INELASTIC LIGHT SCATTERING STUDIES OF QUANTUM PHASE TRANSITIONS IN Cu₄TiSe₂ AND MULTIFERROIC TbMnO₃

BY
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DISSERTATION
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Abstract

In this dissertation, inelastic (Raman) light scattering techniques are used to probe the temperature- and magnetic-field-induced phase transitions of two strongly correlated systems – the magnetoelectric multiferroic TbMnO$_3$ and the layered dichalcogenide TiSe$_2$. In general, strongly correlated materials have a strong coupling between charge, spin, lattice and orbital degrees of freedom. Because of the interplay between various competing orders, these systems have highly complex phase diagrams and exhibit interesting phenomena such as colossal magnetoresistance (CMR), high temperature superconductivity and charge/orbital ordering (COO).

Magnetoelectric multiferroics are an important and interesting sub-class of strongly correlated systems. These are systems whose magnetic and electric orders are strongly coupled, thereby showing exquisite tunability of the electric polarization via applied magnetic fields, and vice-versa. One such system is the perovskite manganite, TbMnO$_3$, which shows magnetic-field-tuned rearrangement of the electric polarization vector in the ferroelectric phase below a critical temperature, $T_c \sim 28$ K. This ferroelectric phase transition is accompanied, and in fact caused, by a magnetic phase transition from an incommensurate spiral magnetic arrangement of the Mn$^{3+}$ ions to a commensurate magnetic phase as a function of applied field. We use Raman scattering to carefully probe this magnetic-field-tuned phase transition in microscopic detail. Our measurements indicate that field-induced quantum fluctuations of commensurate domains, which likely drive the field-induced polarization flop in this material, are found near the field-tuned incommensurate-commensurate phase transition.

The second focus of this dissertation is the study of quantum phase transitions in TiSe$_2$ as a function of temperature and Cu-intercalation, and the comparison of
the effects of intercalation and pressure on the charge-density-wave (CDW) order in this system. All these parameters – temperature, pressure and Cu-intercalation – suppress the CDW state in TiSe₂. Our Raman measurements on CuₓTiSe₂ show that the x-dependent mode softening exhibits identical scaling behavior to thermal mode softening in undoped TiSe₂, suggesting that, like thermal mode softening, the x-dependent mode softening is also associated with a critical point. The softening and significant linewidth broadening of the observed CDW amplitude modes indicate strong fluctuations of the CDW. Even more interesting is the emergence of a superconducting (SC) phase – in CuₓTiSe₂ and pressure-tuned TiSe₂ – indicating a likely coexistence of fluctuating CDW and SC phases near the quantum phase boundary.
Dedicated to my dear grandfathers
S. Rangarajan and T.K.V. Thathachari
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Chapter 1

Introduction

One of the primary areas of research in contemporary condensed matter physics is the study of strongly correlated systems. These are materials that typically have unfilled $d$- or $f$-electron shells with strong local repulsion between the electrons. These strong electronic “correlations” result in the interplay between many internal degrees of freedom of the material – lattice, spin, charge and orbital moments – leading to a delicate balance of interactions that gives rise to a rich variety of physical phenomena. Examples of strongly correlated systems include transition-metal compounds such as the manganites [17], high-$T_c$ cuprates [18], vanadates [19], ruthenates [20], and rare-earth hexaborides [21]. Typical phase diagrams that illustrate the complex phase behavior of these strongly correlated systems are shown in Figs. 1.1(a) and (b).

One of the most fascinating properties of many strongly correlated materials is the presence of complex phase transitions, which results from the interplay between various interactions and the competing orders in these systems. These transitions generally involve a change in both the electronic and magnetic states of the system and are often accompanied or driven by self-organization of the charge, spin, lattice and/or orbital degrees of freedom. Strongly correlated materials exhibit exotic phases, such as charge- and orbital-ordered phases – which involve the self-organization of electrons and/or orbitals in patterns that are often commensurate with the atomic lattice – as well as electronically phase-separated phases, in which distinct electronic and/or magnetic nanometer-scale regions coexist and compete. These coexisting phase regions are often associated with “colossal effects”, wherein the physical properties of the material exhibit enormous responses to external perturbations such as applied magnetic fields, electric fields, and pressure.
The most well-known example of the sensitivity of strongly correlated materials to external perturbations is the Colossal Magnetoresistance (CMR) effect in manganites. In the CMR phase, manganites exhibit a change of several orders in resistance in an applied magnetic field, as shown in Fig. 1.1(c), making them a great prospect for applications such as read/write heads in magnetic recording media, sensors, and spin-polarized electronics. Other strongly correlated materials
show similar sensitivities of physical properties to pressure, doping, electric field, etc., and offer great potential for development of novel technologies. In order to effectively utilize the technological potential of strongly correlated materials, it is important to understand the dynamics of the phase transitions in these materials and the microscopic mechanisms that drive these systems to self-organization. However, the challenges to developing a more complete understanding of these materials are two-fold: the complex correlations responsible for the exotic phases observed are difficult to describe theoretically, and effective experimental probes need to provide microscopic information under extreme conditions of low temperature, high magnetic field and/or high pressure.

In this thesis, we use inelastic (Raman) light scattering to probe the phase transitions of two strongly correlated systems – TbMnO$_3$ and Cu-intercalated TiSe$_2$. Inelastic light scattering is unique in its ability to convey simultaneous energy, lifetime and symmetry information about lattice, electronic and magnetic excitations, all of which are generally influenced during complex phase transitions in correlated systems. Consequently, when combined with the ability to tune the phase behavior of the material as functions of temperature, magnetic field, and/or pressure, inelastic light scattering is capable of providing a great deal of microscopic information about quantum phases and transitions. We have developed the unique ability to perform inelastic light scattering experiments under simultaneous conditions of low temperature, high magnetic field and high pressure. This allows us to study the evolution of the elementary excitation spectra through quantum phase transitions in correlated materials, by exploring the manner in which the energies, lifetimes and symmetries of the excitations evolve as functions of temperature, field and pressure.

1.1 Phase Transitions in Strongly Correlated Materials

The strong coupling between lattice, spin and/or orbital degrees of freedom in strongly correlated systems leads to complex phase transitions. For example, in the ruthenate Ca$_3$Ru$_2$O$_7$, the application of a magnetic field causes a change from
an orbital-ordered to an orbital-degenerate phase as a result of the strong spin-orbit coupling. These transitions also explain the field-dependent change in the conductivity of Ca$_3$Ru$_2$O$_7$ [22]. In addition, phase coexistence at the boundaries of phase transitions and the formation of nanoscale clusters is an important feature of strongly correlated materials. Two nearly degenerate states coexist and compete, with a local tendency toward one phase or the other. The application of an external perturbation then favors the ordering of one of these phases, leading to long-range correlations and the previously discussed “colossal” responses. Such phase transitions – via tuning a parameter such as pressure, magnetic field, electric field, etc., – can occur even at $T=0$ and are called quantum phase transitions.

1.1.1 Quantum Phase Transitions

Classical phase transitions are governed by thermal fluctuations. The phase transitions in water (H$_2$O) are the most well-known and typical example of a classical phase transition. These transitions are driven by a competition between thermal energy and the entropy of the system. At absolute zero, the system is expected to be in its lowest energy state (ground state). However, phase transitions in which the ground state of the system is fundamentally altered can still occur, even at $T=0$. These phases have the same microscopic constituents, but have distinct macroscopic properties [23]. Such phase transitions are caused by changing some parameter, $g$, of the Hamiltonian, as shown in Fig. 1.2 – not by varying temperature, but by varying magnetic field, pressure, doping or electric field. When $g\rightarrow g_c$, an excited state of the system becomes the ground state. Examples of quantum phase transitions are plentiful and include the disorder-induced metal-insulator transition in manganites [17], the superconductor-insulator transition in two-dimensional disordered superconductors [24], and pressure-induced magnetic phase transitions in some magnetic insulators [25, 26]. Understanding quantum phase transitions is vital to explaining the exotic emergent phases and interesting phenomena in strongly correlated materials.

At low temperatures, quantum effects dominate thermal effects and the Heisenberg uncertainty principle demands that the system have quantum fluctuations. In
the absence of thermal fluctuations that drive classical phase transitions, it is quantum fluctuations that drive transitions at $T=0$. The shaded region in Fig. 1.2 are regions of the phase space dominated by thermal fluctuations. For temperatures $T \sim 0$, thermal fluctuations become less important as $g \to g_c$, and quantum fluctuations dominate. The influence of these quantum fluctuations is seen in the behavior of the phase transitions and the physical properties of strongly correlated systems, even at finite temperatures. Unlike classical phase transitions, where the critical length scales are macroscopic, the important length scales in quantum phase transitions are microscopic. Quantum fluctuations play an important role at these length scales, as exemplified in SrTiO$_3$, where it is believed that quantum fluctuation effects are responsible for the absence of a low temperature ferroelectric phase [27]. Thus, in order to gain a more complete understanding of quantum phase transitions, it is necessary to clarify the nature of quantum fluctuations across the quantum phase boundaries. Raman spectroscopy is a microscopic probe that is ideal for studying
the dynamical properties of materials through quantum phase transitions.

