CHARGE DENSITY WAVE INCOMMENSURATION IN TISE$_2$ SYSTEMS MEASURED WITH HARD X-RAY SCATTERING

BY

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DISSEbATION

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Abstract

Unconventional superconductivity cannot be understood independently of the phases that order around it. Characterizing the charge order in modulated superconductors provides essential information that could reveal a common underlying mechanism. We performed low temperature experiments on 1T-TiSe$_2$ crystals tuned by three parameters: pressure, copper intercalation, and sulfur substitution. Resistivity measurements revealed a previously unreported superconductive phase in sulfur substituted samples. Our hard x-ray diffraction experiments determined that the charge order phase does not terminate inside the superconductive phase of these systems, as was formerly believed. The phase diagrams established in this work suggest that incommensurations of the charge density wave could play a role in the emergence of superconductivity.
To my Mother.
I would first like to thank my adviser Peter for his patience, guidance, and support throughout my time as a graduate student. I was extremely lucky to be a member of the friendliest research group in the most amicable physics department.

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# List of Abbreviations

<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CO</td>
<td>Charge order</td>
</tr>
<tr>
<td>SO</td>
<td>Spin order</td>
</tr>
<tr>
<td>SC</td>
<td>Superconductivity</td>
</tr>
<tr>
<td>TMDC</td>
<td>Transition metal dichalcogenide</td>
</tr>
<tr>
<td>BCS</td>
<td>Bardeen Cooper Schrieffer</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical Property Measurement System</td>
</tr>
<tr>
<td>CDW</td>
<td>Charge density wave</td>
</tr>
<tr>
<td>TDS</td>
<td>Thermal diffuse scattering</td>
</tr>
<tr>
<td>DC</td>
<td>Discommensuration</td>
</tr>
<tr>
<td>C-CDW</td>
<td>Commensurate charge density wave</td>
</tr>
<tr>
<td>I-CDW</td>
<td>Incommensurate charge density wave</td>
</tr>
<tr>
<td>QCP</td>
<td>Quantum critical point</td>
</tr>
<tr>
<td>CHESS</td>
<td>Cornell High Energy Synchrotron Source</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
<tr>
<td>DAC</td>
<td>Diamond anvil cell</td>
</tr>
<tr>
<td>MCA</td>
<td>Multi channel analyzer</td>
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<tr>
<td>SCA</td>
<td>Single channel analyzer</td>
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Chapter 1

Introduction

1.1 Context

Antiferromagnetism, ferromagnetism, and superconductivity are well-known physical phenomena that arise from interactions between electrons in solids. Charged particles in these phases of matter cannot be treated as independent entities, one must consider their correlated behavior. Understanding strongly correlated systems comprises one of the central problems in condensed matter physics.

Complex phase transitions result from the interplay between charge, spin, orbital, or structural degrees of freedom in these materials. Phase diagrams of strongly correlated materials can exhibit exotic phases of matter, like charge order (CO), spin order (SO), and superconductivity (SC). These phases often coexist in the phase diagrams, and their order parameters can compete, cooperate, or correlate in a complex manner.

Unconventional superconductors are strongly correlated systems lacking a complete microscopic picture of their phenomena. The Bardeen Cooper Schrieffer (BCS) theory of superconductivity written in 1957 [1] describes only a subset of the superconducting materials known today. Since the discovery of the cuprates in 1986 [2], many compounds surpassing the BCS $T_{SC}$ threshold have been found. Several families of non-BCS superconductors have been established as well. Currently, the unconventional SCs cataloged are more numerous than those described by the BCS theory.

Unconventional superconductors, nonetheless, have properties in common. In terms of their crystal structure, these materials are layered. Experiments on single layers of these compounds have found that their transition temperatures can change drastically compared to their bulk counterparts [3]. SC in these systems is usually found near another ordered phase. Antiferromagnetism, spin order, and charge order are often found within the pseudogap region that overlaps with superconductivity. We know that unconventional SCs have a qualitatively similar phase diagram, but the pseudogap region is not well understood. Characterizing the phases of the pseudogap, how they compete, cooperate, and order, is essential to reveal the underlying mechanism that gives rise to superconductivity.
This work concerns the correlations between superconductivity and charge order in pressure, Cu-intercalation, and S-substitution phase diagrams of 1T-TiSe$_2$.

1.2 Peierls Transition and the Charge Density Wave

Though a charge density wave strictly means a periodic modulation to the electronic structure of a crystal, and can form through different mechanisms [4] [5] [6] [7], a good first approach is to associate it to a Peierls transition [8]. We consider a one dimensional lattice of spacing $a$ and a half filled conduction band (figure 1.1). If the Fermi surface couples with the lattice, it is possible to lower the energy of the system by dimerizing the lattice. This energy lowering is a consequence of a gap forming near $k_F$. Of course, there is an energy cost to distorting the lattice, a charge density wave forms only when energetically favorable. This distortion is a metal to insulator transition.

![Figure 1.1: One dimensional lattice dimerizing after a Peierls transition. The band structure folds and a gap opens at the Fermi energy.](image)

Linear response theory applied to a free electron gas is a simple approach to the problem. An external, space dependent, potential $V_{ext}(r)$ couples to the charge density $\rho(r)$ through an interaction term:

$$H' = \int d^3r V_{ext}(r)\rho(r)$$

(1.1)

This interaction can be treated perturbatively, and $H'$ can be turned on adiabatically from $t = -\infty$. The time evolution of our charge order is given by:

$$\rho(t) = U^\dagger(t)e^{\beta(\Omega-H)}U(t)$$

(1.2)
Where $U(t) = \tau \exp[-\frac{i}{\hbar} \int_0^t dt (H + H')]$ and $\Omega$ is the free energy. To linear order of the potential $V_{\text{ext}}$, the expectation value of the charge order is:

$$
\langle \rho \rangle = \lim_{\eta \to 0} \left( -\frac{i}{\hbar} \right) \int d^r V_{\text{ext}}(r) \int_{-\infty}^0 d't' e^{\eta t'} \langle |\rho(r, t), \rho(r', t')| \rangle_0
$$

(1.3)

The averaged terms on the right of this equation is the density-density correlation function, or the linear electronic susceptibility:

$$
\chi(r, r', t, t') = -\frac{i}{\hbar} \theta(t-t') \langle |\rho(r, t), \rho(r', t')| \rangle_0
$$

(1.4)

If we extend $t \to \infty$ to take care of the step function, we get:

$$
\langle \rho \rangle = \lim_{\eta \to 0} \int d^r V_{\text{ext}}(r) \int_{-\infty}^\infty d't' e^{\eta |t'|} \chi(r, r', t, t')
$$

(1.5)

The susceptibility measures how strongly the charge order responds to the external potential.

If we neglect interactions between the electrons, and assume a static potential (a static lattice distortion), it can be shown that:

$$
\chi(q, \omega = 0) = \sum_k \frac{N_F(\epsilon(k)) - N_F(\epsilon(k + q))}{\epsilon(k) - \epsilon(k + q)}
$$

(1.6)

Stable excitations of the system happen at values of $q$ where the susceptibility diverges. If these happen at $\omega = 0$ then the excitations compete with the ground state. Moreover, if they happen at $q \neq 0$, the excitations form a periodic charge modulation, breaking the translational symmetry.

In a one dimensional lattice, the static response function reads:

$$
\chi(q) = -\frac{e^2 m}{\pi \hbar^2 q} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right|
$$

(1.7)

It is immediately evident that this function diverges at $q = 2k_F$. The charge density response to $V_{\text{ext}}$ is infinitely strong. Any potential will rearrange the electronic density at $q = 2k_F$ and form a CDW. This is only true, however, for a 1-dimensional system; the divergence disappears for higher dimensions (figure 1.2). Nonetheless, states near the Fermi energy dominate the behavior of the correlation function. If enough states make the denominator in equation 1.6 vanish at for same wave vector $q$, the system can form a charge density wave. This nesting happens when segments of the Fermi surface are parallel and can be connected by a single $q$ vector (see, for example [9]).
1.3 Transition Metal Dichalcogenides and TiSe$_2$

Transition metal dichalcogenides (TMDC) are compounds of the form TX$_2$, where T is a transition metal atom and X$_2$ two atoms of the chalcogen family in the periodic table (S, Se, or Te) [10]. TMDCs can form layered or non-layered structures. Group IV-VII generally form tri-layered planes of X-T-X, where the transition metal is sandwiched between two chalcogen layers. They feature a hexagonal lattice which can extend to one, two, or three tri-layers, forming the three common polytypes labeled 1T, 2H, 3R, respectively. Strong bonds within the crystal planes dominate, while the planes are held together by weak van der Waals forces [11].
A reduced dimensionality gives rise to complex phase diagrams in these materials. 1T-TaS$_2$ and 1T-TaSe$_2$ show incommensurate $\sqrt{13} \times \sqrt{13}$ CDWs that become commensurate at low temperature [12] [13]. 2H-TaSe$_2$ and 2H-NbSe$_2$ exhibit a $3 \times 3$ superlattice with an incommensurate to commensurate transitions, the latter shows superconductivity below 7 K. 2H-TaS$_2$ also shows phases of charge order, SC, and a Mott state [14] [15].

1T-TiSe$_2$ is a TMDC that hosts a 2x2x2 charge density wave below 202 K. A schematic representation of the distortion is shown in figure 1.4. The origin of the CDW transition in this material has remained controversial. In contrast with the rest of the dichalcogenides that exhibit charge order, TiSe$_2$ transitions into a commensurate CDW directly, without passing through an intermediate incommensurate state. Many different speculations about the mechanism behind the transition have been made: anisotropic electron-phonon coupling, Fermi surface nesting, Jahn-Teller distortions, and an excitonic effect [16] [17] [18]. The semi-metallic character of the bands is emphasized as well as the importance of electron-hole couplings.

Moreover, TiSe$_2$ hosts a superconductive phase that emerges as charge order is suppressed by Cu-intercalation [19] or hydrostatic pressure [20]. Phase diagrams of the system as a function of these parameters are shown in figure 1.5. These diagrams were established through resistivity measurements, which only indirectly measure the charge order transition. To probe this order directly, we perform x-ray scattering measurements.
Figure 1.4: Periodic lattice distortion in three TMDCs (top) and their corresponding Brillouin zones (bottom). TiSe$_2$ forms a $2 \times 2 \times 2$ superlattice [17].
Figure 1.5: Charge order phase diagrams of TiSe₂ constructed by resistivity measurements. Left: Phase diagram of copper intercalated TiSe₂. SC emerges as the CDW is suppressed with increasing Cu content [19]. Open circles mark the resistive anomaly associated with charge order, closed circles mark region of SC. Right: Phase diagram of TiSe₂ under pressure. Pressure suppresses the CDW and allows the existence of a superconductive phase at low temperature [20]. Blue squares on the top panel mark the increase in resistivity related to the CDW transition, green points mark the superconductive temperature, and red squares mark the residual resistivity at low temperature (right axis). Bottom panel shows the pressure dependence of the thermal exponent of the resistivity.
1.4 Incommensurate CDW

An important observation in this work was the appearance of an incommensurate charge density wave in the phase diagrams of TiSe$_2$. The charge order in pure TiSe$_2$ crystals is always commensurate. After the system is sufficiently tuned by pressure or doping, however, it transitions first to an incommensurate CDW phase before “locking in” to commensurate CDW as the sample is cooled down.

McMillan presented this commensurate-incommensurate phase transition in 2H-TaSe$_2$ using a Landau theory framework [21] [22]. He proposed the incommensurate phase’s spatial form consisted of commensurate regions separated by “phase-slips”, regions he called discommensurations (DCs). It is the average wavelength of the CDW that is incommensurate with the lattice. This picture was later confirmed by NMR [23], and electron microscopy [24].

