C - 650°C temperature gradient and held for 14 days, followed by controlled cooling to room temperature.

Structural characterization was done using a Bruker X-ray diffractometer with Cu k_{α} radiation. Refinements were performed using the FullProf software package [45]. The quantitative chemical composition was determined by electron probe microanalysis (EPMA) using a JEOL JXA 8530F Hyperprobe located at Rice University, Department of Earth, Environmental and Planetary Sciences, and equipped with a Schottky field emitter and five wavelength dispersive spectrometers. The analytical conditions were set to 15 kV accelerating voltage, 20 nA beam current, and beam spot size (~300 nm). The Se L_{α} and Ti K_{α} X-ray lines were simultaneously measured using counting times of 10 seconds per peak and 5 seconds per each lower and upper background, respectively. Each element was simultaneously measured on two different spectrometers in order to increase the accuracy and the statistics of the measurement. Se L_{α} was analyzed on two TAP diffracting crystals, and Ti K_{α} was analyzed on a PETL and a LiFH diffracting crystal, respectively. The standards used to calibrate the spectrometers were Se metal (Se = 99.9990 wt. %) and rutile (TiO₂, where Ti = 59.9400 wt. %). For quantification, the ZAF matrix correction was used. The error of analysis, determined after analyzing secondary standards is below 2%. The instrumental standard deviation (1 σ) for Se and Ti in each analysis is 0.24% and 0.47%, respectively. The quantitative analyses given in element wt. % were converted to atomic ratios, and then the stoichiometry of the analyzed compound was normalized to one Ti atom.

Polycrystalline samples were pressed into pellets without sintering, and shaped into bars for resistivity measurements. DC electrical resistivity measurements were made in a Quantum Design Physical Properties Measurement System with a standard four-point probe technique for temperatures 2-300 K. The technique described in Ref. [46] was used for resistance measurements with current $i \parallel c$. Hall coefficient measurements were performed at constant temperature for selected temperatures sweeping fields from -9 T to 9 T to extract the Hall resistance.

4.3 **Results and Discussion**

4.3.1 Post synthesis cooling rate r

When trying to improve the quality of crystals (*e.g.* decrease extrinsic disorder), two commonly used techniques for metals are: (i) slow cooling to avoid quenching in disorder, and (ii) post synthesis annealing below the synthesis temperature to relieve microstrain and increase grain size [47]. In the present study, both methods were employed to minimize disorder. By contrast, quenching from high temperature was used to study the effect of enhanced disorder.

The first experiment was dedicated to testing the effect of the cooling rate r post synthesis on the electrical resistivity. Three samples were synthesized as described in the Methods. Sample A was air quenched $(r > 2000^{\circ} C/hr)$, sample B was fast-cooled to room temperature at a rate r~= 20°C/hr, and sample C was slow-cooled at r~=4°C/hr. The scaled semi-log $\rho(T)/\rho(300 \text{ K})$ plot is displayed in Fig. 4.4(a). While all three samples show a nearly 5 time increase in $\rho/\rho(300 \text{ K})$ on cooling to 150 K, the air-quenched sample A displays a broad local minimum centered around 60 K, while both samples B and C exhibit nearly two orders of magnitude resistivity increase down to 2 K. Hall coefficient values (not shown) are negative at low temperatures, consistent with reported data [2, 18]. This rules out the possibility of a change in dominant carrier type as the cause of change in the low temperature resistivity. The large change in the resistivity as a function of cooling rate prompted the need to check sample composition for possible non-stoichiometry. The results of the EPMA analysis, displayed in Table 4.1, indicate that all three samples are stoichiometric (to within a 1% error). This does not rule out that the resistivity changes between the three samples may be due to composition variations below the EPMA resolution limit, or, as discussed below, conductive grain boundaries and WL effects. Room temperature X-ray diffraction data (Fig. 4.5) does not show any measurable change in either the peak position or peak shape among the three samples, consistent with invariable lattice parameters.