1.2 The Scope of this Thesis

The two materials studied in this thesis are model systems that exemplify the remarkable properties and complexities of strongly correlated systems, including strong coupling between lattice, spin and electronic orders, charge ordering and emergent phenomena. They also show a strong sensitivity to magnetic fields, doping and pressure.

TbMnO$_3$ is an oxide perovskite that recently revived research interest in a class of materials called magnetoelectric multiferroics [28]. These materials are characterized by a strong coupling between their magnetic and electric orders, so much so that their electric polarization can be tuned via the application of a magnetic field, and vice-versa. This tunability makes magnetic multiferroics exciting candidates for practical device applications such as electrically-controlled magnetic memory and magnetoelectric sensors [9]. In particular, it has been shown that the low-temperature incommensurate magnetic phase in TbMnO$_3$ undergoes a magnetic-field induced transition to a commensurate magnetic phase accompanied by a switching of the direction of electric polarization [28]. In order to achieve greater control over multiferroic materials, it is important to understand the dynamics of the underlying phase transitions.

TiSe$_2$ is a layered dichalcogenide that was extensively studied in order to understand the spontaneous ordering of charge in a charge density wave below 200 K [29, 30]. This order can be “melted” quantum-mechanically by applying pressure [14]. It was recently discovered that intercalation with copper has the same effect on the charge density wave order [16]. In addition, a superconducting phase is seen to spontaneously emerge in both cases [16, 31]. TiSe$_2$ therefore serves as an excellent model system in which to study the quantum transition of an exotic electronic state to a superconducting phase, and to examine the role that critical fluctuations play in driving this transition.

As we will show, Raman spectroscopy provides dynamical information about
the complex phase transitions in these materials and enables us to map out phase
diagrams as a function of temperature, magnetic field, doping and pressure, in
microscopic detail. The distinctly different systems studied in this thesis are a
testament to the diverse applicability of Raman scattering to probe complex phe-
nomena in strongly correlated materials. In the rest of this thesis, I will describe the
theoretical foundations of Raman scattering in solids, and then the experimental
tools used to carry out the experiments in this thesis. Next, I will describe our
results in both TbMnO$_3$ and Cu$_x$TiSe$_2$, before concluding.
Chapter 2

Theory of Raman Scattering

The Raman effect refers to the inelastic scattering of light by molecular and crystal vibrations and gets its name from Sir C.V. Raman, who first observed this effect in liquids. The existence of sidebands in a spectrum of light scattered by a system with two quantized energy levels had been predicted by Smekal in 1923 [32]. Raman’s light scattering experiments on liquids were inspired by his attempts to explain the striking blue of sea water which he observed on his maiden voyage to Europe in 1921.

Raman and his students used telescope objectives to focus sunlight onto their samples and observed the scattered light through a series of complementary filters. During the course of these experiments, they observed, in the scattered light, strongly-polarised peaks that were not originally present in the (filtered) incident light. They initially attributed these peaks to a ‘weak fluorescence’, but soon realized that what they were observing might in fact be the optical analogue of the Compton Effect (which was awarded the Nobel Prize in 1927). A more careful examination of the light scattered from almost 80 different samples, including aromatic, aliphatic and inorganic liquids and vapors, led Raman and his students to conclude that they were observing a new effect, which they initially christened ‘modified scattering’. Their observations were first published in 1928 [33]. The same effect was also observed by Landsberg and Mandelstam in quartz around the same time [34].

The inelastically scattered light can have a frequency greater than or less than the incident light frequency, $\omega$. Scattered light having frequencies $\omega_s < \omega_i$ – where $\omega_s$ is the scattered frequency and $\omega_i$ is the incident frequency – is called the Stokes component of scattered light, and is associated with a gain in the energy $\hbar \omega$ of the
sample, where

\[ \omega = \omega_i - \omega_s \]  \hspace{1cm} (2.1)

Similarly, scattered light having frequencies \( \omega_s > \omega_i \) is called the anti-Stokes component of scattered light, and is associated with a loss in energy \( \hbar \omega \) by the sample, where

\[ \omega = \omega_s - \omega_i \]  \hspace{1cm} (2.2)

It follows, from the above equations, that the scattering medium must have the appropriate energy levels with energy difference \( \hbar \omega \) in order to scatter photons at specific frequencies, \( \omega_s \). Thus, the peaks in the Raman spectrum, shown in Fig. 2.1, correspond to the excitation levels of the medium.

For large scattering samples, the scattering process must also conserve momentum. This is depicted by vector diagrams in Fig. 2.2. The scattering medium gains
momentum $\hbar \mathbf{q}$ for the Stokes component

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s \quad (2.3)$$

where $\mathbf{k}_i$ is the incident photon momentum and $\mathbf{k}_s$ is the Stokes scattered photon momentum. For the anti-Stokes component,

$$\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i \quad (2.4)$$

The differential scattering cross section, $d^2\sigma/d\Omega d\omega_s$, defines the Raman scattering process. It is the rate at which energy is removed from the incident light as a result of scattering in volume, $V$, into the solid angle element $d\Omega$ with a frequency between $\omega_s$ and $d\omega_s$. These quantities are shown in the illustration of an idealized scattering experiment in Fig. 2.3. The scattering cross section is the link between the theory of Raman scattering and a Raman scattering experiment. The next few sections describe the derivation of the differential scattering cross section using two
Figure 2.3: Illustration of an ideal inelastic scattering experiment where light of intensity $I_i$, frequency $\omega_i$ and wavevector $k_i$ is incident on a scattering medium of volume $V$. Light of intensity $I_s$, frequency $\omega_s$ and wavevector $k_s$ is scattered into the detector, whose range of acceptance is limited to the solid angle $d\Omega$ [3].

different methods and discuss how Raman scattering is used to probe elementary excitations. The derivations outlined here closely follow the treatments of Landau and Lifshitz [35], Hayes and Loudon [3] and Lockwood and Cottam [36].

## 2.1 Classical Derivation

In the classical or macroscopic picture, Raman spectroscopy is treated as an electromagnetic phenomena in which light couples to an excitation in a material. The incident light with electric field vector, $E_i$, induces a polarization, $P$, given by

$$P(r, t) = \epsilon_o \chi E(r, t)$$

(2.5)

in the scattering medium. $\epsilon_o$ is the permittivity of free space and $\chi$ is the susceptibility of the medium. This polarization, in turn, produces scattered light whose electric field vector, $E_s$, is described by the driven wave equation, derived from Maxwell’s equations:

$$(\nabla^2 + k_s^2)E_s(r, \omega_s) = -\frac{\omega_s^2}{\epsilon c^2} P(r, \omega_s)$$

(2.6)
where $\epsilon$ is the permittivity of the scattering medium. $k_s = n_s \omega_s / c$ is the wavevector, where $n_s$ is the refractive index of the medium, $\omega_s$ is the frequency of scattered light and $c$ is the velocity of light. When the scattered light is measured far away from the scattering region (where $|r| \gg |r'|$), the solution to the above wave equation is given by

$$E_s(r, \omega_s) = \frac{\exp(ik_s r)}{r} \left( \frac{\omega_s^2}{4\pi \epsilon_o c^2} \right) \int d^3r' \exp(-ik_s \cdot r') P(r', \omega_s)$$

where the integration is over the scattering volume, $V$. The cycle-averaged intensity, $I_s$, of the scattered light with polarization, $e_s$, is given by

$$I_s = 2 \epsilon_o c n_s \langle |e_s \cdot E_s(r, \omega_s)|^2 \rangle$$

The total scattered intensity is obtained from Eqs. 2.7 and 2.8:

$$\bar{I}_s = 2 \epsilon_o c n_s \bar{V} \left( \frac{\omega_s^2}{4\pi \epsilon_o c^2} \right)^2 \int d^3(r_1 - r_2) \exp[i k_s \cdot (r_1 - r_2)] \times \langle |e_s \cdot P^*(r_1, \omega_s)| |e_s \cdot P(r_2, \omega_s)| \rangle$$

where $\bar{I}_s$ d$\Omega$ is the rate at which energy reaches the detector. The differential scattering cross section, which is defined as

$$\frac{d^2\sigma}{d\Omega d\omega_s} = \left( \frac{\omega_i}{\omega_s} \right) \frac{\bar{I}_s}{I_i}$$

can now be calculated by substituting for $\bar{I}_s$ from Eq. 2.9. The prefactor $\omega_i/\omega_s$ accounts for the difference in the rate of loss of energy by the incident beam ($h\omega_i$) and the rate of gain of energy by the scattered beam ($h\omega_s$). Thus,

$$\frac{d^2\sigma}{d\Omega d\omega_s} = \frac{\omega_i \omega_s^2 V}{(4\pi \epsilon_o c^4 n_i |E_i|^2} \int d^3(r_1 - r_2) \exp[i k_s \cdot (r_1 - r_2)] \times \langle |e_s \cdot P^*(r_1, \omega_s)| |e_s \cdot P(r_2, \omega_s)| \rangle$$