The transition is second order, the discommensurations continuously melt with no DCs in the commensurate phase and a finite number of them in the incommensurate phase. The free energy if the $l$th layer of the dichalcogenide has the form:

$$F_l = \int d^2 r \left( a\alpha_l^2 - b\alpha_l^3 + c\alpha_l^4 + d(|\psi_{l1}\psi_{l2}|^2 + |\psi_{l2}\psi_{l3}|^2 + |\psi_{l3}\psi_{l1}|^2) + e \sum_i |(\vec{q}_i \cdot \vec{\nabla} - i\vec{q}_i^2)\psi_{li}|^2 + f \sum_i |\vec{q}_i \times \vec{\nabla} \psi_{li}|^2 \right)$$

(1.8)

Where

$$\alpha(\vec{r}) = \text{Re}[\psi_{l1}(\vec{r}) + \psi_{l2}(\vec{r}) + \psi_{l3}(\vec{r})]$$

(1.9)

contains three order parameters $\psi_{li}(\vec{r})$ representing the three coexisting CDWs in a layer. McMillan looks specifically at the 2H-TaSe$_2$ system, where $|q_{cdw}|$ is 2% less than $\frac{1}{3}K$, the I-CDW wavelength is longer than the C-CDW. In terms of the free energy above, the cubic “umklapp” term, proportional to $b$, lowers the energy when the CDW is locked-in. This term is opposed by the gradient term proportional to $e$, which is a minimum at $q_{cdw}$. Nonetheless, the free energy of the incommensurate phase can be lowered by distorting the plane wave and making use of the cubic term. We keep the wavelength of the incommensurate CDW 2% longer if it is in phase for 25 lattice spacings, then out of phase for the next 25. This makes the umklapp term negative for the in-phase region and positive in the out-of-phase region. It averages out to zero, but we can take advantage of this if we modulate the CDW order parameter (which has the form $\psi = Ae^{i\theta}$). We can modulate its amplitude, making it larger in the in-phase region. We could also modulate its phase, making the in-phase region (domains) larger and the out-of-phase region small (domain walls). It costs much less energy to create a phase distortion than an amplitude distortion.
Simplifying the problem by setting $\psi_2 = \psi_3 = 0$ (considering a single CDW in the layer), McMillan is able to write the difference in the free energy between the commensurate and the incommensurate state as:

$$\Delta F = F^0 \beta \int d^2 s \left( Y \left[ 1 - \cos(3\theta) \right] + (\nabla \theta - 1) \right)$$  \hspace{1cm} (1.10)

where $Y$ contains the temperature dependence and $\theta(x)$ is the phase of the renormalized CDW order parameter $\phi(x) = e^{-i \theta(x)}$. Making the ansatz

$$\theta(x) = \delta x + \sum_{n=1}^{N} A_n \sin(3n\delta x)$$  \hspace{1cm} (1.11)

where $\delta$ and $A_n$ are variational parameters, he minimizes the free energy difference in steps. First at fixed $\delta$ and $Y$ with respect to $A_n$. Then with respect to $\delta$ to find the optimal wavelength at for a fixed temperature. $\delta$ goes continuously to zero at $Y_c$, which establishes the incommensurate to commensurate transition temperature. The function $\theta(x)$ that minimizes $\Delta F$ obtained for $\delta = 0.2$ near the lock in temperature is shown in figure 1.6. The phase slips as a function of position are evident.
Chapter 2

Theoretical Aspects of X-ray Scattering

2.1 X-ray Scattering Theory

This section comprises essential concepts to understand x-ray scattering from a crystal.

2.1.1 Defining the Cross-Section

Theory and experiment converge at the x-ray scattering cross-section. It is important to clearly define this quantity.

We are interested in measuring the number of x-ray photons scattered from our sample into our detector. This quantity is the scattered intensity $I_{sc}$, and it is measured in counts per second. Given a direct beam with an intensity $I_0$, a sample with $N$ particles, and a detector occupying a solid angle of $\Delta \Omega$, we can crudely express the scattered intensity as:

$$I_{sc} = I_0 N \Delta \Omega \left( \frac{d\sigma}{d\Omega} \right)$$

(2.1)

Where the quantity in parenthesis is the differential cross-section. $(d\sigma/d\Omega)$ is a measure of how efficiently radiation is scattered off the particles in our sample.

We can now also define the absorption cross-section. Through this quantity we can describe the change of intensity of the direct beam when placing a sample in the path of the incident beam that directly falls into our detector. As in the scattering case, the number of absorption events, $W_{4\pi}$, is proportional to $I_0$ and $N$. The absorption cross-section is defined as:

$$\sigma_a = \frac{W_{4\pi}}{I_0 N}$$

(2.2)

The subscript in $W_{4\pi}$ notes that the photoelectrons ejected in the absorption process can be emitted into any direction in $4\pi$ steradians.

Finally, if the sample is smaller than the incident beam, then we use $\Phi_0$ rather than $I_0$. $\Phi_0$ is the flux of
the incident beam; the number of photons per second per unit area. The scattered intensity becomes:

\[ I_{sc} = \Phi_0 \Delta \Omega \left( \frac{d\sigma}{d\Omega} \right) \]  \hspace{1cm} (2.3)

where the differential cross-section concerns the whole sample, and the absorption cross-section is given as:

\[ \sigma_a = \frac{W_{4\pi}}{\Phi_0} \]  \hspace{1cm} (2.4)

The experiments constituting this document were performed at different conditions in terms of beam spot size, sample size, and flux. The spot size at CHESS was smaller and more uniform than the one of our source in Urbana. At the synchrotron, we use a gas chamber to measure and then normalize our scattered intensities to the intensity of the direct beam. We assume a constant direct beam in our lab, normalizing only to exposure times. Our samples vary size and thickness. For some the pressure experiments at UIUC, the samples were smaller than our beam spot. Additionally, to reproducibly place the beam in the cell, we maximized the intensity of the transmitted beam. This does not necessarily align the sample and the cross-sectional area of the beam. This experimental consequences make it difficult to normalize the scattered intensities between different samples. The definitions above are fully applicable, however, in the experimental analysis.

2.1.2 Scattering

Classically, an x-ray scatters off an electron by exerting a force on a charged particle, which then accelerates and radiates the scattered wave. The energy of the emitted radiation and the incident radiation is the same for elastic scattering, or Thomson scattering. Compton scattering concerns inelastic scattering processes, in which some energy is transferred to the electron and the scattered x-ray photon has a lower energy than the incident one. Since this investigation concerns the structure of materials, and elastic processes dominate in scattering, we can limit our approach to a classical one that deals only with elastic interactions.

2.1.3 Interaction Between Light and Matter

Scattering of light happens when the electromagnetic wave interacts with particles in the solid. The light mass of the electron makes its interaction with x-ray photons much stronger than that of x-rays and other charged particles. The coupling term in the Hamiltonian is obtained by replacing \( p_i \) in the free electron Hamiltonian \( H_0 = \sum_i p_i^2 / 2m \) with \( p_i - e \tilde{A}(r_i, t)/c \). The interaction term is
\[ H_{int} = \sum_i \left( -\frac{e}{mc} p_i \cdot \hat{A} + \frac{e^2}{2mc^2} \hat{A} \cdot \hat{A} \right) \] (2.5)

and the quantized electromagnetic field can be expressed as

\[ \hat{A}(r, t) = \sqrt{\frac{2\pi \hbar c}{V}} \sum_{i,k} \frac{1}{\sqrt{k}} e_i \left( a_{k,i}(t)e^{ik \cdot r} + a_{k,i}^\dagger(t)e^{-ik \cdot r} \right) \] (2.6)

where \( a \) and \( a^\dagger \) are the photon annihilation and creation operators. The first term in the interaction Hamiltonian is linear in these operators, thus responsible for single photon absorption and emission processes. The second term in the Hamiltonian is quadratic in the operators; it can change the number of photons by 0 or \( \pm 2 \).

**Form Factor**

Scattering x-ray light from a given site \( n \) in a lattice is described in terms of the form factor \( f_n \). This quantity can be written as

\[ f_n = f_n^T + f_n^M + \Delta f_n' + i\Delta f_n'' \] (2.7)

The first two terms correspond to non-resonant charge and magnetic scattering. \( f_n^T \), is Thomson scattering; proportional to the number of electrons in the scatterer. The last part of the expression, \( \Delta f_n = \Delta f_n' + i\Delta f_n'' \) is the dispersion correction, a quantity that depends on the photon energy \( \hbar \omega \) and the polarization of the incoming and scattered beam. The dispersion correction describes the resonant scattering and becomes important near the absorption edges of the scatterer.

\( f_n \) represents the change in phase and amplitude on the incident wave during the scattering process. A plane wave \( \propto e^{ik \cdot r} \) becomes \( \propto f_n e^{ik \cdot r} \) after interacting with a scatterer.

**Kramers-Heisenberg Formula**

Consider the scattering of a single photon with wave vector \( k \) and polarization \( e \) from a lattice in the initial state \( |G\rangle \). After the event, the photon has a wave vector \( k' \) and polarization \( e' \). For elastic scattering, the lattice must remain in \( |G\rangle \). Scattering is a photon-in photon-out process, therefore the contributions to \( H_{int} \) must contain one annihilation and one creation operator.

The first order terms in interacting Hamiltonian are given by the matrix element \( M_1 = \langle G, k', e'|H_{int}|G, k, e \rangle \).

Only the term proportional to \( \hat{A} \cdot \hat{A} \) contributes to \( M_1 \) because it is the only term in the Hamiltonian containing products of the \( a \) and \( a^\dagger \) which do not change the number of photons.

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The $p \cdot \hat{A}$ term does not contribute to $M_1$, but it must be considered in second order perturbation theory. The second order matrix element $M_2$ includes two successive $p \cdot \hat{A}$ interactions. The dominant contributions to $M_2$ come from processes where an incoming photon is annihilated first and then the scattered photon is created passing through an intermediate state $|I\rangle$ in between, that is $M_2 \sim \langle G, k', e' | (p \cdot \hat{A})^\dagger | I \rangle | p \cdot \hat{A} | G, k, e \rangle$.

The scattering cross section can be derived from $M_1$ and $M_2$ as:

$$\frac{d\sigma}{d\Omega} = r_0^2 |e \cdot e' \langle G | \rho(Q) | G \rangle - m \sum_l \frac{\langle G | e' \cdot J(k') | I \rangle \langle I | e \cdot J(k) | G \rangle}{E_I - E_G - \hbar \omega - i\Gamma_I/2} |^2$$

where $r_0$ is the classical electron radius, $\rho(Q)$ is the Fourier amplitude at the momentum transfer vector $Q = k' - k$ of the charge density, $E_G$ and $E_I$ are the energy of the ground and intermediate states, $\Gamma_I$ is the life time of the intermediate state, and $J(k) = 1/m \sum_i p_i e^{ik \cdot r_i}$ is the current operator describing transitions between the states.

The equation for the cross section above is the Kramers-Heisenberg Formula. It is related to the form factor by $d\sigma/d\Omega = |f|^2$. Therefore, we have an expression for $f_n$. The first term in the K-H equation corresponds to Thomson scattering from the first order matrix element. $f^T$ is a non-resonant effect that depends on the total number of electrons in the scatterer. The second term in the K-H formula is the dispersion correction $\Delta f$. It is due to the $M_2$ matrix element and corresponds to resonant-scattering.

**Scattering from a Crystal**

A crystal is a highly ordered periodic arrangement of atoms. The scattering of x-rays of wavelength $\lambda$ from a crystal lattice is in its most basic form governed by Bragg’s law:

$$2d \sin(\theta) = n\lambda$$

where $d$ is the distance between lattice planes, $\theta$ the angle of incidence, and $n$ is an integer. While immensely useful, this is just a condition for constructive interference between two scattering waves of light, it lacks intensity information at the Bragg condition.

We need information about the scattering amplitude of a crystal. We take a lattice of unit vector $R_m$ and atomic positions $r_n$ within each lattice site, so that the position of any atom of the crystal is found by $R_m + r_n$. The scattering amplitude of a crystal is then:
\[ F(Q) = \sum_j f_n(Q) e^{iQ \cdot r_n} \sum_n e^{iQ \cdot R_m} \] (2.10)

Where the term for the form factor has been reduced from \( f_n(\hbar \omega, e, e', Q) \) to \( f_n(Q) \) for Thompson scattering, and is independent of the position of the atoms in real or momentum space. The first term in equation 2.10 is the unit cell structure factor describing the interference of particles within a unit cell, the second term is a sum over the lattice sites of the crystal. \( e^{iQ \cdot r} \) is the relative phase of scatterers in a unit cell.

The scattering amplitude is related to the cross section, and the scattered intensity as:

\[ I_{sc} \propto \left( \frac{d \sigma}{d \Omega} \right) = |F(Q)|^2 \] (2.11)

which is the measured quantity in our experiments.
Chapter 3

Experimental Procedures

3.1 Crystal Growth

Our role in the experiment begins at the samples’ origin. All the varieties of TiSe$_2$ were grown by the Chemical Vapor Transport (CVT) method. The Cu-doped series of crystals were grown by the Goran Karapetrov group at Drexel. We grew pure TiSe$_2$ for the pressure measurements and TiSe$_{2-x}$S$_x$ for the S-substitution measurements at our home institution. This section explains the procedures we followed to obtain our crystals.