When plotting $\rho(T)$ on a semi-log scale (Fig. 4.4(b)), all three samples A-C show a $-\ln T$ dependence of $\rho(T)$ upon cooling below the broad local maximum near 150 K. Since no magnetic impurities are present in any of the samples, the $-\ln T$ increase of ρ cannot be attributed to Kondo or other extrinsic magnetic effects. In TiSe₂, the low dimensionality enhances two quantum corrections to the resistivity: Altshuler-Aronov corrections due to the coherent scattering of electrons by impurity-induced Friedel oscillations [48–50], and WL due to self-intersecting scattering paths [51, 52]. Upon an application of finite transverse magnetic field $H \perp i$, the shape of the magnetoresistance MR = $[\rho(H) - \rho(0)]/\rho(0)$ is insensitive to Altshuler-Aronov cor-



Figure 4.4 : (a) A comparison of the normalized resistivity $\rho/\rho(300 \text{ K})$ as a function of temperature for samples: A, air quenched; B, cooled at 20°C/hr; C, cooled at 4°C/hr. (b) A semi-logarithmic plot of $\rho(T)$. (c) and (d) show the magnetoresistance MR measured at 15 K for the polycrystalline samples A-C and the single crystal, respectively.

Cooling rate $r~(^{\circ}\mathrm{C/hr})$	Se
A: > 2000 (air quench)	2.02 ± 0.01
B: 20	2.01 ± 0.01
C: 4	2.00 ± 0.01

Table 4.1: EPMA results for polycrystalline TiSe₂ with variable cooling rates post synthesis corresponding to Figs. 4.4 and 4.5. Data is normalized to 1 Ti.

rections, while WL can be suppressed in finite magnetic fields leading to a negative MR. Fig. 4.4(c) shows a pronounced peak of MR centered at zero field for samples A-C, which is typical for WL effects. However, the absolute MR values for the different samples reflect not only the WL effects, but also extrinsic effects likely due to the different cooling rates. Therefore, possible explanations for the low temperature increase in resistivity $\rho(T)$ with decreasing r include disorder, or grain boundaries more conductive than TiSe₂. It has been shown that grain boundaries in polycrystalline samples can be conductive [53]. Slow cooling (small r) would be expected to increase grain size, reducing disorder and the number of grain boundaries, and thus increasing the low temperature resistivity.

For comparison, the single crystal sample with iodine inclusions does not show WL behavior either in $\rho(T)$ or in MR (Fig. 4.4(d)). EPMA reveals a 1% iodine impurity per formula unit in the single crystalline samples. In our single crystal sample, the iodine inclusions might dope the system and dominate the transport property which leads to a suppression of WL behavior. A recent electrical transport study on iodine-free TiSe₂ single crystals does show a large increase in electrical resistivity on cooling, qualitatively consistent with what is seen in our polycrystalline Samples B and C [18]. It will be informative to investigate the magnetic field effects on the transport properties in these iodine-free single crystals to quantitatively analyze the characteristic parameters from the WL correction. The WL effect noted here for the first time in TiSe₂ had been previously reported in another TMDC, VSe₂ [54].



Figure 4.5 : Room temperature powder X-ray diffraction patterns for the polycrystalline samples (symbols), with refinements shown as solid black lines, and the difference between measurement and calculation shown in red. The vertical marks below each pattern correspond to the calculated peak position for TiSe₂. Inset: a zoomed in view of all three of the measured patterns plotted.

Cooling samples slowly after synthesis was expected to decrease the extent of disorder in the crystals and increase the average grain size. In an attempt to characterized disorder, we turn again to the X-ray refinements. There are at least four contributions to peak width in powder X-ray diffraction [47]: instrumental broadening, thermal vibrations, grain size, and microstrain. Instrumental broadening is a function of beam optics and geometry. Thermal vibrations increase the peak width with increasing temperature. Peak width increases with reduced grain size and increasing microstrain. No variations in the X-ray peak widths are measured in the current pollycrystalline samples (inset of Fig. 4.5). Differential instrumental or thermal peak broadening can be ruled out, since all samples were prepared and measured at room temperature on the same instrument. Because all peaks are of similar width, no difference due to grain size or microstrain can be resolved between samples A, B and C.