Replacing $P(r, \omega_s)$ by the Fourier transform in k-space, we get

$$\frac{d^2\sigma}{d\Omega d\omega_s} = \frac{\omega_i \omega_s^2 V}{(4\pi \epsilon_o c^4 n_i |E_i|^2} \langle |e_s \cdot P^*(k_s, \omega_s)| |e_s \cdot P(k_s, \omega_s)| \rangle$$
The term \( \langle \mathbf{e}_s \cdot \mathbf{P}^*(\mathbf{k}_s, \omega_s) | \mathbf{e}_s \cdot \mathbf{P}(\mathbf{k}_s, \omega_s) \rangle \) is called the pair correlation function. It relates the scattering cross section to fluctuations in the polarization. Any excitation that can modulate the polarization can give rise to inelastic scattering, be it vibrational, rotational, crystal field or electronic excitations. These excitations in the material can be represented by the dynamical variable \( X(\mathbf{r}, t) \). The effect of these excitations is to produce the fluctuating term in the polarization \( \mathbf{P} \), by modulating the susceptibility, \( \chi \), defined in Eq. 2.5. The susceptibility, \( \chi \), is expanded around the static susceptibility, \( \chi_o \), in powers of \( X(\mathbf{r}, t) \), as

\[
\chi_{ij} = (\chi_{ij})_o + \sum_k \left( \frac{\partial \chi_{ij}}{\partial X_k} \right)_o X_k + \frac{1}{2} \sum_{k,m} \left( \frac{\partial^2 \chi_{ij}}{\partial X_k \partial X_m} \right)_o X_k X_m + \ldots \quad (2.13)
\]

Including only the first-order inelastic contribution of the susceptibility in the polarization Eq. 2.12, can be rewritten as

\[
\frac{d^2\sigma}{d\Omega d\omega_s} = \frac{\omega_i \omega_s^3 V n_s}{(4\pi)^2 c^4 n_i} |\mathbf{e}_s \cdot \chi' \cdot \mathbf{e}_i|^2 \langle X(\mathbf{q}, \omega)X^*(\mathbf{q}, \omega) \rangle \quad (2.14)
\]

where \( \chi' = d\chi(\omega)/dX \). This final expression of the scattering cross-section contains several important insights into the inelastic scattering process. It shows that the differential scattering cross section relies not only on the magnitude of the fluctuating susceptibility, but also on the material’s optical response. It is seen that the differential scattering cross-section is proportional to the scattering volume, \( V \), and the ratio of refractive indices of the incident and scattering media, \( n_s/n_i \).

In addition, the differential scattering cross-section also depends on the scattering geometry. This means that by varying the polarization of the incident and scattered light, \( \mathbf{e}_i \) and \( \mathbf{e}_s \), one can couple to different components of \( \chi' \), the Raman tensor. This places restrictions on the allowed symmetries of the scattering cross-section and allows us to identify the symmetry of the excitations in the scattering medium. The use of polarization studies to identify excitation symmetries is a powerful and unique feature of Raman scattering and is described in further detail in Section 2.5. The scattering geometry of a Raman scattering experiment is commonly represented by \( \mathbf{k}_i(\mathbf{e}_i, \mathbf{e}_s) \mathbf{k}_s \), where \( \mathbf{k}_i \) and \( \mathbf{k}_s \) are the wavevectors of
the incident and scattered phonons, respectively, and \( e_i \) and \( e_s \) are their respective polarizations. All our experiments were performed in what is known as the “back-scattering” geometry, which, in this nomenclature would have \( k_i = z \) and \( k_s = -z \), indicating that the incident and scattered wavevectors are directed along the \( z \) and \(-z\) axes, respectively.

### 2.2 Quantum Mechanical Derivation

The microscopic or quantum mechanical description of Raman scattering models the coupling of the scattering medium with the incident light. The calculation of the cross-section is based on the quantum mechanical Hamiltonian that describes the interaction of radiation and matter:

\[
\hat{H} = \frac{1}{2m} \left[ \hat{p} - \frac{e}{c} \hat{A}(r) \right]^2 + e\phi(r) \tag{2.15}
\]

where \( \hat{p} \) is the momentum operator, \( \hat{A}(r) \) is the vector potential and \( \phi(r) \) is the scalar potential.

The scattering cross-section is defined as the rate of removal of energy from the incident beam divided by incident-beam intensity. The rate of removal of energy can be written as \( \hbar \omega_i / \tau \), where \( \tau \) is defined as the rate of transition from the initial to final states. The incident beam energy is given by

\[
\bar{I}_i = \frac{c^2 k_i}{n_i^2 V} N_i \tag{2.16}
\]

where \( N_i \) is the number of photons incident in the scattering volume, \( V \). Using \( k_i c = n_i \omega_i \) and the above expression for \( \bar{I}_i \), the cross-section can now be written as

\[
\sigma = \frac{\hbar \omega_i}{\tau \bar{I}_i} = \frac{n_i V}{\tau c N_i} \tag{2.17}
\]

Thus to calculate \( \sigma \), one needs to determine \( \tau \), which has contributions from interaction terms in the Hamiltonian, defined in Eq. 2.15. The Hamiltonian can be
conveniently divided into three terms:

\[
\hat{H} = \hat{H}_o + \hat{H}'_{ER} + \hat{H}''_{ER}
\]  

(2.18)

where,

\[
\hat{H}_o = \frac{\hat{p}_j^2}{2m} + V(r)
\]  

(2.19)

\[
\hat{H}'_{ER} = \frac{e^2}{2mc^2} \sum_j \hat{A}(r_j) \cdot \hat{A}(r_j)
\]  

(2.20)

\[
\hat{H}''_{ER} = \frac{e}{2mc} \sum_j \hat{A}(r_j) \cdot \hat{p}_j
\]  

(2.21)

\(\hat{H}'_{ER}\) and \(\hat{H}''_{ER}\) constitute the interaction terms of the Hamiltonian and represent the electron-radiation interaction. The former describes the interaction of the radiation field with itself, while the latter describes the interaction between the radiation field and the charge.

The transition probability between the initial state \(|i\rangle\) and a final state \(|f\rangle\) is given by Fermi’s Golden Rule as

\[
W_{i\rightarrow f} = \frac{2\pi}{\hbar} \sum_f |\langle f|H_{int}|i\rangle|^2 \delta(E_f + \hbar\omega_s - E_i - \hbar\omega_i)
\]  

(2.22)

where \(\langle f|H_{int}|i\rangle\) is defined as the \(T\)-matrix. The differential scattering cross-section is calculated from \(W\) as

\[
\frac{d^2\sigma}{d\Omega d\omega_s} = \frac{n_i c}{V} \frac{d^2\langle W\rangle}{d\Omega d\omega_s}
\]  

(2.23)

where \(n_i c/V\) is the photon flux. The final expression for the differential scattering cross-section reads

\[
\frac{d^2\sigma}{d\Omega d\omega_s} = \frac{\omega_i \omega_s^3 V}{(4\pi\epsilon_o)^2 c^4} \sum_f |\langle f|H_{int}|i\rangle|^2 \delta(E_f + \hbar\omega_s - E_i - \hbar\omega_i)
\]  

(2.24)

The \(T\)-matrix for a specific excitation needs to be computed in order to determine the differential cross section. As an illustration, in the following section, we calculate
the differential cross-section for phonons – the excitation most frequently studied in this thesis work – using both classical and quantum mechanical approaches outlined above.

2.3 Phonons

![Feynman diagram for phonon light scattering process](image)

Figure 2.4: Feynman diagram for phonon light scattering process [3].

The normal modes of vibration in a crystal are called phonons. In other words, phonons are quantized lattice vibrations and any dynamic distortion in a crystal can be described in terms of its phonons. Phonons couple indirectly to the light in a third-order process, illustrated in Fig. 2.4, in which an incident light photon creates electron-hole pairs and the excited electron subsequently interacts with the lattice via electron-phonon coupling. The phonon motion can be modeled classically as a driven harmonic oscillator with a natural frequency $\omega_q$, damping rate $\gamma$ and driving frequency $\omega$, from the application of force $F(t)$. The equation of motion for the amplitude $X(r)$ can be written as,

$$X(\omega_q^2 - \omega^2 - i\gamma\omega) = F(\omega)$$  \hspace{1cm} (2.25)

where $F(\omega)$ is the Fourier transform of the generalized force, $F(t)$. The average
displacement, $X$, can be written in terms of the generalized force, $F$, and the linear response function $T(\omega)$,

$$\bar{X} = T(\omega)F(\omega) \quad (2.26)$$

From Eqn. 2.25, the response function can be written as

$$T(\omega) = \frac{1}{\omega^2 - \omega^2 - i\gamma\omega} \quad (2.27)$$

The fluctuation-dissipation theorem relates the power spectrum of the amplitude fluctuations of the dynamical variable, $X$, to the imaginary, or dissipative part of the response function:

$$\frac{1}{2} \langle X^*X + XX^* \rangle = \frac{\hbar}{\pi} \left( n(\omega) + \frac{1}{2} \right) ImT(\omega) \quad (2.28)$$

After substituting for the response function, $T(\omega)$, the differential scattering cross section can be calculated from the above equation:

$$\frac{d^2\sigma}{d\Omega d\omega_s} = \frac{\omega_0^2}{(4\pi^2\epsilon)\epsilon d^4} |e_s^*e^i|^2 \frac{\hbar}{\pi} (n(\omega) + 1) \frac{2\gamma\omega}{(\omega^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (2.29)$$

Eq. 2.29 predicts a Lorentzian lineshape for phonon excitations when using monochromatic light, provided the phonons can be modeled as driven harmonic oscillators. When other degrees of freedom couple with the phonon, additional anharmonic contributions to the imaginary part of the phonon self-energy must be considered. For example, interactions between a phonon and the electron continuum result in a Fano lineshape, which is described by

$$I(\omega) = I_o \frac{(q + \epsilon)^2}{1 + \epsilon^2} \quad (2.30)$$

where $I(\omega)$ is the modified intensity of the phonon, $I_o$ is a constant and $q$ is an asymmetry parameter [37].