We start from pure powders of titanium, selenium, and sulfur, and weigh them inside an argon glove box. The powders’ weight correspond to the desired stoichiometry, and we measured 1 gram total of powder. Given that the molecular weights of Ti, Se, and S are 47.867 g/mol, 78.96 g/mol, and 32.065 g/mol respectively, to grow $x = 0.05$ TiSe$_{1.95}$S$_{0.05}$, for example, we use:

- Ti = 235.285 mg
- Se = 756.834 mg
- S = 7.881 mg

Once properly weighed, we proceed to mix and grind the powders using a mortar and pestle. This mixture is then compressed into a small 1/4 inch pellet by a hydraulic press. The pellet is placed into a graphite crucible that prevents Se sublimation while close to a flame used during the steps involving glassblowing. We put the crucible inside a small open ended quartz tube. The tube should be long, it must hold the length of the crucible and allow space above it for sealing. Next, we place a Swagelock valve on the open end of the tube, close the valve, take the setup out from our argon environment, and attach it to a vacuum station. We pump out the Ar gas to a pressure of about 100 mTorr. We now take a blowtorch and seal the tube. Figure 3.1a shows our preparation at this point. The closed tube is placed inside a 720 K furnace, where the Se, Ti, and S powders prereact for 48 hrs. This process yields TiSe$_{2-x}$S$_x$ powder.

After the prereaction, the quartz tube is carefully broken inside the Ar glove box. The crucible is opened and the remains of the pellet are pulverized once more between a mortar and pestle. We then transfer the
powder into 18 cm long, 1 cm inner radius, quartz tubes. 1.4 mg/cm$^3$ of iodine is added (or 80 mg for the volume of our container). We close the open end of the tube using a valve, evacuate, and seal the glass with a blowtorch as done above. Careful handling of the tube must be observed; most of the TiSe$_{2-x}$S$_x$ powder should remain near one end when we put the tube in the middle of a two-zone furnace. This type of furnace creates a temperature gradient, allowing the iodine vapor transport to take place. TiSe$_2$ crystals will grow in the cooler part of the oven, the powder side of the tube should be kept at a higher temperature. We grew successful batches using a 680-780 °C gradient. We applied a reverse temperature gradient for 1 day to clean the crystal side of any powder. After that, we applied the correct gradient and waited 10 days for completion of the growth.

If everything went well TiSe$_2$ crystals will form inside the tube (fig. 3.1b). We then carefully crack the glass and extract the samples.

Notes on Growths and Nomenclature

Each growth is unique in its own way. Following identical procedures will rarely result in identical batches in terms of crystal size and thickness. Some small variations in the growths cannot be controlled for: nucleation sites, small deformations on the glass vials, small variations in pressure, sublimation while blowtorch sealing, temperature differences inside the furnaces, loss of material while transferring. It may be possible to avoid these and other small differences between batches, but given limited financial and temporal resources, it is not practical. When we can control only so many parameters, repetitions and failures become part of the process.

It is necessary to clarify the meaning of $x$, or the doping of the sample. $x$ has a different meaning in a
Cu-intercalated sample than in a S-substituted sample. Cu intercalates between Se-Ti-Se layers, presumably not affecting the amount of titanium nor selenium. Thus, an $x$ value of 1 indicates a 1-1-2 Cu-Ti-Se ratio; a total of 4 atoms that changes with the amount of copper. On the other hand, S substitutes Se in TiSe$_{2-x}$S$_x$, and an $x$ value of 1 corresponds to a 1-1-1 S-Ti-Se ratio. This total of 3 atoms is invariant with $x$ since we subtract Se when we add S. We must apply this information to correctly calculate the proportions of powder needed to attain the desired $x$ of a growth, and to compute $x$ after sample characterization measurements.

Interchanging “$x = 0.04$” and “4% doped” is common in the Cu$_x$TiSe$_2$ literature. A 4% S-substitution, however, means $x = 0.08$ because 0.08 atoms of S are needed to replace 4% of the 2 Se atoms. To avoid confusion, the quantity $x$ in our samples is explicitly declared throughout this document, and not a percentage. Finally, the word “doping” may be adequate for Cu-intercalated TiSe$_2$ since intercalation introduces an atom to the lattice. Copper also electron-dopes the samples. “Doping” is less fitting in S-substituted TiSe$_2$, where neither the amount of atoms nor the valence of the compound changes. The distinction might be trivial, but both samples take a part in our study. The more precise terms of substitutions and intercalations are preferred outside of the Cu$_x$ and S$_x$ sections.

3.2 Sample Characterization

X-ray Fluorescence

Small irreproducibilities are natural in the growth process. Batches of the same nominal doping usually have a different measured stoichiometry. Moreover, crystals from the same batch also have small doping variations. Measuring $x$ for each crystal is necessary.

We determined the amount of copper or sulfur in each crystal through x-ray fluorescence measurements (XRF). XRF uses the characteristic energy levels of an atom to determine a compound’s composition. Electrons removed from a core shell of an atom will create a vacancy that is filled by an outer shell electron. An x-ray photon is emitted as the higher energy level electron falls into the core-hole. This photon either leaves the atom, or scatters with another electron which is in turn ejected from the atom (Auger effect). The energy of the ejected particles corresponds to a transition of an atom in the sample. The fluorescence intensity at a given energy increases with the concentration of the corresponding element.

A Shimadzu EDX-7000P instrument is used to perform this measurement. The system uses a rubidium Kα x-ray source to bombard the target with photons. A silicon drift detector bins the energies of the x-rays generated in the samples. The elemental content of every sample was measured using the C line fluorescence signal from Ti, Se, S, and Cu atoms. Several spectra at different spots of the sample were taken to ensure
Good structural quality of a crystal must be guaranteed before taking it to a synchrotron run. Preliminary x-ray diffraction measurements are necessary; only about one in ten or twenty samples selected under the microscope by eye passes a quality test under x-rays. We have a source in our lab, but obtaining a quantitative measure of the crystal quality with our setup takes a long time. Instead, we use a Philips X’Pert 1 diffractometer and Cu-K\(\alpha\) source in the MRL central facilities to do this characterization.

The samples are flat and their crystallographic c-axis points normal to the surface. Finding an out-of-plane reflection of the crystal, optimizing it, and taking a theta (or omega) rocking curve can be done in 15 minutes. One such curve is shown in figure 3.2. We look for sharpness and symmetry in the Bragg peak as measures of quality.

### 3.3 Resistivity Measurements

Charge density waves manifest as superlattices, which occupy charge carriers. The reduced availability of free carriers associated with the opening of a gap at the Fermi level results in an abrupt increase to the otherwise metal-like behavior of the resistivity in TiSe\(_2\). This effect is used to label the charge density wave’s critical temperature \(T_{CDW}\). The “resistive anomaly” shown in figure 3.3 is a standard way to make a map
Figure 3.3: Resistive anomaly of pure TiSe$_2$. Each curve represents a sample grown at the labeled temperature [25]

![Resistive anomaly of pure TiSe$_2$](image)

Figure 3.4: Sample wired to a PPMS chip ready for a resistivity measurement.

![Sample wired to PPMS chip](image)

of the charge order phase boundary in a temperature vs doping (or pressure) phase diagram.

We carried out our four contact resistivity experiment using a Physical Property Measurement System (PPMS) machine manufactured by Quantum Design. This device is a common workhorse in many research facilities and preparing the samples for measurements is straightforward. We start by making electrical contacts between four leads and our sample using silver epoxy. We then use N-grease to stick our sample onto the PPMS chip, thereby ensuring thermal contact. Next, we use Crystalbond to stabilize the wires onto the chip. This way we can manipulate the open ends of the wires without worrying about breaking contact with or damaging the sample. These ends are then soldered to the appropriate voltage and current pins on the PPMS chip. A connected sample and chip are shown in figure 3.4.

During a resistivity measurement current passes through the sample via two leads. The remaining two leads measure the voltage across the sample. The voltmeter used has a high impedance and draws minimal current. Both the current and voltage drop are thus known, and calculating the resistance is a matter of using Ohm’s law. The PPMS is able to reach temperatures down to $\sim 0.5$ K and has a resolution of $20 \mu\Omega$. 

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using a 5 mA current.

Observing the emergence of a resistive anomaly is a perfectly reasonable way to obtain $T_{CDW}$, but it has some inherent limitations. Resistivity is an *indirect* way of measuring the order parameter. This experiment reveals no information about the robustness of the charge order nor its behavior as a function of temperature.

A weak CDW, or one that fractures into domains, reduces the magnitude of the resistive anomaly, sometimes to the point of invisibility. If the charge order is confined to pockets in the sample, due to domains or inhomogeneities, carriers will (literally) take the path of least resistance and avoid the CDW regions. The sample’s bulk resistivity will barely increase, if at all, at the critical temperature. This is certainly the case in samples with higher Cu and S content in Morosan’s [19] and in DiSalvo’s [25] resistivity data. It is why the phase diagrams in figures ?? and Kusmartseva are incomplete and the quantum critical point of charge order was extrapolated using data from lower doped (and pressurized) samples.

Finally, while the four contact measurement is in principle not destructive, it is difficult to recover an unscathed sample after the process. TiSe$_2$ is buttery soft, and the flake-like crystals are fragile. Removing the silver epoxy contacts will almost certainly compromise the crystallinity of the sample. When we performed multiple experiments on the same crystal, we scheduled the resistivity one at the end.

### 3.4 X-ray Sources

We used three different sources to obtain our data. The pressure phase diagram was obtained using a Rigaku rotating anode source at UIUC and the C-1 beam line at CHESS. The Cu-doped data was obtained using the C-1 and A-2 lines at CHESS. S-substituted crystals were measured with a Genix-3D microspot source at UIUC and the C-1 line. This section contains an overview of each x-ray source.

**Rigaku Rotating Anode and Considering the Energy**

A rotating anode x-ray source produced the photons in our initial pressure experiments. We had the option to equip it with a copper or a molybdenum anode. The Cu anode produces a greater photon flux, but the higher energy of the Mo-$K\alpha$ emission line tilts the balance in favor of the latter.

Changing the beam energy affects any scattering experiment in two important ways. It modifies both the attenuation length of the target, and the scattering angle of the beam. Attenuation lengths of a material shorten in general as a function of increasing energy. A pressure experiment is executed via a diamond anvil cell and scattering is measured in transmission geometry. Detected x-ray photons must pass through the diamond window of our cell, scatter on the crystal, pass through the rest of the sample, and exit through
Figure 3.5: Energy spectra from a Mo anode in the Rigaku source before and after passing through the monochromator. Measured with our multi-channel analyzer.

a second diamond window of the cell. If we want to take temperature dependent measurements, the beam needs to go through two additional Be windows. A 17.4 keV (Mo) photon has a higher probability of surmounting these layered obstacles than a 8.04 keV (Cu) photon. The way the scattering angle is affected by the energy can be read directly in Bragg’s Law: \( 2d \sin(\theta/2) = n\lambda \). A larger energy (shorter wavelength) results in a smaller value of \( \theta \). This is an important consideration in a pressure cell experiment. Our cell has an aperture of \( \pm 45 \) deg. If the scattered beam has too large an angle, it will impinge on a wall of the cell and never on our detector. Using a higher energy allows a larger number of Bragg peaks to occupy the angle space compatible with the aperture of the cell.

The energy spectrum of our rotating anode source using a Mo anode can be seen in figure 3.5.

**Genix-3D Source and Considering the Size of the Beam**

For years the Rigaku rotating anode doubled as a source of photons and a source of sorrow. It required constant repairs and soon after the pressure experiments we replaced it with a micro-spot Genix-3D source developed by the Xenocs company. This source has a smaller overall flux than the rotating anode, but it
has higher brightness. That is, the photon flux of the $\sim 200 \, \mu m$ diameter beam-spot of the Genix machine is greater ($\sim 1 \times 10^7 \text{photons/second}$) than the photon flux passing through a spot of the same diameter somewhere within the larger beam spot ($\sim 1 \times 1 \text{mm}$) the rotating anode produced.

Concentrating the x-rays into a small area has some obvious advantages. Photons scatter off the sample only if they hit the sample. If our crystal is much smaller than the beam then a large portion of our beam goes to waste. This is the case in our pressure experiments, where the sample must be smaller than the 400 $\mu m$ hole in the gasket, for example. Another advantage is reduced sensitivity to domains within the sample. Depending on the material, the handling of the sample, the growth process, the grower, and other stochastic processes, a single crystal is often only nominally a “single” crystal. A beam will illuminate as many crystal domains as it contacts. Distinguishing and labeling a few domains is usually straightforward, especially with an area detector. With a small beam spot, however, we could possibly target a single domain or a part of the crystal with better, sharper, more intense Bragg peaks. Once again, this is a more efficient use of the beam.