4.3.2 Post synthesis annealing time t

The next set of experiments focuses on the effect of annealing time t. Different pieces of sample A were annealed at T = 200°C, for times t ranging from 1 to 6 days, followed by air quenching. The low anneal temperature was chosen to relieve quenched-in disorder without adding more disorder from quenching at a high temperature. Resistivity shows a general upward, albeit small trend at low temperatures for increasing t (Fig. 4.6a). As before, no change is recorded in the X-ray peak width and lattice parameters (not shown). By comparison with the cooling rate r (Fig. 4.4 and Table 4.1), the change in the low temperature resistivity is much smaller when varying the annealing time t at T = 200°C: at the lowest measured temperature, the relative change in ρ as a function of r (Fig. 4.4) is $\rho_C/\rho_A \sim 30$, even for stoichiometry changes less than 1% (Table 4.1). The corresponding change in ρ at low temperature with annealing time t (Fig. 4.6) is $\rho(6days)/\rho_A \sim 1.5$ with larger composition variation (Table 4.2). The latter reinforces the idea of the possibly intrinsic semiconductor state in TiSe₂, which is approached with longer annealing. Conversely, the role of stoichiometry variations, while unclear, appears to be minimal compared to the disorder and WL effects.

A similar study with anneal time was done on single crystals. The normalized $\rho(T)$ is plotted in Fig. 4.6b. Annealing did not change the low temperature transport properties when compared to the polycrystalline samples. EPMA studies looking for only Ti and Se show all similar ratios as seen in Table 4.2. However, as stated earlier, EPMA measurements reveal iodine inclusions around 1% in single crystals for which the Ti:Se ratio is found to be 1:2. The additional density of states near the Fermi energy due to iodine accounts for the metal-like low temperature electrical transport down to 2 K in single crystalline TiSe₂.

4.3.3 Post synthesis annealing temperature T

The next experiment aims to purposefully induce disorder into the TiSe₂ by quenching, followed by annealing at different temperatures T. Different single crystal pieces were annealed for 2 days at different temperatures T between 200 and 1200°C. After annealing, all samples were quenched. Normalized $\rho(T)$ data is plotted in Fig. 4.7.

For anneal temperatures T below the growth temperature $T_{growth} = 650^{\circ}$ C (triangles, Fig. 4.7(a)), the low temperature resistivity of the polycrystalline samples increases compared to that of the as-grown sample, much the same as the result shown in Fig. 4.6(a). For anneal temperatures at (square) or above (star) the synthesis temperature, the low temperature resistivity decreases. However, below 20 K the resistivity increases on cooling for all annealing temperatures T. Our EPMA data



Figure 4.6 : (a) Comparison of polycrystalline $\rho/\rho(300 \text{ K})$ for TiSe₂ samples annealed at 200°C in one day increments up to six days. With increase in anneal time, the low temperature resistivity increases. (b) The same comparison for TiSe₂ single crystals. The low temperature resistivity is dominated by iodine impurities.

shows no systematic loss of selenium with increased anneal temperature (Table 4.3), whereas X-ray diffraction patterns (Fig. 4.8) indicate significant peak broadening for samples quenched from 1200°C (star) indicating microstrain caused by quenching at such a high temperature. Though there are small variations in lattice parameters, the variations are less than 0.1% of the as grown (upwards triangle), so the change in resistivity is not due to a change in the unit cell.