For the quantum mechanical description of the phonon scattering process, best summarized by the Feynman diagram in Fig. 2.4, the differential scattering cross
section is computed from the \( T \)-matrix after accounting for time-reversal symmetry. Stated without proof, the \( T \)-matrix for this process is given by,

\[
T = \sum_{i_1,i_2} \frac{\langle f | H_{ER} | i_1 \rangle \langle i_1 | H_{ER} | i_2 \rangle \langle i_2 | H_{EP} | i \rangle}{(E_i - E_1 - \hbar \omega_i - \hbar \omega_{ph})(E_i - E_2 - \hbar \omega_i)}
+ \frac{\langle f | H_{ER} | i_1 \rangle \langle i_1 | H_{EP} | i_2 \rangle \langle i_2 | H_{ER} | i \rangle}{(E_i - E_1 - \hbar \omega_i - \hbar \omega_{ph})(E_i - E_2 - \hbar \omega_i)}
+ \frac{\langle f | H_{EP} | i_1 \rangle \langle i_1 | H_{ER} | i_2 \rangle \langle i_2 | H_{ER} | i \rangle}{(E_i - E_1 - \hbar \omega_i - \hbar \omega_{ph})(E_i - E_2 - \hbar \omega_i)}
\] (2.31)

where \( H_{ER} \) is the electron-radiation interaction Hamiltonian, \( H_{EP} \) is the electron-phonon interaction Hamiltonian and \( i_1 \) and \( i_2 \) are intermediate states.

### 2.4 Soft Modes and Critical Fluctuations

When a solid undergoes a structural phase transition, at a critical temperature \( T_c \), from one crystal structure to another, the transition is very often characterized by the anomalous behavior of the frequency, linewidth and/or intensity of a phonon. In particular, a phonon which becomes unstable, and whose frequency, \( \omega \), exhibits an anomalous decrease as a structural phase transition is approached with changing temperature, is called a soft mode. The phonon softening is a result of a temperature-dependent renormalization of the phonon frequency that is brought on by anharmonic interactions in the crystal that drive the transition. The renormalization conditions and damping parameters represent the relation between the static and dynamic properties of the system.

The eigenvector of a soft mode mimics the lattice distortion and is important in determining the new structure of the crystal below \( T_c \). The soft mode serves as the order parameter for second-order structural transitions, which proceed by a continuous distortion. The frequency of the soft mode in a second-order transition goes continuously to zero, as shown in Fig. 2.5.

The soft mode and its fluctuations are of vital importance in describing a structural phase transition. Systems exhibit spontaneous fluctuations about the equi-
Figure 2.5: Temperature dependence of soft-mode frequency for a second-order phase transition below the critical temperature, $T_c$.

librium state, which are brought about by inherent thermal motion in the classical regime and are explained by the uncertainty principle in the quantum regime, $\hbar \omega \gg kT$. These spontaneous fluctuations are characterized by the so-called noise spectrum, which contains information about the spatial and temporal behavior of the fluctuations. The noise spectrum is found to be related to the dynamic response of the system to external perturbations via the fluctuation-dissipation theorem. Thus, measuring the noise spectrum can give information about the system’s response to external perturbations that may be hard to produce experimentally [5].

Fig. 2.6 shows the process by which a fluctuation, $x_q(\omega)$, scatters light inelastically. It follows that Raman scattering can be used to measure the noise spectrum directly. For measurements at a given wavevector $q$, the noise spectrum describes the temporal behavior of the fluctuations at that wavevector. The fluctuation spectrum of a soft mode near a phase transition would show that the corresponding
peak in the noise spectrum moves towards $\omega=0$, while its height goes to infinity and its width tends to zero. This indicates that the “critical fluctuations” in the system attain a macroscopic size and drive the system to the new phase as the phase transition is approached [5].

\subsection{Soft Modes and the Charge Density Wave Transition}

“Phasons” and “amplitudons” are examples of soft modes. They are excitations of a ground state called the charge-density-wave (CDW) state, which is a periodic charge density modulation that is accompanied by a periodic lattice distortion [38]. The CDW state is frequently observed in low-dimensional materials at low temperatures, because the low dimensionality enhances the electron-phonon interactions, resulting in the development of a CDW ground state. To form a CDW state, the energy gain due to the modulation of the charge density has to be greater than the energy lost in deforming the lattice in order to minimize the free energy of the system and allow the transition to the CDW phase. The periodic lattice distortion results in the opening of an energy gap at the Fermi surface ($k=\pm k_F$), thus reducing the total electronic energy. This compensates for the increased elastic energy caused by the
spontaneous ordering. The phase transition to the CDW state occurs at an onset temperature, $T_{CDW}$. The dichalcogenide $1T$-TiSe$_2$, studied in this work, has quasi-two dimensional character and is known to transition to a CDW ground state at $T_{CDW} \sim 200$ K.

In the mean-field approximation, the charge density wave gap in a CDW system approaches zero as $T \to T_{CDW}$ and the temperature dependence is described by

$$\frac{\Delta(T)}{\Delta(0)} = \Delta_0 \left(1 - \frac{T}{T_{CDW}}\right)^{1/2}$$  \hspace{1cm} (2.32)

The CDW gap, $\Delta$, acts as the order parameter of the phase transition,

$$\Delta = |\Delta| e^{i\phi}$$  \hspace{1cm} (2.33)

where $|\Delta|$ is the amplitude of the order parameter and $\phi$ is the phase. Oscillations of the amplitude and phase of the order parameter are associated with excitations which are called amplitudons and phasons, respectively. The amplitude mode is Raman active and serves as an excellent means to probe the evolution of the CDW state using Raman spectroscopy. Its frequency exhibits a temperature dependence given by $\omega_o(T) \sim (1 - T/T_{CDW})^\beta$, where $\beta$ is a critical exponent [39].

### 2.5 Symmetry Selection Rules

The symmetry of a given excitation can be determined from the expression for the differential scattering cross section in Eq. 2.14. The term $|e_s \cdot \chi' \cdot e_i|$ is required to be invariant under the group symmetry operations of the scattering crystal by Neumann’s principle. The incident and scattered light polarizations, $e_i$ and $e_s$, transform like polar vectors and are described by the three-dimensional polar-vector representation $\Gamma_{PV}$ of the scattering crystal’s point group. The excitation symmetry is defined by the irreducible representation $\Gamma_x$, which describes the spatial properties of the excitation. It follows from Neumann’s principle that only the excitation symmetries $\Gamma_x$ that are contained in the decomposition of $\Gamma_{PV} \times \Gamma^*_{PV}$ are non-zero in
a Raman scattering measurement. In other words, only excitations that satisfy this condition can scatter light in the Raman process. In addition, Neumann’s principle places constraints on the components of the allowed Raman tensors, requiring some of them to vanish and for others to be related. The matrix elements for the different crystal point groups have been computed and listed in several references [3, 40]. To illustrate, we list, in the sections below, the Raman tensors and the allowed modes for the perovskite manganite, TbMnO$_3$, and dichalcogenide 1T-TiSe$_2$, on which the experiments described in this thesis were performed.

2.5.1 TbMnO$_3$

Oxide perovskites have the general chemical formula ABO$_3$, where A and B are cations of different types that bond to the O$^{2-}$ anion. The ideal perovskite structure, which has cubic symmetry, belongs to the space group $Pm\bar{3}m$. All its atoms are at centrosymmetrical sites and there are no Raman allowed modes for this structure. TbMnO$_3$ is an orthorhombically distorted perovskite which is described by the $Pnma$ space group at room temperature. Some texts represent the TbMnO$_3$ structure with the $Pbnm$ space group, which is simply a non-standard representation of $Pnma$. $Pnma$ designates lattice parameters according to the condition $a>b>c$, whereas, in $Pbnm$, $b>c>a$.

As mentioned previously, the allowed phonon modes in a crystal can be computed from its space group symmetry. The crystal symmetry is determined from x-ray scattering and the site-symmetry of each species of atom is found. In the case of TbMnO$_3$, the Tb ions have site symmetry $C_s$, the two non-equivalent oxygen ions, O1 and O2 have site symmetries $C_s$ and $C_1$, respectively, and the Mn ions have site symmetry $C_i$. The Raman tensors for these symmetry groups are listed in Table 2.1 where, the missing elements have zero values and the lettered elements represent different non-zero values. Equal components are indicated by the occurrence of the same letter.

Using these tables, it is possible to calculate the scattering geometry needed to probe a specific excitation:

$$z(x', x')\bar{z} : A_g + B_{2g} \quad (2.34)$$

22
\[ z(x, x) \hat{z} : A_g \]  
(2.35)

\[ z(x', z') \hat{z} : A_g(\text{weak}) \]  
(2.36)

\[ z(x', y) \hat{z} : B_{1g} + B_{3g} \]  
(2.37)

\[ z(x, z) \hat{z} : B_{2g} \]  
(2.38)

where \( y \) coincides with the \( b \)-axis of the crystal and \( x' \) and \( z' \) are two mutually orthogonal directions in the \( ac \) plane, rotated by 45° with respect to the crystallographic axes [7].