A smaller beam spot comes hand in hand with additional technical complications. The large beam of the Rigaku made targeting the sample an easy task. Switching to the Genix source implied improving our control of the sample positioning. Large samples are not much more complicated with a reduced spot size, but targeting smaller crystals can be more challenging. Threading the needle of the pressure cell, for example, requires fine and tight control on the sample motions. Tighter constraints also arise in terms of the center of rotation. If the beam or the sample deviate from the COR, diffractometer motions that rotate the crystal will also make it stray away from the beam. Temperature changes that move the sample due to thermal contraction in our system also need to be corrected for in a more careful manner. To compensate for these restrictions we built a motorized cryo-carrier that allows for fine sample adjustments.

Having talked about the consequences of the smaller spot size, let us now focus on the Genix-3D source itself. We again had a choice between Cu and Mo anodes, but we are not able to swap between these without making major changes in the machine. Similar considerations about energy and momentum space mapping explained above lead us to use the $17.4 \text{keV} K_{\alpha}$ beam from a Mo anode.

Though it operates at much lower power, the working principles of this source are similar to the rotating anode. A tungsten cathode raised to a 50 kV voltage ejects electrons that impinge onto a Mo cathode with a current of 1 mA. Colliding electrons accelerate other electrons and ions in a static Mo anode. Most of the energy is released as heat, which dissipates through a loop of running water generated by our chiller. Some of the energy is emitted as useful x-ray radiation. The beam is focused by a multilayer, parabolic mirror to a size of $\sim 200 \, \mu m$ at the focus. It has a divergence of 4 mrad and a focal length of 270 mm. The energy
profile of the source is shown in figure 3.6 as measured by a high quality Si single crystal.

**C-1 Line at CHESS**

A bending magnet produces a high flux x-ray beam at the C1 end-station at CHESS. High energy electrons are accelerated through the magnetic field and emit radiation. Particles in the synchrotron travel in a circular path and eject x-rays tangent to this circle. The angular spread of this radiation is focused tightly in the vertical direction, and to about $\pm0.12\,\text{deg}$ in the horizontal direction by a rhodium mirror. The photon energy at this end-station was selected by a Si(220) monochromator to 18 keV for the pressure experiments and to 12 keV for the Cu-intercalation and S-substitution experiments. The energy was calibrated using Zr and Se, elements with K-edge absorption energies of 17.997 keV and 12.666 keV, respectively.

**A-2 Line at CHESS**

Radiation is generated by a 1.5 m compact undulator accelerating high energy particles at the A-2 beam-line at CHESS. A high-heat-load diamond (111) monochromator is used to select the energy in the range from 5 to 70 keV. Our experiments here were ran at 12 keV and the flux delivered was of $1 \times 10^{14}$ photons/sec.
3.5 Detectors

Amptek Photodiode

We used an Amptek XR100CR silicon photodiode detector for the pressure experiments using the Rigaku rotating anode. This detector has an energy resolution of $\sim 145\text{eV}$. With it, we can account for fluorescence or x-rays at a harmonic energy of our beam. The upper boundary of this detector’s dynamic range is at 12kHz. For pressure experiments limited to low count rates, we were never close to saturation.

mar345 Area Detector

The mar345 is an image plate detector composed of a collection of Farbe centers in a phosphor screen. The x-y position of the collected x-ray photons are represented by the spatial distribution of the F-centers. The intensity of the scattered x-rays on the plate corresponds to the intensity of the fluorescence induced by a He-Ne during the detector read-out.

The detector measures 345 mm in diameter, and on high resolution mode, each pixel is $100 \times 100 \, \mu \text{m}^2$. We have about 9.3 million pixels sensitive to x-rays. The sensitivity of our detector is 1 x-ray photon per analog to digital converter unit at 8 keV. Each pixel saturates at about 65000 counts. The phosphor screen absorption efficiency reduces to about 0.96 at 17.4 keV. A plot of its efficiency is shown in figure 3.7. In our current setup, the image plate sits 223.6 mm away from the sample, as calibrated with a Si (111) peak. It is off-center with respect to the direct beam in order to accommodate larger magnitudes of our momentum transfer vectors. Our setup grants us 53.8 degrees in two-theta for our momentum transfer vector.

An area detector is a major upgrade over a point detector in an x-ray crystallography laboratory. We capture information that was otherwise thrown away. A single motor scan grants us access to many Bragg reflections. For each temperature, we take a step in our diffractometer’s $\theta$ motion, expose our sample to light, and measure what scatters on the mar345. Numerous Bragg peaks lead to greater confidence on the orientation matrix of the crystal. It also enables us to distinguish between and define different crystallographic domains, if any. Data collected out of the scattering plane on the area detector can be interpreted as being inside the scattering plane after specific rotations of the diffractometer.

This detector is quite large and weighs about 70 kg. Its position is fixed and swapping the detector is not a trivial task. The advantages over a point detector clearly outweigh the disadvantages, but they exist. For an experiment measuring extremely low signals, one might try to use a point detector in conjunction with a set of slits to reduce overall noise. The major disadvantage of the area detector, however, is its lack of energy resolution. In our $\text{TiSe}_2$ experiments, as explained below, it is essential to clearly resolve the fundamental
and harmonic energies of our beam in order to measure the degree of commensurability of the charge density wave. We are able to measure only the magnitude of the CDW order parameter with the area detector.

**Sodium Iodide Scintillator**

We used a sodium iodide scintillator detector for the pressure experiments on the C-1 line at CHESS. The energy resolution of this detector is worse than the Amptek’s at around 1 keV. It is, however, perfectly adequate for distinguishing between 18 keV radiation and harmonic 36 keV radiation. We use a pair of single channel analyzers to separate the photons into two bins in our data.

**Vortex Detector**

The NaI detector used in the pressure experiments was upgraded to a Vortex-EX silicon drift detector by the time we performed the Cu and S experiments. This detector features better energy resolution (180 eV), and more importantly a lower noise baseline. We were also able to record the energy spectrum for every scan, confirming no leaking of harmonic energy beam in the fundamental energy window we set on the detector. The Vortex has an active area of 80 mm² (which is slitted down during an experiment). It leaves its linear operating regime at about 900 kHz.
Pilatus 300K Detector

The A-2 beam line is equipped with a Pilatus 300K area detector. The “300K” label refers to the number of $172 \times 172 \mu m^2$ silicon diode pixels comprising its active region (and its cost in USD). The detector is light and was mounted on the two-theta arm of the Huber diffractometer at A-2. The distance of the detector can be adjusted with a mount and was calibrated using LaB$_6$ powder diffraction.

This area sensor has the advantages over a point detector already discussed above, but there are additional aspects that also make it superior to our mar345 detector. The Pilatus saturates at 200,000 counts, about thrice the limit of our detector. It also has a much faster 2.6 ms readout time. A typical exposure of the mar345 is taken for 60 s. After collection, one has to wait an additional ninety seconds for the image plate to read out and erase the x-ray imprint on the detector. The mar345 manual advices against collection times shorter than 30 s (we can cut the x-ray exposure time, but the detector collection time must be greater than this lower limit). Measuring a very intense peak in our lab, still implies waiting 2 minutes per point. The Pilatus is order of magnitudes faster than this. With it, we make decisions in real time; this is extremely valuable in a synchrotron experiment.

A-2 uses a diamond(111) monochromator (there is no (222) reflection in a diamond lattice), and the Pilatus is not energy resolving. Our experiments in this beam line collected information only about the magnitude of the charge order parameter, and not its commensuration to the ionic lattice. On the other hand, due to short readout times, high flux from the undulator, and quick orientation building using the area detector, construction of the TiSe$_2$Cu$_x$ phase diagram was very efficient.

3.6 The “Harmonic Trick”

The preceding sections painstakingly speak about fundamental and harmonic energies of the beam. The detectors’ ability to separate these two was also emphasized. In particular, we mentioned that if our detector is not able to resolve the two, then we are not able to measure the degree of commensurability of the CDW. This section describes how we are able to take such a measurement in our TiSe$_2$ crystals, and filter the harmonic and fundamental x-ray frequencies.

We used the ”harmonic trick” in our lab setup with the Rigaku and at the C-1 beam line. Let’s take C-1 at CHESS as an example, where the energy can be tuned between 5 keV and 35 keV. The use of a Si(220) monochromator at C-1 was no accident. In a diamond structure, like the Si lattice, Bragg reflections are forbidden unless their Miller indices are all odd or when they all add up to multiples of 4. The Si(440) reflection is thus allowed, its planes are parallel to the (220) plane, and they are separated by half the lattice
It is evident from Bragg’s law $2d \sin(\theta/2) = n\lambda$ that halving both $d$ and $\lambda$ leaves the angle untouched. Harmonic beam with twice the fundamental energy will bounce off the monochromator through the (440) reflection at the same angle as the fundamental beam bouncing off the (220) plane. (Similar arguments can be given for the $2^{nd}$, $3^{rd}$ and $n^{th}$ harmonics, but the energy band width of the white beam and the structure factor for the corresponding Si reflections make the presence of higher harmonics in the beam negligibly small).

Superposition of harmonic and fundamental energy radiation is usually bad. Many end-stations put in a lot of work to avoid it. Imagine using this beam to measure the temperature dependence of a (001) peak on a given sample. As the fundamental beam illuminates this reflection, the harmonic beam shines on the (002). Again, photons of both energies scatter off the sample at the same angle. If the detector cannot resolve the two, (001) data will be contaminated with (002) scattering. An energy resolving detector separates the two peaks and, depending on the experiment, collects additional information of the sample.

TiSe$_2$ has a half-ordered commensurate charge density wave. Resolving the two energies means measuring both the CDW reflection and the corresponding ionic Bragg peak with twice the CDW Miller indexes. We get information about two peaks in a single motor scan. For pressurized TiSe$_2$, measured in transmission geometry, we simultaneously collected data from the ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) and the (111) reflections. For Cu-intercalated and S-substituted TiSe$_2$, measured in reflection geometry, we simultaneously collected data from the ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) and the (117) reflections. The percentage of harmonic to fundamental signal in the beam was about 0.02%. The signal of a crystallographic Bragg peak in one of our pure samples, however, is a factor of about 1000 larger than the CDW peak. The ionic Bragg peak signal was always easy to observe.
Figure 3.9: Detector view of the harmonic trick. All figures are raw data from the same Cu$_{0.075}$TiSe$_2$ scan. 

a) Total counts of the detector as a function of L at $q_{cdw}$. The shoulder of this peak could be interpreted as poor sample quality reflected on the CDW peak. 
b) Energy spectra of a single point on the curve in a), collected at $L = 3.496$. Two distinct peaks appear at channels 750 and 1500 of the detector corresponding to the fundamental and harmonic frequencies of the scattered beam. 
c) Same L scan after setting windows in the data discriminating the two energies. The shoulder is resolved, it is not a product of sample polycrystallinity, but of an incommensurate lattice.
Separating the two energies not only cleans the superlattice Bragg peak from ionic lattice contamination, we can also measure its position in momentum space relative to the lattice peak. If the superlattice in TiSe$_2$ is half-ordered and truly commensurate with the ionic lattice, the fundamental and harmonic peaks should fall directly on top of each other in an angle scan. If they do not, we measure the momentum difference between the centers of the two peaks. This displacement is the degree of incommensuration $\delta$. It is zero for unpressurized and pure samples of TiSe$_2$, but it is a very small, yet resolvable quantity in some of these crystals. Measuring $\delta$ in the same scan muffles questions on accuracy of the orientation matrix and reproducibility of the diffractometer motions that would otherwise arise if we measured the superlattice and lattice peaks separately.

Applying the “harmonic trick" requires an energy resolving detector, a small amount of harmonic contamination in the beam, and a sample with a half order superlattice. The Vortex and Amptek detectors can bin photons into different energy channels on their own. To hasten collection and processing, however, we used two single channel analyzers (SCAs) that set two non-overlapping energy windows in the detector separating harmonic from fundamental frequencies of the beam. An energy spectrum of the scattered beam on the Vortex detector can be seen in 3.9 b) as measured on a CDW and ionic lattice peak simultaneously. The two energies can be clearly resolved. No overlapping tails cross our SCA windows set on the channels of Vortex. 3.9 c) shows a momentum scan illustrating data obtained through the use of this technique.