For comparison, analogous data is shown in Fig. 4.7(b) for TiSe₂ single crystals. Besides the differences in low temperature resistivity, which can be explained



Figure 4.7 : (a) A comparison of normalized $\rho(T)$ for polycrystalline TiSe₂ samples annealed at different temperatures post synthesis. For anneal temperatures below the growth temperature, there is an increase in normalized $\rho(T)$, while at higher temperature anneals, their is a decrease in low temperature normalized $\rho(T)$. (b) The corresponding study for single crystals.

by iodine impurities, the normalized $\rho(T)$ shows qualitatively similar features as the polycrystalline samples. The trend of decreasing peak height below the CDW transition is qualitatively similar to that previously attributed to non-stoichiometry or disorder, or both [2, 35]. Though a Se deficiency is seen in the sample annealed at 1200°C, the polycrystalline counterpart suggests that the decrease in the anomaly height is not due to doping, but rather an increase in quenched disorder. Remarkably, the 1200°C single crystal (star, Fig. 4.7(b)) shows metallic behavior for the whole temperature range, and no anomaly in $\rho(T)$. Consistent with the observations of the



Figure 4.8 : Zoomed in comparison of X-ray patterns for different anneal temperatures. At 1200°C there is an increase in disorder from microstrain as evidence by severe broadening of the peaks.

most substantive structural changes at this temperature (Fig. 4.8), this signals that self doping, disorder, grain boundary freezing, or more, inhibit the plausible intrinsic semiconducting behavior of $TiSe_2$ at excessively high annealing temperatures.

In summary, our results on polycrystalline $TiSe_2$ are consistent with this system being a small band gap semiconductor at low temperatures. When synthesis conditions favor disorder, the semiconducting behavior is concealed by enhanced metallicity. Though all polycrystalline samples in the current study are close to stoichiometry, the small band gap causes even the smallest deviations from the 1:2 stoichiometry to add impurity states, which, in turn, affect the low temperature transport. These impurity states become localized at low temperature, resulting in a logarithmic increase of the resistivity on cooling rather than the exponential increase expected from an activated gap. These observations are consistent with transport in polycrystalline $TiSe_2$

Anneal t	Polycrystal	Single Crystal
(days)	Se	Se
As Grown	2.00 ± 0.02	2.013 ± 0.02
2	2.03 ± 0.02	
3	2.03 ± 0.03	2.017 ± 0.02
4	2.01 ± 0.02	
5	1.98 ± 0.02	
6	2.00 ± 0.03	2.012 ± 0.02

Table 4.2 : Se normalized to 1 Ti in $TiSe_2$ samples annealed at 200°C in one day increments up to six days corresponding to Fig. 4.6.

Anneal $T~(^{\circ}\mathrm{C})$	Polycrystal	Single Crystal
	Se	Se
As Grown	2.00 ± 0.02	2.013 ± 0.007
200	2.03 ± 0.05	
400	2.02 ± 0.04	2.04 ± 0.01
650	2.026 ± 0.006	2.05 ± 0.01
1200	2.03 ± 0.02	1.882 ± 0.007

Table 4.3: EPMA results for TiSe₂ samples annealed for 2 days at variable temperatures corresponding to Fig. 4.7.

emerging from both semiconductor physics and localization physics, more commonly discussed in disorder metals.

4.4 Conclusions

We have systematically studied the effects of the cooling rate r, and temperatureand time-dependence T and t of post-synthesis annealing on the observed electrical transport properties of TiSe₂. For the first time, the weak-localization effect is found in polycrystalline TiSe₂ samples, embodying the quantum corrections to the electrical transport properties in low dimensional systems. At low temperatures results on polycrystalline TiSe₂ are consistent with a small gap semiconductor behavior, with low temperature $\rho(T)$ and MR dominated by the weak localization effect due to residual impurities. This study is intended to serve as a guide in the synthesis of TiSe₂, by pointing out the intrinsic and extrinsic properties as a function of the preparation method.

Chapter 5

Outlook

While I have identified synthesis conditions that systematically vary the electrical transport properties measured in $TiSe_2$, it has been hard to pin point the microscopic mechanism responsible for such variations. Since all samples were very close in stoichiometry, I hypothesize that some of the variation may come from local structural disorder. While powder x-ray diffraction is only sensitive to the average global structure, pair distribution function analysis, a total scattering technique is indeed sensitive to local structure. To further investigate the role of local disorder in $TiSe_2$, we have applied for beam time to study the local structure of $TiSe_2$ samples that vary most in transport.

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