Conversely, the symmetries of specific excitations can also be calculated using the correlation method, which can predict the phonons allowed in Raman, infrared and acoustic methods. The correlation method can be written mathematically as [41]

\[ \Gamma_{\text{allowed}} \Gamma_{\text{site}}(T_x, T_y, T_z) = \sum C_R \Gamma_{\text{space}} \]  
(2.39)

where the allowed phonon symmetries are found in expansions of the site group irreducible representations which transform like translation vectors \((T_x, T_y, T_z)\). Calculations based on the correlation method predict that the Raman-allowed phonon modes in \( \text{TbMnO}_3 \) are [7]:

\[ \Gamma_{\text{Raman}} = 7A_{1g} + 5B_{1g} + 7B_{2g} + 5B_{3g} \]  
(2.40)

Below \( T_N \sim 42 \) K, \( \text{TbMnO}_3 \) undergoes a magnetic phase transition to an antiferromagnetic (AFM) phase in which the Mn ions are sinusoidally modulated. A second magnetic transition to a spiral magnetic phase has also been observed below \( T_c \sim 28 \) K. The modulation in both phases is incommensurate with the underlying lattice periodicity. This means that no two atoms are displaced by the same distance from their positions in the undistorted phase. New modes in the Raman spectrum have been observed in the incommensurate phases of many materials [42, 43]. In addition, Sousa and Moore [44], using a phenomenological Landau theory framework, explain how the incommensurability of the magnetic ordering can result in the appearance of magnetodielectric resonances in the optical spectra of multifer-
Indeed, we observe new modes in the Raman spectrum that appear below the Néel temperature, $T_N$. These modes are discussed in greater detail in Section 4.2.1.

### 2.5.2 1T-TiSe$_2$

The dichalcogenide, 1T-TiSe$_2$ crystallizes in the D$_{3d}^3$ symmorphic space group, with the Ti ions having a site symmetry D$_{3d}$ and the Se ions having a site symmetry C$_{3v}$. The Raman tensors for these point groups are listed in Table 2.2.

The excitation symmetries that can be probed in the different scattering geometries are found, by calculating $(\mathbf{e}_i \cdot \mathbf{\Gamma} \cdot \mathbf{e}_s)$ using the Raman allowed tensors $\mathbf{\Gamma}_x$ associated with the point group D$_{3d}$, to be,

$$z(x, x) \bar{z} : A_1g + E_g$$

(2.41)
Table 2.2: Raman tensors for $D_{3d}$ and $C_{3v}$

\[
\begin{align*}
D_{3d}: & \quad \begin{pmatrix}
a & a \\
b & b
\end{pmatrix} \quad \begin{pmatrix}
d & -d & e \\
e & -d & -e
\end{pmatrix} \\
& \quad A_{1g} \quad E_g \\
C_{3v}: & \quad \begin{pmatrix}
a & a \\
b & -c
\end{pmatrix} \quad \begin{pmatrix}
d & d & e \\
e & -d & -e
\end{pmatrix} \\
& \quad A_1 \quad A_2 \quad A_{1g}
\end{align*}
\]

\[z(x, y) \vec{z} : E_g \quad (2.42)\]

Using the correlation method for the normal state of $1T$-TiSe$_2$ it can be shown that allowed optical modes are,

\[\Gamma = A_{1g} + E_g + A_{2u} + E_u \quad (2.43)\]

The $A_{2u}$ and $E_u$ modes are infrared active and the only modes expected in the Raman spectrum are the $A_{1g}$ and $E_g$ modes, both of which involve displacements of the Se ions.

The low-temperature, charge-density-wave (CDW) state of $1T$-TiSe$_2$, described in Section 2.4 above, belongs to the nonsymmorphic space group $D_{3}^{4}$, with two non-equivalent groups of Ti ions having site symmetries $D_3$ and $C_2$ and two non-equivalent Se ions having site symmetry $C_1$ and $C_3$. The corresponding Raman tensors can be found in Ref. [3]. Again, applying the correlation method, one can
show that the Raman-allowed modes in this CDW state of $1T$-TiSe$_2$ are

$$
\Gamma_{Raman} = 4A_{1g} + 11E_g,
$$

(2.44)

However, only about 5 of these new modes are observed in our experiments, as will be seen in Section 5.3. The other modes may be too weak to detect with our system.
Chapter 3
Experimental Details

3.1 Raman System

The Raman scattering system used to make our measurements is described in this chapter. Figure 3.1 shows the key components of our Raman scattering system. It consists of an excitation source, incident and collection optics, a spectrometer and a detector. Our Raman system also is distinguished by a unique capability that allows simultaneous and independent control of the temperature, magnetic field and pressure of the sample environment, simultaneously but independently. The functions of all these different elements of our system are explained in detail in the following sections.

3.1.1 Excitation Source

Lasers are the light source of choice for Raman scattering experiments. They made obsolete discharge lamps and other excitation sources that were used in the past, because they have several properties that make them better suited to Raman measurements. These include:

- **High Intensity**: Raman scattering is an inherently weak process and a high powered excitation source makes it easier to detect and monitor weak excitations.
- **Monochromaticity**: Lasers have a very narrow bandwidth and since Raman peaks are measured as the energy difference from the exciting wavelength, a highly monochromatic source ensures better data quality.
- **Tunability**: Frequency selection allows the determination of the spectral range and is particularly useful in resonance Raman measurements when the frequency
Table 3.1: Major operating wavelengths of the Innova-90K krypton-ion laser.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>476.2</td>
<td>0.05</td>
</tr>
<tr>
<td>482.5</td>
<td>0.03</td>
</tr>
<tr>
<td>520.8</td>
<td>0.07</td>
</tr>
<tr>
<td>530.9</td>
<td>0.20</td>
</tr>
<tr>
<td>568.2</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>647.1</strong></td>
<td><strong>0.50</strong></td>
</tr>
<tr>
<td>676.4</td>
<td>0.12</td>
</tr>
<tr>
<td>752.5</td>
<td>0.10</td>
</tr>
</tbody>
</table>

of the source needs to be chosen such that the incident light energy coincides with an electronic transition of the sample, thus greatly enhancing the scattered intensity from vibrational modes associated with that transition.

- **Collimation:** Laser light is highly collimated. This allows the beam to be directed easily over long distances with little dispersion. This also enables the light to be focussed to a rather tight spot and is very useful in probing very small samples (<1 mm²).

- **Polarization:** Finally, laser light has a definite polarization, which can be subsequently manipulated, in order to probe a specific excitation symmetry. A more elaborate discussion of this property follows later in this section.

We used a water-cooled, model Innova-90K, krypton-ion laser made by Coherent Inc., to make all our measurements. It is a continuous wave (CW) gas laser, whose major operating wavelengths are listed in Table 3.1. We used the 647.1 nm line with an output power of 5–10 mW in our work. Some disadvantages of gas lasers are that they produce plasma lines that appear in and confuse the detected signal, and they are bulky and expensive; however, these drawbacks are outweighed by their merits – these lasers can be operated at relatively high powers with very good power stability and emit many discrete wavelengths that allow greater tunability.
Figure 3.1: Schematic illustration of a Raman scattering system comprising of a prism monochromator (PM), a spatial filter (SF), a polarization rotator (PR), a polarizing beamsplitter (PB), a Berek compensator (B), a polarization analyzer (PA), lenses (L_1 and L_2), mirrors (m_1, m_2 and m_3) and a CCD detector.

3.1.2 Optics

The entrance and collection optics, shown in Figure 3.1, reject unwanted laser light and optimize the detected Raman signal. The functions of the different components are described in detail below:

- **Frequency selection**: The function of a monochromator is to filter out the unwanted plasma lines and any adjacent lasing frequencies that may be emitted by the laser. These plasma lines will not only appear in, and confuse, the spectrum, as mentioned above, but can also excite the sample and cause spurious lines to appear. We use a prism monochromator (PM) which is continuously tunable over a wide range of wavelengths (400–900 nm). It allows 75% transmission and has a very narrow bandpass of ~1 nm in this wavelength range.
- **Light Path**: Mirrors (M1, M2 and M3) are used to direct the beam to
the sample. Light from the monochromator is passed through an attenuator (A), which is used to adjust the laser power to the desired level. The lens L1 doubles up as the entrance lens (L1) as well as the collection lens in this configuration, also called the backscattering configuration. L1 focusses the incident laser light - to a spot size of \( \sim 50 \, \mu m \) - onto the sample. L1 also collects the scattered light and directs a collimated beam to the spectrometer, for which purpose it is required to have very low spherical and chromatic aberrations. The spectrometer coupling lens (L2) focusses the light scattered from the sample onto the entrance slit of the spectrometer. L2 is chosen to have an f/# – a number that provides a measure of the light collecting ability of an optical system – that matches that of the spectrometer, to optimize the throughput. An improper choice of lens leads to loss of photons and increased stray light by underfilling or overfilling the gratings.