### 3.7 High Pressure Setup

We used a diamond anvil cell (DAC) to reach the high pressures required to explore the TiSe$_2$ phase diagram. A diagram of this set-up is shown in figure 3.10. Two diamonds with flat culets sit opposite to each other on top of hardened beryllium seats. A gasket with a circular hole, typically half the size of the diamond culets sits in between the two diamonds. The gasket hole is filled with a pressure medium, wherein a ruby crystal and our sample are placed. Tightening the screws on top of the cell brings the diamonds closer together, squeezing the gasket and raising the pressure inside the hole.

Our cell was purchased from the Almax-easylab company; we used the Diacell Bragg-LT(S) model in which the screws are hand tightened. A picture of the cell can be seen in 3.11. There is a threaded hole on the short flat side of the cell. A set screw mates the DAC to the top of the cryostat’s cold finger. Spacers between the cell and the cold finger place the sample is at a height close to the direct beam (within the range of the vertical motion of our setup) and ensure good thermal contact. Finally, we use silver paint to glue our temperature sensor to the side of the cell.
Having described the basic working principles of a diamond anvil cell above, we now zoom into the specific characteristics of our cell and explain their *raisons d’être*.

**Diamonds and Alignment**

Hardness and high transparency to x-rays and visible light make diamonds ideal anvils for pressure and diffraction experiments. The culets and tables of the diamonds are aligned horizontally to the hole in the beryllium seats. This allows radiation interacting with our sample and ruby to pass through and out of the cell. It also allows use of a microscope for loading and inspecting the cell during our experiments.

The cell’s upper pressure limit is inversely related to the size of the culets. Since the charge order phase of TiSe$_2$ is observed only for low pressures (relative to a typical high pressure experiment) up to $\sim$ 6 GPa, we chose to use culets of 800 $\mu$m in diameter. Using large culets allows us to drill a larger gasket hole, which can accommodate a bigger crystal and simplifies the surgical-like task of loading the sample and the ruby.

Alignment of the diamonds is extremely important. The planes of the culets must be parallel to each other. If they are misaligned, uneven strains can be applied that can cause them to break.

**Gaskets**

Several parameters of the gasket can be tuned which can affect the boundaries of the experiment. We will first focus on preparation of the gasket, then on the tunable features and their consequences.

To make gaskets, we start with blanks; small circles punched out of sheet metal 10 mm in diameter and 0.4 mm in thickness. We scratch a mark on the blank and center it on the diamond anvils using a holder and...
tighten the cell. This creates an indentation on the gasket. The thickness at the indentation is measured until it is about half the blank gasket thickness. Ideally one gets to the desired thickness indentation in a single cell compression. If it is still too thick, we align the mark with a previous reference and try again. We limit ourselves to pressing the blank twice. When many compressions have been made, the gasket might not sit flat on the culets and loading can become difficult.

With the indentation finished, we then use electrical discharge machining to drill a hole through our gasket. The hole is centered on the diamonds’ imprint and its diameter is close to 400 $\mu$ half culet size. (Larger diameters can be used to accommodate larger samples, at an increased risk of gasket failure). The hole is then inspected under a microscope to check for deformations due to a tilted drill or gasket, and to see how well it is centered. Upon passing these inspections, the gasket is cleaned in an ultrasonic methanol bath, it is now ready for loading.

There are several adjustments we can make to the gasket. First, we must consider its material. We had the option to use copper, stainless steel, or rhenium gaskets. Pressure is adjusted by manually turning two screws on the cell, which requires strength and finesse in the experimenter’s hands. A harder material is more difficult to compress and demands more force to turn the screws. Copper, out of the three options above, is the softest and easiest to drill and indent. Unfortunately, this also means it is prone to deformations of the hole. At some point in pressure the gasket fails, and one must reload the cell. We had success with Cu and steel, Rh is expensive and hard to drill and indent. There was no real advantage to use rhenium in a TiSe$_2$ experiment.

The indentation amount and the size of the hole are, to some extent, debated topics in the high pressure community. An indentation to half the thickness of the gasket and a hole of half the diameter of size is what we used in our experiment, but different labs use different conventions (a bulk of which were probably set by a “if it ain’t broke, don’t fix it” type proverb). In particular I have found most experimenters prefer indenting to a thinner thickness, often to less than 100 $\mu$m. Ideally, the size of the hole will not change throughout the experiment. In practice, the hole can shrink or expand as the diamonds come closer together. Thinner thicknesses of the indentation tend to make the hole smaller as pressure rises. Thicker indentations can make the hole expand, and the pressure might not rise as much as the cell is tightened. If the hole expands beyond the culet, the pressure media will leak out and the cell must be reloaded.

Naturally, one has to consider the size of the sample while making decisions about the gasket. Cutting small pieces of TiSe$_2$ is difficult, the crystals are soft and deform easily. Once an appropriate sized, high quality crystal is found (among the vast amounts of poor quality samples tested), we try to accommodate our setup to it. The indentation must be thicker than the sample, the hole diameter must be larger than
the longest side of the crystal, and we should still be able to fit a piece of ruby next to the sample. We sometimes bend our rules of thumb for thickness and diameter. In our last two pressure measurements (chronologically), our copper gaskets failed at ∼ 3.5 GPa. We used 250 µm thick gaskets with a hole 450 µm in diameter. For subsequent pressure experiments in our lab we opted for using stainless steel in this section gaskets and had no trouble reaching pressures up to 12 GPa.

Pressure Medium and Sample Loading

At this point our culets are aligned, our gasket indented, and hole was pierced through it. Two more elements in our pressure experiment need to be detailed. The ruby crystal used for measuring the pressure along our phase diagram will be discussed in the following section. Here, we briefly describe our pressure medium before going over a step by step loading procedure.

We use a 4:1 methanol:ethanol volumetric mixture as our pressure medium. Our choice of this mixture over other commonly used media, such as Ne and He, is due to the design of our cell, and to the lack of loading apparatuses near us that can harmonize with the cell’s particular shape. Noble gases will better (homogeneously) distribute the pressure within the gasket hole. He will not freeze at the lowest temperatures of our experiment. The alcohol mixture, however, worked well for our cell and we reached the necessary pressures.

Loading the cell in preparation of a scattering experiment takes patience and practice. Following a
systemic procedure often helps with such tasks. We take the following steps:

- Using gloves, place the bottom part of the cell under a microscope and place the focus on the culet. Clean the culet if needed.
- Place three small clay spheres around the culet in the bottom part of the cell.
- Balance a clean gasket on the clay, making sure the mark on the gasket aligns with a reference (we use the red mark on the cell as shown in figure 3.11). This allows the indentation to match the diamond faces and make a tighter seal with the culet.
- Using a hypodermic needle, place a drop of pressure medium in the gasket hole. If it leaks out, the indentation may not be flat on the culet. Try to re-balance the gasket if this is the case.
- Using the tip of a needle or a specialized tool, grab a sample and place it in the hole. Static electricity, or rubbing the needle on a bit of scotch tape is often enough to get a hold of small samples. The alcohol will likely detach it from the needle upon contact. Pushing the sample through extra pressure medium if it fell close to but not inside the hole helps the positioning. Evaporation of the alcohol might also help since the gasket hole can act like a sink.
- Once the sample is in the hole, repeat the same steps for a ruby crystal. The ruby should sit next to, not on top of the sample; ruby fluorescence is measured in transmission geometry and the sample could be crushed due to the added thickness otherwise.
- Drop additional pressure media if it has evaporated, take the piston side of the cell and carefully slide it until it makes contact with the gasket. Press down firmly with gloved hand.
- Place the clamp on top of the cell, slightly and evenly tighten the screws on the clamp. Check the loading under the microscope. Sometimes, a small bubble will form on the medium, as the screws are tightened, the bubble will shrink and disappear. This is a good indication that pressure media was trapped.

If done correctly, we now have a loaded cell ready for an experiment. Tightening the screws will increase the pressure. Pressure cannot be reduced by loosening the screws without the medium leaking because the gasket deforms plastically. Additionally, the sample quality deteriorates as it is pressurized. We do not reuse our crystals.

Since the methanol-ethanol mixture is transparent, to ensure it was trapped in the hole one measures the ruby spectra. Before a scattering experiment, we take a spectra at room temperature and ambient pressure
Figure 3.12: A loaded pressure cell viewed through a microscope.

(slight variations between rubies are expected). We make one more measurement with the ruby inside the cell, at the lowest pressure right after loading. Finally, to ensure the cell is functioning properly, we measure again after a slight turn of the screws if we are starting our series at the lowest possible pressure, or after tightening to whichever point we choose. The next section describes the nature of such measurements.

**Pressure Calibration**

We need to tag each scattering curve with a temperature and a pressure label. To do this, we use a well established reference: ruby. The R1 and R2 fluorescence peaks of ruby have been extensively studied, and their behavior as a function of pressure and temperature are well understood [26].

The ruby is excited via a 50 mW, 532 nm portable green laser. The spectra is then collected by an Ocean Optics URB 2000 miniature fiber optic spectrometer and a 5 mm focal lens collector is used to enhance the signal. The R1 line of a typical ruby at room temperature and one bar fluoresces at 695 nm. This line follows an empirical equation as a function of T and P:

\[
P = \frac{A}{B} \left(1 + \frac{\Delta \lambda}{\lambda_0}\right)^B - 1\]  

Where \( P \) is the pressure, \( A \) and \( B \) are constants, and \( \Delta \lambda \) is the shift of the R1 line wavelength from its room temperature and ambient pressure value \( \lambda_0 \).

The ruby fluorescence signal is collected and pseudovoigt functions are fit to the R1 line to determine its
center. Figure 3.13 shows the line’s spectral shift with temperature. The temperature is read from our sensor and inserted into the equation above to determine the pressure. To travel across the T vs P phase diagram, first take a step along the x-pressure axis by tightening our screws. We attach the cell to the cryostat and cool down to base temperature. We take an x-ray measurement here, then apply heat with our controller to take a step up in the y-temperature axis, and collect more scattering data. Once a temperature line is completed, we vent the cryostat, take out the cell, tighten the screws to take one more step in pressure, and repeat our procedures to gather temperature data here.

We must take a pressure measurement at every temperature point. The DAC undergoes thermal expansions and contractions. Perhaps due to small misalignments and asymmetries, the pressure can change a small amount at each temperature.

**Rotating Cryostat Head**

Photons produced by the synchrotron have a very different wavelength than the ones originated in our green laser. Both x-rays and visible light have to pass through the single aperture in our cell. Since the cryostat must be covered before it can get cold, we need to make the cryostat head out of a material that is...
transparent to both wavelengths of light.

We used two pairs of windows built into a rotatable head to solve this problem. Beryllium windows are visibly opaque, but barely scatter hard x-rays. Glass windows were used for the ruby measurements with the green light. Each pair of windows sit opposite and parallel to each other on the four walls of the cryostat head. To position the windows for an x-ray or ruby measurement, the head was designed to rotate manually. It maintains the vacuum necessary to keep the cryostat cold while rotating. Figure 3.14 shows a picture of our design. The Be windows are large and do not set additional limitations on the entrance and exit angles of the beam.

![Figure 3.14: Cryostat head used in the pressure experiments. O-rings on the windows and at the bottom maintain a vacuum in the cryostat. The Teflon collar minimizes friction between the head and the jacket while rotating.](image)

**Transmission Geometry**

As previously discussed, our scattering experiment using the diamond anvil cell is necessarily done in transmission geometry. That is, the surface normal of our flake-like TiSe$_2$ crystals are near parallel to our x-ray beam. The beam must scatter in and traverse the sample, come out of the cell, and hit our detector.

Our transmission geometry sets limits on the thickness of our sample. Too thick and the beam will be severely attenuated, too thin and the beam will not scatter enough with our sample. For x-rays of 18 keV energy, TiSe$_2$ has an attenuation length of 40 µm at 90 deg. Most of the samples used were around 60 µm thick as measured by a profilometer. A thicker sample may be used, however, if it has exceptional crystalline quality and appropriate dimensions. Though TiSe$_2$ layers cleave easily like graphene with scotch tape, it is hard to control the amount of layers cleaved and thus the thickness of a given crystal. This handling may also damage the quality of a sample at risk. Instead of cleaving or cutting our samples, we choose one of
suitable size from the many crystals in a batch.

We studied scattering from the \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) CDW reflection in the pressure experiments. The Bragg peak is reachable in transmission geometry.