- **Selecting Polarization:** The polarization dependence of an excitation gives clues that facilitate accurate identification of the excitation’s symmetry. This feature, which is unique to Raman scattering, arises because the polarizations of the incident and scattered beams couple to specific components of the Raman tensor, as discussed in section 2.5. The polarization dependence of an excitation is studied by using polarizers and other optics to adjust the polarization of both the incident and scattering light. A polarization rotator (PR) is used to select the incident polarization and a polarizing beamsplitter (PB) is used to selectively transmit the p-polarized component, producing a clean beam of linearly polarized light.

Our experiments often employ a magnetic field, which can destroy the linear polarization of light because of Faraday rotation effects. To circumvent this problem, we use a Berek compensator to produce a circularly polarized incident beam. The Berek compensator consists of a single plate of uniaxial material whose extraordinary axis is perpendicular to the plate. At normal incidence, light passes through the plate unchanged. If the Berek compensator is tilted so that the incident light is no longer at normal incidence, the component of the light polarized along the direction of incidence is retarded while the component of
light polarized perpendicular to the direction of incidence is not retarded. The amount of retardation depends on the angle of tilt and the wavelength of the light. Thus, by varying the tilt appropriately, it is possible to adjust the output polarization.

The polarization of the scattered beam is controlled by a polarization analyzer (PA), which is adjusted such that the polarization of the beam entering the spectrometer falls along the grating’s most efficient direction. Knowledge of the scattered beam’s polarization is also necessary to identify the excitation symmetry when performing polarization-dependent measurements.

### 3.1.3 Triple Stage Spectrometer

Light scattered off the sample is collected and directed to the spectrometer, whose function is to extract the inelastically scattered light (by effectively rejecting the more intense elastically scattered light) and to disperse it onto a detector. A schematic of the home-made, triple stage spectrometer used in our measurements is shown in Figure 3.2. The first two stages are identical Czerny-Turner Acton Research AM-503 spectrometers which are set in a “subtractive-dispersion” mode. In this mode, the dispersive action of the gratings are arranged so as to cause no net dispersion, but rather to reject unwanted stray light and act as an excellent bandpass filter. The final stage is a Czerny-Turner Acton Research AM-505 spectrometer, which disperses the light onto a mirror, which then projects a flat image onto the CCD detector.

The spectral resolution of the spectrometer is defined, in this subtractive mode, primarily by the final stage grating. It is useful to understand how these gratings function in order to better optimize the system’s resolution, and we begin by looking at the grating equation, which describes the angular distribution of light from the grating shown in Fig 3.3:

\[ m\lambda = d(sin\phi + sin\theta) \]  

(3.1)

where \( \lambda \) is the wavelength of the incident light, \( \phi \) is the angle the light makes with the normal to the grating surface, \( \theta \) is the angle the diffracted light makes
Figure 3.2: Illustration of a triple stage subtractive spectrometer, based on the layout of a Spex 1877 Triplemate [6]. The gratings G1-G3 disperse the light which is guided by mirrors through the various stages. The slits S1-S3 act as stray light filers, that control the light entering and exiting the different stages.

with the grating normal, \( d \) is the line spacing of the grating, and \( m=0,1,2, \ldots \) is the order of the diffracted light. For fixed incident angle of the light, the angular dispersion is obtained by differentiating Eq. 3.1 with respect to wavelength \( \lambda \) [45].

\[
\frac{\partial \theta}{\partial \lambda} = \frac{m}{d \cos \theta}
\]  

(3.2)

From this, one can obtain the linear dispersion of the spectrometer in the focal
Figure 3.3: Diffraction by a multiple slit aperture or grating. The spacing of the gratings is denoted by \( d \). \( \phi \) is the angle of incidence of the light and \( \theta \), the angle of diffraction.

It is given, quite simply, by

\[
\frac{\partial h}{\partial \lambda} = f \frac{\partial \theta}{\partial \lambda}
\]  

(3.3)

where \( f \) is the focal length of the exit mirror. It follows from Eq. 3.2 and 3.3 that the dispersion and consequently, the resolution, depend inversely on the grating spacing and the focal length. Our third stage monochromator has a focal length of 0.66 m. However, the resolution of the spectrometer is ultimately limited by the resolving power of the grating, which can be derived, starting from its intensity distribution function [46], as

\[
RP = \frac{\lambda}{\partial \lambda} = N m
\]  

(3.4)

where \( N \) is the number of grooves. The gratings in our system are blazed so that the diffracted light intensity primarily goes into the first order (\( m=1 \)) response; therefore, the resolving power is determined by the number of grooves or, for a grating of fixed width, the groove density. The greater the groove density, the greater the resolving power. We use a 1800 grooves/mm grating in conjunction with the 647.1 nm Krypton-ion laser to optimize the spectral resolution.

Another important consideration in the overall effectiveness of the spectrometer
is throughput, i.e., the amount of light incident on the system that is ultimately transmitted to the detector. The throughput of the spectrometer – which depends on both the wavelength and polarization of the incident light – needs to be maximized to optimize the measured intensity of the Raman spectrum. For the 647.1 nm light source used in our experiments, light polarized perpendicular to the grating rulings results in better transmission; this condition is achieved by appropriately adjusting the polarization analyzer, as discussed in the previous section.

3.1.4 Detectors

Since Raman signals are inherently weak, recording them requires efficient detection. Historically, the first detectors used in Raman scattering experiments were photographic plates. They were cumbersome and time-consuming and were replaced by photo-multiplier (PM) tubes, which convert photons into an electric signal.

These tubes contain a cathode with a photo-emissive surface that emits electrons when photons strike it, followed by a series of dynodes that emit several secondary electrons for every electron that strikes them. This produces a large current on the order of $10^6$ electrons which are collected as an output signal by an anode. The detection is done for each frequency and the entire spectrum is obtained by scanning through the frequency range of interest. PM tubes have high sensitivity, low background and are very reliable. However, their response is not linear and the process of scanning over the entire frequency range is time-consuming and poorly suited to the study of dynamic systems. Multichannel detectors, such as the intensified photodiode array, are more useful in this case, as they can simultaneously detect Raman signals over the entire frequency range.

These days, however, the charge-coupled device (CCD) detector is a popular choice for Raman detection systems because of its higher quantum efficiency, lower readout noise and sensitivity over a wider frequency range. The CCD is an analog, metal-oxide semiconductor (MOS) device. The chip consists of a doped silicon base that is coated with a silicon dioxide layer and topped with another doped polysilicon layer. The surface of the CCD is divided into pixels or picture elements, each of which represents one tiny piece of the imaged object. The resolution of the
A spectrometer is limited by the size of these pixels, since the pixel dimension defines the smallest amount of linear dispersion that can be detected.

When light strikes the chip, photons with energies greater than the bandgap will create electron-photon pairs. A positive sine-shaped potential applied via an array of electrodes repels the holes to the base and captures the electrons in the potential well. Manipulating the electrode voltages suitably enables the transfer of the collected charge in each pixel to a data processing device, one pixel at a time, where it is converted to a voltage and measured using a load resistance. This output is converted to a digital signal that is integrated over time, from which a profile of photon intensity vs pixel can be generated.

To obtain the best possible results, care must also be taken to eliminate or reduce noise. The possible noise sources include:

- **Electronic noise**, which refers to the uncertainty in the number of electrons counted by the detector. This uncertainty can be caused both by lack of reproducibility in the process of analog-to-digital conversion and by random, unwanted signals from the sensor or electronics that get added to the pixel charge. Altering the gain of the electronics and increasing the signal-to-noise ratio by increasing the exposure time can help reduce such noise.

- **Electrical noise**, or the “dark count” of the detector, which is caused by generation of charge in the pixels due to thermal activation. Lowering the temperature of the detector is an effective way of mitigating noise from this source.

In addition to the above sources of noise, the CCD is also sensitive to cosmic rays. These are recorded as random spikes in the spectrum, seldom on the same pixel, and can, therefore, simply be identified and subtracted out by taking more than one set of data.

In our experiments, we used a Princeton Instruments LN/CCD, composed of a 1340 x 400 imaging array of 20 µm x 20 µm pixels, to record data. The CCD was cooled to $-110^\circ$C using liquid nitrogen to reduce electrical noise. Liquid nitrogen cooled CCD detectors (LN/CCDs) are ideal for low to ultra-low light level applications requiring very long integration times. They have a wide spectral range, a high dynamic range, high thermal and temporal stability, and excellent geometric
accuracy and stability.

### 3.1.5 Sample Environment

To spectroscopically probe the complex phases and transitions of strongly correlated materials, in addition to the highly efficient spectroscopic system, we need a sample environment that can be tuned to any desired region of the sample’s phase space. Most often, the phases of interest in these systems are at extremely low temperatures and the quantum phase transitions are induced by the application of high magnetic fields or pressures. Accordingly, our system has the unique ability to tune – simultaneously, but independently – the following three variables: temperature, magnetic field and pressure.

The sample itself is initially mounted in a pumped vacuum space to eliminate any Raman lines that may be excited by air molecules. Temperature control of the sample is achieved by means of a pumped Oxford continuous-flow cryostat. The sample space is cooled with liquid helium forced through a needle valve down to a temperature of 3 K. The sample temperature can be precisely controlled in the 3–300 K range, either by altering the helium flow or by applying a voltage across a carbon resistor.