### 3.8 Copper and Sulfur Series Setup

As seen above, mapping a pressure phase diagram requires additional equipment and expertise. The amount of variables in such measurements blurs the boundaries between experimenter and artisan. Risk of failure on the cell is always present. In contrast, though questions about sample homogeneity arise, Cu-intercalated and S-substituted TiSe\(_2\) experiments demand a much simpler scattering setup. We used the same setup to measure both sets of copper and sulfur.

We chose to measure these Cu and S samples in reflection geometry. Here, worries about the sample being too thick dissolve. Since low penetration is no longer a concern, the x-ray energy was lowered to 12 keV to optimize the photon flux in the synchrotron. Having no option to tune the energy in our lab, we kept using our 17.4 keV Mo \(K\alpha\) beam.

In reflection geometry, the normal vector to the sample surface points perpendicular to the beam. Measuring the \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\) CDW peak is not possible, because the crystallographic c-axis vector of TiSe\(_2\) is normal to the surface as well. Instead, we studied the \((\frac{1}{2}\frac{1}{2}\frac{7}{2})\) reflection of these crystals.

The sample was mounted flat on an aluminum holder using silver paint. Our holders were machined at UIUC, and were used both in our lab and at CHESS. They screw directly onto our cryostat. Holder height can be adjusted with spacers, and thermal contact is attained placing copper grease or a small piece of indium between the bottom of the holder and the top of the cold finger. For each synchrotron run, we took a set of holders with pre-oriented crystals. Swapping to a crystal with a different composition was a quick task. The speed of a swap was only limited by the warm-up time of the cold finger (ice builds up inside the cryostat if we vent while it is cold) and the few seconds taken to replace the holder with a new one.

Since optical windows are not required for the experiment, a Be dome topped our cryostat. It is a hemispherical head transparent to x-rays.

### 3.9 X-ray Scattering at UIUC

Though our x-ray source in Urbana is not as bright as a synchrotron source, the photon beam is sufficiently intense to perform several sample checks and to conduct preliminary experiments. We are able to cool our samples down to 4.5K, and can determine the temperature and characteristics of structural phase
transitions. We can do the same for some CDW transitions on samples where the modulation peaks show a high intensity. Coupled with our area detector and diffractometer, our home system becomes a very powerful research tool. This section describes the details of our setup and breaks down a typical scattering run in our lab.

3.9.1 Diffractometer and He Cryostat

Our sample is mounted on a Huber 4-Circle Diffractexploitometer model 5020. The four circles of our diffractometer (two-theta, theta, chi, and phi) enable us to rotate and orient our crystals, and to manipulate the direction of the momentum transfer vectors in order to place the scattered beam into our detector. When using an area detector instead of a point detector, we can map a large area of momentum space by rotating only about the theta axis of the diffractometer leaving the other motors fixed. The pixels on either side of our scattering plane capture information equivalent to chi or phi angle rotations.

We cool our samples down to temperatures as low as 4.5 K using a Displex DE-202 cryostat. It is a closed cycle He gas cryocooler that mounts onto the diffractometer. Helium is supplied from the high pressure line of our compressor onto the cold finger (or expander). The refrigeration cycle takes place here: the gas expands, removes heat from the system, and returns to the compressor through the low pressure gas line. A vacuum shroud with Be windows surrounds the cold finger. At the tip of the cold finger, we place the sample stage with our crystal. We raise the temperature of our samples via a resistive heater attached to the cold finger’s tip, and we measure the temperature through a silicon diode glued onto the sample stage. These components are connected to a PID circuit, part a LakeShore 325 temperature controller on which we set our desired temperatures. The whole assembly is capable of motorized fine motions in x, y, and z directions. We can then ensure that the sample is at the center of rotation of our diffractometer at each temperature in our measurement.

We used the same diffractometer, He cryostat, and temperature controller for the experiments in our lab at UIUC and at the Cornell High Energy Synchrotron Source. We do use a different cryo-carrier in our lab; it was built in house at our machine shop. The cryo-carrier at CHESS is commercially available from the Huber company. Both serve the same purpose (moving the sample in 3-D space without moving the diffractometer’s center of rotation).

3.9.2 Execution of a Scattering Experiment

Figure 3.15 is a picture of our scattering experiment. In it, we see the x-ray source, diffractometer, mar345 area detector, and the cryostat showing an exposed cold finger. A closer inspection of the image reveals
some details of these central components.

The cryostat’s helium supply and return lines are visible in the figure. They hang suspended by elastic bungee chords which prevent strain and alleviate tension that can potentially damage the lines or misalign the diffractometer during motor motions. Attached to the cryostat as well, between the detector’s supporting legs covered in yellow envelope paper to reduce friction on the table, lies a bellow that connects to a vacuum pump sitting below the table (not pictured). Through it we achieve the insulating vacuum required to operate our cryostat and cool our sample. Moving our gaze up through the cryostat, we see the cryo-carrier that allows automated fine motions of the sample. Continuing upwards, and zooming into the cold finger, three sets of electrical wires that plug into the temperature controller can be found. The first set connects to a resistive heater buried under the copper top of the cold finger. The second set of wires, stabilized by white Teflon tape, go to a small temperature diode that screws onto the copper top. The third set, shown hanging off the top of the cold finger, end in a disk-shaped Si temperature sensor. This sensor is glued directly onto the sample holder (or the side of the DAC) that screws on the cold finger.

The image plate is circular and resides behind the black protective cover of the mar345. Off-center placement and a short distance between the active area and the diffractometer’s COR allows us to capture Bragg peaks lying at high two theta values. The detector sits on a plate supported by two aluminum extrusions. In figure 3.15, the diffractometer is at a $\theta = 0$ angle. The placement of the aluminum extrusions was carefully considered so that the cryostat passes between them as $\theta$ moves to its highest limit.
Through one more view of figure 3.15, we notice a slit placed right in front of the source. To our surprise, we found the x-ray optics produced a weak secondary beam. There is a finite angle between this ray of photons and what we call the direct beam. Blocking the secondary beam with a slit prevented confusion in the data.

**Setting up the Sample**

For simplicity, we first describe an experiment which does not involve pressure. An aligned beam and diffractometer are assumed. Preparing an experiment begins with the following steps:

1. Glue the sample as flat and centered as possible to the top of a machined holder using conductive silver paint.

2. Screw the holder onto the cryostat, first placing a small piece of indium or aluminum foil between the holder and cold finger. The soft metal will squeeze as the holder is tightly fastened, making good thermal contact.

3. Place the sample at the center of rotation using the cryo-carrier. The COR is marked by cross hairs shown in the monitor of a telescope camera (figure 3.16).

4. Using a diode monitoring the direct beam, scan the height of the cryostat. At some point of this scan, the holder will eclipse the direct beam on the diode. This scan should look like a step function, take the derivative. Place the holder at the derivative’s maximum (or minimum, depending on the direction...
of the scan). At this point the sample is centered height-wise on the beam. The diode measuring the direct beam is visible in figure 3.17.

Figure 3.17: One more view of the scattering setup. A circular Si diode monitors the direct beam. Lead tape behind it protects the detector from the beam. The sample is located inside the Be cryostat head. The source can be seen mirrored on the image plate’s protective cover.

5. Take long integrated theta scan: open the x-ray shutter, setup a single long collection (∼ 200 s) on the detector, and move theta from 0 to 20 deg. This scan quickly tests for adequate sample quality, and confirms the sample is on the beam. Integrated scans of a “good” and a “bad” crystal are presented in figure 3.18.

6. Given a satisfactory crystal quality and position, glue the temperature sensor onto the side of the holder.

7. Seal the cryostat using the Be dome head seen in figure 3.17.

8. Turn on the vacuum pump and wait until the pressure reaches $1 \times 10^{-4}$ Torr.

9. The He compressor can now be turned on. Water must flow through the compressor’s radiator. Turn on the water valve at this time. The temperature reading of the sensors should start dropping.
10. Upon reaching base temperature, take another cryo-carrier height scan. The cold finger should have shrunk one or two millimeters. Place the sample on the beam once more.

**Data collection**

We are now ready to begin measurements of the crystal. A general approach to data acquisition is adopted:

1. At base temperature, perform a large theta motor scan (0 to 20 deg or wider), taking one image at every 0.05 angular step. A wide and fine scan will reveal numerous Bragg reflections and will have a good momentum resolution. Depending on the strength of the scattering, a longer or shorter x-ray exposure time can be chosen. A 60 s exposure per image is a good starting point.

2. Establish the orientation matrix of the crystal. Label each reflection with a Miller index for refinement. Figure 3.19 shows a theta integrated image in which the Bragg peaks have been labeled.

3. Using this matrix and given it is low temperature data, explore the images for CDW peaks. Label and compare their intensities.

4. Find a suitable charge order peak to study its full temperature dependence. If studying TiSe$_2$ varia-
Figure 3.19: A theta-integrated scan of Cu$_x$TiSe$_2$ at 9 K. Bragg peaks have been indexed, an orientation matrix was chosen and two charge density wave peaks have been found. They are labeled in red: (1 $\frac{1}{2} $ $\frac{1}{2} $), and (1 $\frac{1}{2} $ $\frac{1}{2} $). The latter is equivalent to the (3 $\frac{1}{2} $ $\frac{1}{2} $) reflection.

5. Input a new temperature set-point to the PID controller. Wait for the temperature to stabilize.

6. Scan the cryo-carrier and compensate for thermal expansion.

7. Take a narrow angle scan centered on the CDW peak at this temperature.

8. Repeat the three steps above to obtain a full T-dependence of the CDW peak.

9. If useful, take a wide angle scan at room temperature for further lattice refinement.

At this point we have obtained an intensity vs temperature plot for one sample. We turn off the compressor, warm up the cold finger, vent the cryostat, unscrew the holder, and get ready to measure a new crystal.
3.9.3 Conversion of Image Data

An image is taken after each exposure of the detector. Each pixel in a collected image contains three quantities: x position, y position, and intensity. To this image we append information about the geometry of the diffractometer: the values of the two-theta, theta, chi, and phi motors. We rotate the crystal, take another exposure, and collect the new image with the new diffractometer information. By repeating this process, we map a volume in the reciprocal space of the crystal.

Recipes for establishing an orientation matrix and fundamental diffractometer equations are given in [27]. Additional discussions on lattice refinement and using different diffractometer configurations are given in [28] and [29].

The area detectors are used as 6-Circle diffractometers during the data processing. Pixels outside of the scattering plane are assigned a value in terms of the delta and gamma angles in a 6-C geometry. Once the orientation of the sample is determined, we use it to transform the six angles into $hkl$ values of the crystal.

Binary files containing $h$, $k$, $l$, and intensity information are then created and stored for each set of images. Through these files, it is possible to obtain an $h$-$k$ plane cut at a fixed $l$ value, for example. When slicing the data we can tune the thickness of the slab (e.g. $l$) and the size of the bin where the pixel will be stored (the $h$ and $k$ steps). The data in each bin is normalized by the number of pixels. A typical value of the slab thickness is $Q = 0.02$, the bin size is usually 0.005x0.005 r.l.u.. The size of the bins and the slab thickness are adjusted from sample to sample to prevent smearing of the data, or sparse data points. Finally, we can take $h$, $k$, or $l$, or any other preferred line cuts in our plane to closely inspect the data.
3.10 X-ray Scattering at CHESS

The scattering setup at CHESS is shown in figure 3.20. The familiar sights of a Huber diffractometer and the cryostat greet us. A point detector at the end of the two-theta arm is used for harmonic filtering. Without an area detector we must use the rotations of the diffractometer to put our reflections in the scattering plane. An orientation matrix must be built before finding superlattice reflections. We illuminate the differences of an experiment at C-1, by following its execution.

**Setting up the Sample**

Positioning Cu-intercalated and S-substituted samples on the beam is attained by the same steps described above in our lab setup. It is more useful to look at a pressure experiment. We assume the DAC has been loaded with the sample and a ruby measured at ambient or very low pressure.

1. Screw the cell into the cryostat. It is important to consider the experiment’s geometrical limitations. Bellows, He lines, and the cryostat can collide with objects with motor motions. The window of the DAC must face the direct beam. Spacers between the cell and cryostat are preferred over compensations.
using the phi motion of the diffractometer.

2. Glue the temperature sensor to the side of the cell.

3. Place the center of the cell as close as possible to the COR marked by cross hairs in a downstream monitoring camera.

4. A Si diode monitors the direct beam. Scan the cell’s z and x directions (the height and the other orthogonal direction to the beam) to find the hole in the gasket using the diode.

5. Cover the cryostat with the Be windows facing the beam, vent, cool down to base temperature, and compensate for the height lost due to thermal contractions.

6. Find two Bragg reflections to orient the crystal, we used (110) and (200) in transmission geometry. Beam attenuation is necessary to avoid detector saturation.

7. Find the CDW \((1/2 1/2 1/2)\) peak using the orientation matrix found. Optimize this peak and then use it as one of the orientation vectors.

8. Set up two separate single channel analyzers to discriminate between fundamental and harmonic parts of the beam.

**Data Acquisition**

1. Take the necessary momentum line cuts centered at \(Q_{CDW}\).

2. Collect the ruby spectra to take a low temperature pressure measurement. Return the cryostat to a vertical position. Rotate the cryostat head so that aperture is visible through the optical windows. Position the laser beam spot on the sample, and the collector as close as possible to the optical window. Collection time depends on the ruby signal, a distinct peak must be resolved.

3. Raise the temperature an appropriate amount and take another pressure measurement once the temperature stabilized.

4. Return the cryostat head to the original x-ray position, and go to the CDW peak’s diffractometer angles.

5. Measure the scattering signal of the superlattice at this temperature.

6. Move another temperature step and perform an x-ray measurement.
7. Alternating between scattering-then-pressure and pressure-then-scattering measurements after each temperature step to cut the setup time, repeat the procedures above until a complete temperature dependence is finished.

8. Warm up, vent, and open the cryostat. Remove the temperature sensor and unscrew the DAC from the cold finger.

9. Tighten the clamp of the cell to raise the pressure of the sample. One should be conservative while tightening the screws, turning them a small amount and measuring the shift in the spectra each time until the desired value is achieved. Pressure can only be applied monotonically.

10. At the new pressure point, set up the sample on the cold finger once more to begin a new temperature dependence. The diffractometer angles of the Bragg peaks used for the orientation matrix should be similar. It is possible, however, for the sample to shift inside the cell.
Chapter 4

Experimental Results

The main results on the effects of pressure, copper intercalation, and sulfur substitution in TiSe$_2$ can be condensed into three phase diagrams. We explained above how we were able to move along the x (pressure, copper, or sulfur content) and y (temperature) axes in a controlled manner. This chapter summarizes our results and describes the construction of the phase diagrams from our x-ray diffraction data.

4.1 TiSe$_2$ Under Pressure

Charge order manifests as a superlattice distortion in TiSe$_2$ below 202 K. Applying pressure to the crystal suppresses the CDW and gives rise to a superconducting phase [20]. A quantum critical point of charge order ($T_{CDW} = 0$) is argued to lie within the dome-like superconductive region of the T-P phase diagram. If so, TiSe$_2$ is an example of the “universal” phase diagram of unconventional superconductors, where SC emerges near the suppression of another ordered phase.

To understand the relationship between CO and SC we need to directly probe the CDW order parameter. We used x-rays and our diamond anvil cell, and a He-cryostat to explore the charge order of this system. Specifically, we studied the (1$rac{1}{2}$1$rac{1}{2}$1$rac{1}{2}$) reflection.

Pressure and Temperature Dependence

The temperature and pressure dependences of the CDW peak are summarized in figures 4.1 and 4.2(a,d) [30]. Figure 4.1 depicts temperature dependent integrated intensities from H cuts at several low pressures. This curves were measured with our lab setup. To find $T_{CDW}$ the data is fit to an empirical formula:

$$f(t) = I_0 \left(1 - \frac{t}{(t - \alpha)/(1 + \alpha)}\right)^\beta$$

(4.1)

where $t = T/T_{CDW}$, $\alpha = 0.248$, and $\beta = 3.85$. $\alpha$ and $\beta$ were determined by least squares fitting. After linear scalings, one can collapse the integrated intensities at different pressures into a single curve.

It was concluded from these measurements that the CDW must have a $T = 0$ critical pressure above 3.0
Figure 4.1: Temperature dependence of the CDW (111) at different pressures. Raw data (solid lines) can be linearly scaled to $f(t)$ and then collapsed on top of each other (dashed lines).

GPa. To access this regime of the phase diagram, where the magnitude of the CO order parameter is small, we took our diamond anvil setup to CHESS. The pressure QCP was found at 5.1 GPa (fig. 4.2d). We were able to scale the CDW intensity from different experiments at 3.0 GPa and 3.1 GPa that showed similar temperature dependences.

Residual peaks for all the samples were visible outside of the CDW phase, but their integrated intensities were temperature independent. Figure 4.2b) shows these peaks for crystals at three different pressures. Diffuse scattering above $T_{CDW}$ should be contained in the diffraction signal, but the measured curves showed no change in the linewidth. Long range order should be weak, but still present in TiSe$_2$. Therefore, we interpret this signal as one originating from a symmetry breaking field.

Fluctuations near $T_{CDW}$ were not observed in the samples. Sample degradation occurs as pressure is applied, and the CDW peaks broaden following the ionic Bragg peaks. This broadening, however occurs in the constant momentum transfer direction. Our resolution in the H momentum direction was still mostly determined by the slits of our detector, and not mosaicity of the sample. Diffuse scattering measured for pure TiSe$_2$ by Holt [31], however, was not observed in our high pressure measurements. Though pressure might suppress these fluctuations, the diffuse scattering signal could be buried in the high background natural to a DAC.
Figure 4.2: Temperature and pressure dependences of the CDW. a) Low temperature momentum cuts showing suppression with increasing pressure. b) Residual peak observed outside of the charge order phase boundary. c) Pressure dependence of the CDW coupling constant $g$. d) $T_{CDW}$ as a function of pressure, gray points are from reference [20].
Figure 4.3: Out-of-plane synchronous CDW and Bragg peak line scans for two different pressures: 1.9 GPa and 3.0 GPa.

Incommensurate CDW

Figure 4.3 [30] show L momentum cuts for several temperatures of samples with two different pressures. The intensities of the superlattice and lattice peaks were measured simultaneously using our harmonic trick. The gray and green curves for the lower pressurized sample, at 1.9 GPa, stack on top of each other, indicating a commensurate lattice within our resolution. At a higher pressure of 3.0 GPa, we observe a commensurate to incommensurate transition as the temperature is raised above 70 K. The coexistence of both incommensurate and commensurate peaks makes this a first order transition, similar to the ones in other dichalcogenides [32, 15].

Our data is summarized in figure 4.4 [30]. The distance between the QCP and the superconducting dome-like region of the phase diagram implies SC is not directly associated with instabilities of the CDW. We also see how the commensurate to incommensurate transition lies at the same pressure as the superconductive phase. Domain walls of charge order may have a more direct connection to SC.
Figure 4.4: Pressure-temperature phase diagram of charge order in TiSe₂. White circles mark points of data acquisition. Data where the harmonic filtering technique was applied is labeled “C” and “I”, representing a commensurate or incommensurate CDW, respectively; the “C/I” label indicates coexistence. Superconducting phase in red was taken from reference [20]. a) Wide view of the data showing the full diagram showing the quantum critical point. b) Close-up of the commensurate to incommensurate boundary.
4.2 Cu-intercalation in TiSe$_2$

Two novel observations were made in pressurized TiSe$_2$. First, the quantum critical point of the charge order phase lies outside of the superconducting dome-like region of the phase diagram. Second, the charge density wave of this system undergoes a commensurate to incommensurate transition at higher pressures. Kusmartseva’s phase diagram was constructed via resistivity measurements, and it needed revision. The QCP was extrapolated from this data to an inaccurate point of the pressure axis. Morosan’s Cu$_x$TiSe$_2$ phase diagram was built on the same techniques, and the QCP of charge order was extrapolated in the same manner. It was therefore sensible to hold the suggested QCP suspect.

Several consequences follow increasing $x$ in Cu$_x$TiSe$_2$. As copper intercalates between titanium diselenide layers, the lattice parameters $a$ and $c$ expand up to $x = 0.1$ [19]. This is the upper limit of solubility in TiSe$_2$, and the compound will not crystallize beyond this level of copper. Cu intercalation also raises the chemical potential [33] and suppresses the CDW transition temperature. It has been argued that this suppression originates from the suppression of exciton formation [34]. Finally, the superconductive phase of Cu$_x$TiSe$_2$ exists for $x = 0.04 \pm 0.10$.

For higher values of copper intercalations the resistivity anomaly, used to establish $T_{CDW}$, becomes unmeasurable. X-rays provide a better probe to the CDW than bulk resistivity measurements. A more precise phase diagram can be constructed based on diffraction. X-rays also provide information of the CO correlation length and will reveal the existence, if any, of CDW domain walls.

The diffraction experiments in this section took place at the C-1 and A-2 beamlines at CHESS, and in our home institution using the Genix source and area detector setup. A set of nine copper intercalated samples with $x = 0 - 0.91$ were measured. Only five of those were measured at C-1, where we can apply the harmonic filtering technique. The degree of incommensuration was measured only in those samples.

**Cu$_x$ and Incommensuration**

Our crystals were glued onto aluminum holders and cooled to a base temperature of 11 K. Representative cuts of the CDW ($\frac{1}{2} \frac{1}{2} \frac{7}{2}$) and the Bragg ($\frac{1}{2} \frac{1}{2} \frac{7}{2}$) reflections for different levels of Cu-intercalations are shown in figure 4.5 [35]. These plots display the power of our harmonic trick, and reveal the developing incommensurate superlattice. Figure 4.5a shows a commensurate resolution limited peak in a pure TiSe$_2$ sample. With increased intercalation, the locations of the Bragg and CDW reflections drift apart from each other in reciprocal space. This is clearly evident in figures 4.5c and 4.5d. The degree of incommensuration $\delta$, the difference between the positions of the peaks, is independent of temperature within error.

A slight CDW incommensuration in the TiSe$_2$ system is interpreted as domain walls or stacking faults
in the superlattice [36]. In terms of amount of copper intercalation, the appearance of these stacking faults coincides with the emergence of superconductivity. This can be seen in figure 4.8 [35]. We can estimate the average distance between stacking faults from our measure of incommensuration. For the sample optimally doped for superconductivity, at \( x = 0.073 \), this average is \( \sim 1/(2\pi\delta) \simeq 22 \) lattice units in the out-of-plane direction. A CDW incommensuration was not observed in the in-plane direction in this experiment due to instrumental resolution, but STM studies have confirmed domain walls within the plane as well [37].

Only the pure TiSe\(_2\) peak was resolution limited, and superlattice reflections broadened with increased intercalation. The inverse linewidth is a good measure of the correlation length, which is shown in figure 4.6 [35].

**Temperature Dependence**

The bottom two panels of figure 4.5 show the CDW persisting for highest doping intercalation. Though the resistivity anomaly is no longer measurable, increased copper content only quantitatively changes the
Figure 4.6: Low temperature inverse linewidths of H and L momentum cuts across the CDW reflection.

CDW. To draw a full phase diagram, we measured the temperature dependence of the order parameter for each of our samples. Figure 4.7 [35] shows representative H-cuts through the superlattice peak at several temperatures for two samples: pure TiSe$_2$ and $x = 0.06$. The intensities are normalized to the direct beam. The integrated intensity of each curve is plotted as a function of temperature and then fitted to the empirical fit (equation 4.1). $T_{CDW}$ for the pure sample was found to be lower than reported in the literature, at 185 K, this is likely due to Se vacancies in the sample. For the plotted Cu-x sample, and all the other copper intercalations, a rounding of the integrated intensities, indicated with an arrow, is seen close to the transition temperature. A residual peak remains above of our $T_{CDW}$ label found using the fit function.

Figure 4.8 summarizes our data in a phase diagram. We see two distinct regions of charge order in it. For lower values of intercalations $x \leq 0.055$, $T_{CDW}$ rapidly decreases and then levels out at higher amounts of copper. This contrasts with our pressure measurements, where the transition temperature does not plateau with increasing pressure. Our incommensuration measurements coincide with the emergence of superconductivity. This agrees with experiments that highlight the importance of domain walls of charge order in the origin of a superconductive phase.

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Figure 4.7: Temperature dependence of H-cuts for the CDW in pure (left) and $x = 0.06$ Cu$_x$TiSe$_2$ (right). Insets plot the normalized integrated intensity for each sample, the red line corresponds to the fitting function used to find the transition temperature.
Figure 4.8: (Top) Degree of incommensuration in the L direction as a function of Cu-intercalation. (Bottom) Completed phase diagram for Cu$_x$TiSe$_2$. The red points in both panels were taken from [19].
4.3 S-Substitution in TiSe$_{2-x}$S$_x$

Studying the TiSe$_{2-x}$S$_x$ system was a natural follow-up to the pressurized TiSe$_2$ experiment. Sulfur and selenium are both part of the chalcogen family. The elements sit on top of each other in the periodic table and have identical atomic valence configuration. Substitution neither electron nor hole dopes our samples. However, having fewer core electrons than selenium, sulfur has a smaller Bohr radius. Se is about 15% larger than S. Replacing Se with a smaller atom makes this substitution act as chemical pressure on the crystal. This affects the c-lattice parameter of the crystal, which shrinks as the presence of sulfur increases (figure 4.9). It has been suggested that increasing sulfur concentration can also raise the conduction band [38].