The cryostat itself is mounted horizontally in the open bore of an Oxford superconducting magnet. This unique arrangement was chosen in order to overcome the limitations of traditional bath cryostats. In the conventional arrangement, the large separation between the sample and collection optics restricts the f/# of the collection lens used, which restricts throughput and makes the system unsuitable for studying weak excitations. In our arrangement, however, it is possible, as shown in Figure 3.4, to place the collection optics as well as the cryostat in the open bore of the magnet. This allows the use of an achromatic, 70 mm focal, collection lens with a large f/# of 1.4, allowing us to effectively study the field dependence of weak excitations.

The superconducting magnet is capable of generating fields as high as 10 Tesla. The sample can be mounted on the sample rod in two different geometries, as shown in Figure 3.4. When it is affixed directly to sample rod, magnetic measurements
Figure 3.4: The two configurations of mounting samples for magnetic field-dependent measurements: (a) Faraday (q∥H) and (b) Voigt (q⊥H) geometries.

are made in the Faraday geometry (q∥H), as shown in Figure 3.4(a), where \(q\) is the wavevector of the incident light and \(H\) is the direction of the magnetic field. Alternatively, the sample can be mounted on an 8-sided polygon, one side of which is mounted on the sample rod along with a 45° mirror, as shown in Figure 3.4(b). This allows us to make in-plane magnetic measurements in the Voigt geometry (q⊥H). Rotating the octagon on its side enables the field direction in one plane of the material to be varied in 45° increments.

Our system is also equipped with the unique ability of making pressure measurements using a miniature cryogenic diamond anvil cell (MCDAC), which fits into the cryostat in the magnet’s open bore as shown in Figure 3.5. The DAC is made
of beryllium copper, which has high thermal conductivity and is non-magnetic. The DAC contains a pair of anvils, which exert hydrostatic pressure on the sample through a pressure transmitting medium such as argon or helium. The anvils also double as optical windows through which incident and scattered light is transmitted to and from the sample; therefore, the optical properties of different anvil materials need to be carefully considered when choosing suitable anvils. We commonly use moissanite (6H-SiC) anvils in our experiments. Moissanite is a good choice since it is chemically inert and transparent in the wavelength range of our experiments. It cannot match diamond’s hardness, but can withstand pressures up to 300 kbar [47], which meets our experimental requirements. Moissanite is much cheaper than diamond, making it affordable to buy high quality anvils with far fewer impurities. Using better quality anvils reduces fluorescence from the anvil which could overwhelm the Raman signal from weak excitations of the sample.

The hydrostatic medium is held trapped in the cell by means of a metal gasket fitted between the anvils. The use of a gasket also enables higher pressure to be achieved by providing massive support to the edge of the anvils [48]. Also enclosed between the anvils is a small piece of ruby, whose $R_1$ and $R_2$ fluorescence lines have been calibrated and shown to be linear below pressures of 200 kbar for the entire temperature range of our experiments [49, 50, 51]. Measuring the ruby line gives a fairly accurate estimation of the pressure in the cell, allowing the pressure to be monitored in-situ. Pressure is generated outside the cryostat by means of a hydraulic ram that pulls on cables wrapped around the end of the MCDAC, allowing the pressure to be varied even at low temperatures or high fields.

### 3.2 Sample Preparation

#### 3.2.1 TbMnO$_3$

The single crystal samples of TbMnO$_3$ used in our experiments were grown by our collaborators at the Hahn-Meitner Institut in a floating zone image furnace under an Ar atmosphere. The phase purity of this crystal was checked by crushing, and performing X-ray and neutron diffraction measurements on a small part of, the
Figure 3.5: Schematic illustration of the sample environment, that enables independent and simultaneous control of temperature, magnetic field and pressure. The sample is mounted between anvils in a MCDAC which is inserted into a continuous flow cryostat. The cryostat is mounted horizontally inside the bore of a superconducting magnet.

The resulting diffraction patterns indicate that the sample was single phase orthorhombic, while specific heat measurements on the same sample indicate three successive transitions with decreasing temperature at $T_N(Mn)=41$ K, $T_c=29$ K and $T_N(Tb)=7$ K, in good agreement with published measurements.

3.2.2 Cu$_x$TiSe$_2$

Undoped and Cu-intercalated single and polycrystalline samples of TiSe$_2$ were provided to us by E. Morosan and R. Cava from Princeton University. To prepare the polycrystalline, pressed-pellet samples of Cu$_x$TiSe$_2$ ($0 \leq x \leq 0.06$), stoichiometric amounts of elemental powders were sealed in evacuated silica tubes and heated from room temperature to 350°C in about 1 hour. The temperature was then increased
at 50°C/hr to 650°C, after which it was maintained at 650°C for 20 hours. The powders were then pressed into pellets, re-sealed in silica tubes under vacuum, and annealed at 650°C for 50 hours. Homogeneous, purple-grey pellets were obtained. Powder X-ray diffraction measurements were employed to characterize the samples.
Chapter 4

Field-Tuned Quantum Phase Transitions in Multiferroic TbMnO$_3$

TbMnO$_3$ is one of several multiferroic materials in which strong magneto-elastic coupling results in an interaction between magnetism and ferroelectricity, and in particular in magnetic-field-induced rearrangements of the polarization vector [11, 28]. The possibility of controlling the electric polarization via applied magnetic fields and magnetization using applied electric fields in these materials makes them technologically attractive. A deeper insight into the microscopic details of the magnetic-field-induced transitions in multiferroic materials would help realize their technological potential effectively. In this chapter, I will present the results of our temperature- and magnetic field-dependent inelastic light scattering studies of TbMnO$_3$. By carefully examining the evolution of magneto-elastic modes in various phases of TbMnO$_3$, our studies allow us to map out the temperature and field phase diagram, and reveal several features of the field-induced incommensurate-commensurate (IC-C) transition in TbMnO$_3$.

4.1 Phase Transitions in TbMnO$_3$

TbMnO$_3$ has a distorted orthorhombic perovskite structure, as shown in Fig. 4.1(a). The low-temperature magnetic and orbital structures of TbMnO$_3$, schematically depicted in Fig. 4.1(c), are best understood by examining the structures of the family of perovskite manganites, RMnO$_3$. The end member of this series, LaMnO$_3$, is known to be an A-type antiferromagnet—consisting of ferromagnetically aligned planes of Mn-ions, shown in Fig. 4.1(b), that are stacked antiferromagnetically. This magnetic configuration arises because of the antiferro-orbital arrangement of
Figure 4.1: (a) Crystal structure of TbMnO$_3$ [Reprinted figure with permission from [7] ©(1998) by the American Physical Society]. Also shown, are the magnetic structures in the $ab$-plane, for (b) LaMnO$_3$ (c) TbMnO$_3$ (d) HoMnO$_3$, below the Néel temperature, $T_N$ [8].
the $3d_{3z^2-r^2}$ orbitals, which favors a ferromagnetic (FM) nearest-neighbour (NN) superexchange (SE) interaction between the Mn sites in the plane and an antiferromagnetic SE interaction along the $c$-axis [52, 53]. However, substitution of La with a smaller trivalent R cation decreases the Mn-O-Mn bond angle, $\phi$, which leads to an enhanced cooperative rotation of the MnO$_6$ octahedra. This enhances next-nearest-neighbour (NNN) SE interactions in the plane; these interactions are antiferromagnetic and lead to spin frustration. For $R = \text{Gd, Tb, and Dy}$, A-type antiferromagnetic order is supplanted by more complex, incommensurate (IC) magnetic order, while HoMnO$_3$ has an E-type (or “up-up-down-down”) antiferromagnetic order (see Fig. 4.1(d)) [52].

For example, below a Néel temperature of $T_N \sim 41$ K, TbMnO$_3$ exhibits a longitudinal spin density wave (SDW) associated with the Mn spins, with a modulation wave vector that is directed along the $b$-axis, $k_m^{Mn} = (0, k+\delta_m^{Mn}, 0)$, where the incommensurability $\delta_m^{Mn} \approx 0.29$ at $T_N$ [12, 28]. Accompanying the magnetic ordering is a lattice modulation having $\delta_l = 2\delta_m$. At still lower temperatures, below $T_c = 28$ K, TbMnO$_3$ exhibits a second transition to a spiral magnetic phase, in which the spins have an elliptic cycloid structure with spins rotating around the $a$-axis [12, 28]. It has been shown that the magnetic structure of the high temperature incommensurate AFM phase is a collinear, sinusoidal spin density wave, shown in Fig. 4.2(a), with the modulation of the Mn$^{3+}$ moments described by

$$\vec{M} = \{0, M_b\sin(\vec{q} \cdot \vec{R}), 0\}$$

(4.1)

The modulation wavevector $\vec{q}$ is directed along the $b$-axis. The low temperature incommensurate spiral magnetic phase, on the other hand, has Mn spins ordered such that the tip of the spins sweep out a cycloid, as shown in Fig. 4.2(b). This noncollinear modulation of the Mn$^{3+}$ spins in this phase is given by,

$$\Delta\vec{M} = \{0, 0, M_c\cos(\vec{q} \cdot \vec{R})\}$$

(4.2)