![Figure 4.9: Room temperature c-lattice parameter of TiSe$_{2-x}$S$_x$ as a function of Sulfur content. This measurement is in agreement with reference [39].](image)

The sulfur series of experiments called for a simpler and more reliable setup than the pressure series. Moreover, compared to the Cu-intercalated samples, a larger portion of the charge order phase diagram can be explored in S-substituted samples. There is a limit to how much copper one can intercalate between the Se-Ti-Se layers, after which the compound does not crystallize. The upper limit of Cu content in Cu$_x$TiSe$_2$ lies at around $x = 0.11$, and sample quality worsens as this boundary is approached. In contrast, there is no limit to the amount of sulfur that can be substituted into our samples. TiS$_2$ crystallizes and can be obtained through the same CVT method used in TiSe$_{2-x}$S$_x$ growths.
4.3.1 Discovery of Superconductivity in TiSe$_{2-x}$S$_x$

We found a previously unreported superconductive phase for some of our TiSe$_{2-x}$S$_x$ samples. Our results are summarized in 4.10. The transition occurs close to the lower temperature limit of our experiment ($\sim 0.5$ K). The measured transition is thus incomplete, but the onset of the SC phase is clear. To establish the onset’s value, two lines were fit on the data: one fit to the points above the transition temperature, and a second one fit to the data below it. We calculated the point of intersection of the two lines and labeled it as the onset of superconductivity. Figure 4.11 depicts this process. Noise in the curves comes from applying a higher current to the sample. It is necessary to get a stable resistivity reading on the chip before cooling down. Using a high current value can accomplish this at the expense of increased noise at low temperatures.

Finding SC in this sample was pretty surprising. Resistivity measurements in S-substituted TiSe$_2$ were reported in 1976 by DiSalvo [25], and later in 1987 by Lopez-Castillo [40]. It is possible the superconductive phase remained hidden because their setup was limited to a 4 K liquid helium base temperature, and superconductivity becomes visible in these samples at around 1 K. The large range of sulfur contents available for TiSe$_{2-x}$S$_x$ could also have contributed to the phase’s elusiveness. As mentioned in the previous chapter, it is possible to observe transition to a charge ordered state through a resistivity measurement. The tools necessary to detect the resistive anomaly in our samples are standard in a laboratory and were readily available in our campus. We began our experiments by trying to reproduce DiSalvo’s. Performing them four decades later on the PPMS gave us the option of using a now common He-3 setup. This technological improvement resulted in a lower base temperature that revealed a superconductive phase.
Figure 4.11: Resistivity measurement showing a superconducting transition of a single sample. Labeling an onset of the superconductive phase is done by fitting two lines to data above (red) and below (dashed black) the transition, and finding their intersection.

Figure 4.12: Resistive anomaly in a sample of $x = 0.05 \text{ TiSe}_2 - x \text{ S}_x$ measured using a PPMS device.
We were able to accomplish our original goal of observing the spike in the resistivity associated with the formation of a CDW, but only for some samples. Figure 4.12 depicts a measurement of this phenomenon. Shape and features of the resistive anomaly vary from batch to batch and sample to sample. Some of our resistivity measurements show an absence of features near the charge order transition temperature. “Sample dependence” in resistivity measurements is well known among dichalcogenide growers. Variation in the anomaly for samples with identical compositions, is likely due to variations in crystal quality. Charge density wave reflections of poor crystals have a reduced magnitude (but not a lower transition temperature), and they can be hard to observe at synchrotrons if they are quite bad. Naturally it is just as difficult, if not more, to measure the resistive anomaly of damaged or poor crystals.

Additionally, DiSalvo et al [25] showed how temperature of the crystal growth affects the phenomenon’s magnitude in TiSe$_2$ (figure 3.3). Two stoichiometrically identical crystals should have the same properties, therefore growth temperature affects the stoichiometry of the samples. Nonetheless, one could still see magnitude variations of the resistive spike in two doped samples with the same measured atomic composition—if the doping homogeneity of the two is different. The CDW is also affected by disorder at the ionic level. It is then not unreasonable that we failed to see the phenomenon for some samples on which the superlattice peaks were measured with x-rays.

4.3.2 X-ray Scattering Data

All the experiments in this section, with the exception of pure TiSe$_2$, were performed at the C-1 line at CHESS. Our datasets consist of simultaneous K and L momentum cuts of the superlattice reflection centered at $Q_{CDW}$ and of a Bragg peak at $2\times Q_{CDW}$. Temperature dependences of these cuts were taken for each of the samples measured. A representative plot of the momentum scans of one crystal is shown in figure 4.13.

To establish $T_{CDW}$ we measure the scattering intensity of the superlattice Bragg peak as a function of temperature. K and L scans depicting these measurements are shown for a, $x = 0.13$, representative sample in the left panels of figure 4.13. The integrated intensity of these curves is shown for every measured S-substitution as a function of temperature in figure 4.14. Though our empirical equation $f(t) = I_0 \left(1 - [(t - \alpha)/(1 + \alpha)]^\beta\right)$ fitted our pressure and Cu-intercalated data, and fits the lower $x$ values for TiSe$_{2-x}$S$_x$ quite nicely, it performs poorly on higher S-substitutions. The rounding observed on the temperature and Cu-$x$ intensity curves near $T_{CDW}$ (inset of figure 4.7, marked by black arrow), returns with a vengeance in S-$x$ samples. Sample heterogeneity becomes more pronounced due to much higher proportions of sulfur in our measured TiSe$_{2-x}$S$_x$ crystals. One cannot superimpose the curves with linear scalings to
Figure 4.13: (Left) In and out of plane cuts of the CDW lattice peak for several temperatures of TiSe$_{2-x}$S$_x$. $x = 0.13$. Intensities are normalized to the direct beam. Color scale qualitatively depicts the temperature. (Right) Temperature dependence of K and L linewidths of the CDW and lattice peak.
Sulfur-substitution mimics pressure (to some extent), but it also introduces disorder. As the composition is tuned from TiSe$_2$ towards TiSeS, rare Se-rich spatial regions can develop inhomogeneously in the sample. A superlattice can form within these pockets, and scatter x-ray photons. Consequently, the global phase transition smears for higher S contents. This kind of quenched disorder would then make the transition temperature nonzero over the entire range of compositions $x < 2$. $T_{CDW}$ is not a well defined quantity, but we still can empirically label the phase transition. To do this we passed a Savitzky-Golay filter through our curves and computed derivatives to find their inflection point. Therefore, one is still able to observe charge order signal above this empirical $T_{CDW}$. These $T_{CDW}$ labels are shown as blue dots in our phase diagram (figure 4.18).

In addition to line cuts, 2-dimensional intensity maps of in-plane and out-of-plane momentum, centered on the CDW reflection, were acquired for each sample at base temperature (figure 4.15). These depict our instrumental resolution, and speak of the effects of disorder in our samples. The Bragg peaks lose their quality as $x$ in TiSe$_{2-x}$S$_x$ increases. This is evident from the elongation of the (117) reflection in the direction of constant momentum transfer, indicating a long range scale disorder in the system. The CDW is expected to and does follow the lattice broadening, losing sharpness in this direction. An additional stretching along the L direction, however, manifests for the CDW as more sulfur is introduced. Sulfur substitution also reduces the superlattice’s correlation length in this direction. The inverse linewidth of a reflection is a good estimate of this quantity. Figure 4.16 shows the evolution of the inverse linewidth for the studied charge order peak as a function of sulfur content.
Figure 4.15: Simultaneous K-L plane cuts of the CDW and lattice Bragg peaks for three different values of sulfur substitution. Dashed red lines mark the direction of constant momentum transfer. A powder ring signal from the sample holder can be seen for the $x = 0.87$ color plot.
Through our harmonic filtering technique, we were able to resolve an incommensurate to commensurate CDW transition in the samples. Figure 4.17 shows this incommensurate parameter for a sample with $x = 0.047$ substitution. There is an appreciable incommensuration for both the in-plane and the out-of-plane directions (top four panels of 4.17). As we go from high to low temperature, the CDW locks-in, and becomes commensurate (bottom panel 4.17). As the amount of S-substitution increases, disorder makes the CDW peak too broad to resolve small incommensurations within error. The CDW domain walls would then be farther apart than the correlation length of the superlattice, a statement meaning that the degree of incommensuration $\delta$ becomes ill defined.

We see once more that our phase diagram shows a incommensurate to commensurate transition at concentrations of sulfur where the superconductive phase appears. Our data is summarized in figure 4.18. A closer inspection of the curves of the samples over the superconductive phase shows an increase of its linewidth at low temperature (figure 4.13). This makes a stronger statement for correlations between superconductivity and the emergence of charge order domain walls.

Finally, we performed preliminary thermal diffuse scattering measurements close to the phase transition temperature. Though we observed no diffuse scattering signal in the pressure experiments, and did not have enough time for these type of measurements in the copper intercalated samples, we saw evidence of thermal diffuse scattering in a $x = 0.047$ sulfur substituted sample. The measured CDW peak for this sample was strong and saturated our detector at low temperature. After obtaining a full temperature dependence for the
Figure 4.17: Measurement of the incommensuration parameter $\delta$ of sample $x = 0.047$. A commensurate to incommensurate temperature dependent transition is evident for both the K and L momentum line scans (top four panels). (Bottom) The incommensuration parameter $\delta$ for both momentum directions as a function of temperature.
Figure 4.18: Phase diagram of TiSe$_{2-x}$S$_x$. Regions marked C-CDW and I-CDW label the commensurate and the incommensurate phase. Yellow circles mark the temperature below which the superlattice correlation length shortens.
sample, we removed the direct beam attenuation and set our temperature controller close to the determined $T_{cdw}$.

2d reciprocal space maps are shown for this sample at low temperature and close to the transition temperature in figure 4.19. The scattering from the CDW elongates in the out-of-plane direction close to $T_{cdw}$. We compare out-of-plane and in-plane scattering in figure 4.20. Line scans at different temperatures in figure 4.21. We were not able to see thermal diffuse scattering in the in-plane direction within our resolution for the sample.
Figure 4.19: Two dimensional reciprocal space scans showing thermal diffuse scattering close to $T_{\text{cdw}}$ in the L direction. The TDS can be seen in the bottom left panel. Scans at base temperature (top panels) and simultaneous Bragg peaks are shown for comparison (right panels). Note the change in scale in the x and y axes between base temperature and $T_{\text{cdw}}$. Red dashed lines pass through $q_{\text{cdw}}$ and mark constant momentum transfer.
Figure 4.20: In-plane and out-of-plane 2d scans of TiSe$_{2-x}$S$_x$, $x = 0.047$, close to the charge order phase transition temperature. TDS is visible in the L-momentum direction, no TDS is apparent in the in-plane scans. Red dashed lines mark direction of constant momentum transfer, some mosaic spread is seen in the CDW bottom left panel.
Figure 4.21: In-plane and out-of-plane line scans of TiSe$_{2-x}$S$_x$, $x = 0.047$, at several temperatures close to the charge order phase transition temperature.
Chapter 5

Conclusions

The overlap of superconductivity and charge order phases in TiSe$_2$ makes it a good candidate to study intertwined order. We measured the effect of three parameters on this system: pressure, copper intercalation, and sulfur substitution. The charge density wave phase diagrams of pressure and copper intercalation established in the literature by resistivity measurements were revised by our x-ray scattering experiments. In particular, we found that a charge density wave persists beyond pressure and Cu concentrations previously thought. The quantum critical point of charge order then lies not within the superconductive region of the phase diagrams, as was believed. In sulfur substituted TiSe$_2$, an unreported superconductive phase was revealed. The CDW in this system was observed well away from the SC phase in the sulfur content axis. Additionally, we employed a harmonic filtering technique to measure small deviations from commensurability between the 2x2x2 superlattice and lattice Bragg peaks. All three phase diagrams showed a commensurate to incommensurate transition close to the pressure, Cu-intercalation, and S-substitution optimal for SC. Our findings suggest that domain walls in the superlattice might be more closely related to emerging superconductivity instead of charge order fluctuations near the quantum critical point.
References