It was observed [28] that the transition to the low temperature incommensurate spiral magnetic field was accompanied by the appearance of a spontaneous electric
polarization, $\mathbf{P}$, along the $c$-axis. The appearance of ferroelectricity in correlation with a spiral magnetic phase has also been observed in other materials, including $\text{Tb}_2\text{MnO}_5$, $\text{Ni}_3\text{V}_2\text{O}_6$ and $\text{MnWO}_4$. It has been subsequently shown that a magnetic spiral ordering induces an electric polarization, $\mathbf{P}$, due to an inverse Dzyaloshinskii-Moriya (DM) coupling between pairs of noncollinear spins $\mathbf{S}_i$ and $\mathbf{S}_j$ separated by a distance $r_{ij}$: $\mathbf{P} \propto r_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)$ [54, 55, 56]. The Dzyaloshinskii-Moriya (DM) interaction is induced by the spin-orbit interaction with an antisymmetric component in the exchange coupling in magnetic systems with low symmetry. This interaction favors non-collinear spin ordering and explains, for example, the magnetic spiral ordering in $\text{BiFeO}_3$ [57, 58, 59]. The effect of the inverse DM interaction, on the other hand, is to induce ferroelectric lattice displacements as a result of the exchange striction in a magnetic spiral. The vector product $\mathbf{S}_i \times \mathbf{S}_j$, has the same sign between pairs of neighbouring spins in a magnetic spiral. Thus, the DM interaction

Figure 4.2: Illustration of (a) the sinusoidal spin density wave and (b) the cycloidal spiral spin order [9].
pushes the negative oxygen ions in one direction, perpendicular to the line joining the transition metal ions (Mn ions in the case of TbMnO$_3$), inducing a polarization perpendicular to the spin chain, as shown in Fig. 4.2. In addition, the DM interactions also help to stabilize the spiral magnetic structure at low temperatures [56].

The inherent magnetic frustration and noncollinear magnetic order responsible for multiferroic behavior in TbMnO$_3$ is understandably sensitive to an applied magnetic field, and leads to strong magnetoelastic coupling and hybridized phonon-magnon excitations [54, 60, 61]. Recent field-dependent neutron and x-ray diffraction measurements demonstrated that an applied magnetic field above $H_c \sim 4.5$ T (along the $b$-axis direction at $T \sim 2.6$ K) relaxes the magnetic frustration caused by the GdFeO$_3$-type distortion [52]. The applied field thereby induces a linear magnetoelastic coupling that drives a magnetostructural transition from an IC phase with $\mathbf{P} || c$ to a commensurate (C) phase in which $\mathbf{P}$ flops along the $a$-axis, $\mathbf{P} || a$ [12, 62]. Schematic representations of the magnetic structures of the various phases of TbMnO$_3$ are shown as insets in the temperature vs. field phase diagram shown in Fig. 4.4. The critical field, $H_c$, at which this IC-C transition occurs is a function of temperature, increasing for instance to $H_c \sim 6$ T at $T \sim 10$ K [11]. X-ray diffraction measurements by Aliouane et al. [62] showed that for fields applied along the $b$-axis, $\mathbf{H} || b$, there is a discontinuous transition from the IC to the C phase at 4.5 T that is coincident with the polarization flop. In addition, these measurements demonstrated that there is a co-existence of IC and C phases between 4–5.5 T in TbMnO$_3$ for $\mathbf{H} || b$ at 2.6 K.

The IC-C transition coincides with a ferroelectric polarization flop from $\mathbf{P} || c$ to $\mathbf{P} || a$, which is driven by the change in the spin-rotation axis of the spiral from the $a$-axis to the $c$-axis [55]. This flop of the Mn spin cycloid has been confirmed by recent neutron diffraction data that established the high field magnetic structure of TbMnO$_3$ [13]. This change in the spin-rotation axis requires a degree of magnetic anisotropy that is most likely provided by the rare-earth spins [55]. However, the change to a commensurate phase appears to be accidental, as $\delta$ is close to the commensurate value of 1/4. Indeed, DyMnO$_3$ exhibits a field-induced polarization flop $\mathbf{P} || a$ similar to that in TbMnO$_3$, but this flop is not associated with a commensurate
high field phase [63].

Whatever the exact mechanism of the polarization flop in TbMnO$_3$, the phase co-existence of the IC and C states in the intermediate field regime suggests the possibility of dynamical (fluctuational) contributions to the phase transition that are commonly observed at discontinuous magnetic transitions [64, 65, 66]; unfortunately, there has been little or no investigation of TbMnO$_3$ using inelastic scattering techniques that would be sensitive to the fluctuational dynamics near the temperature- and field-dependent phase transitions of this system. In the rest of this chapter, we discuss our temperature- and field-dependent Raman measurements aimed at studying the structural and magnetic dynamics through the quantum phase transitions of TbMnO$_3$.

4.2 Results and Discussion

4.2.1 Temperature-dependent Spectra

The room temperature Raman spectrum of TbMnO$_3$ is presented in Fig. 4.3(a), showing several optical phonon modes in the 110–550 cm$^{-1}$ spectral range, including a number of modes that have been previously observed and identified by Martín-Carrón et al. [67] and Iliev et al. [68, 69]. For example, the 147 cm$^{-1}$ phonon mode in Fig. 4.3(b) is an $A_g$-symmetry mode associated with displacements of the Tb$^{3+}$ ions (R-mode) [67]. In order to explore the low temperature ($T<T_N$) and field-dependent phases of TbMnO$_3$ in this study, it is sufficient to focus attention on the temperature- and field-dependence of the Raman spectrum between 115–160 cm$^{-1}$.

Fig. 4.3(b) illustrates the temperature dependence of the Raman spectrum in the range 115–160 cm$^{-1}$, highlighting several interesting spectroscopic features. For example, Fig. 4.3(b) shows that a broad mode near 125 cm$^{-1}$ evolves below the transition to the incommensurate longitudinal spin density wave (SDW) phase at $T_N \sim 42$ K. We attribute this “incommensurate phase” (IC) mode to the magnetoelastically induced lattice modulation that accompanies IC magnetic ordering below $T_N$ [11, 28, 62]. Such a lattice modulation is expected to result in the appearance of new modes associated with the incommensurate wavevector of the lattice modu-
Figure 4.3: (a) Room temperature Raman spectrum of TbMnO$_3$. (b) Temperature-dependence of the zero-field Raman spectra in the 115-155 cm$^{-1}$ spectral range showing the evolution of the IC mode at 125 cm$^{-1}$; the dashed line is a guide to the eye. (c) Field dependence of TbMnO$_3$ at T=10 K for H$\parallel b$ (top) and H$\parallel a$ (bottom) axes. The C mode is induced at 137 cm$^{-1}$ for H$>4$ T along the b-axis but is not present up to H = 8 T for applied fields along the a-axis [10].

Incommensuration in TbMnO$_3$ ($\delta_l = 2\delta_m \sim 0.58$ at $T_N$, where $\delta_l$ and $\delta_m$ are the lattice and spin incommensurabilities, respectively [62]). In particular, an incommensurate lattice modulation is known to be associated with the appearance of both amplitude and
phase vibrational modes [70]; the amplitude mode involves lattice fluctuations that preserve the symmetry of the incommensurate lattice modulation and are therefore Raman active [42].

Our interpretation of the 125 cm\(^{-1}\) IC mode as an amplitude fluctuation of the incommensurate lattice modulation is supported by several features of the data: first, the 125 cm\(^{-1}\) IC mode softens and broadens as \(T \rightarrow T_N\) (dashed line in Fig. 4.3(b)), as expected of ‘soft’ amplitude modes; and second, the intensity of the 125 cm\(^{-1}\) IC mode not only disappears above the IC phase transition, \(T > T_N\), but also disappears with increasing field into the field-induced commensurate “C” phase (\(H = 8\) T spectra in Fig. 4.3(c)); the latter is associated with the field-induced destabilization of the lattice modulation that leads to commensuration of the magnetic and atomic lattices above \(H_c \sim 5.5\) T at 10 K (\(H\|b\)) [62]. In addition, our interpretation of the 125 cm\(^{-1}\) mode as the IC phase mode is also supported by more recent Raman data measured by Rovillain et al. In particular, their studies provide evidence that suggests that this mode is a magnetic mode, likely associated with a magnon-phonon process [71, 72]. We also note that the broad linewidth associated with the 125 cm\(^{-1}\) IC mode is consistent with inhomogeneous broadening associated with a slight k-smearing of the incommensurate wave vector; indeed, a smearing of the incommensurate wavevector in the IC phase of \(\text{TbMnO}_3\) is supported by the observation that the width of the second harmonic IC lattice reflection in x-ray diffraction measurements is significantly broader than that associated with the C lattice reflection for \(H > H_c\) [62].

### 4.2.2 Field-dependent Spectra

Fig. 4.3(c) shows that, in addition to a high-field suppression of the IC mode, a narrow field-induced mode near 137 cm\(^{-1}\) appears at \(H \sim 4\) T for \(H\|b\) in the vicinity of the field-induced IC-C transition. The integrated intensity of this commensurate phase (“C-phase”) mode grows with increasing field in the C phase, saturating at \(H = 6\) T, the field at which the electric polarization flops from \(P\|c\) to \(P\|a\) [28, 11]. This is shown in Fig. 4.4, which summarizes some of the temperature and field values at which the IC (green circles) and C (red squares) modes are observed.
on the established phase diagram of TbMnO$_3$ [11, 62]. We attribute this C-phase mode near 137 cm$^{-1}$ to a zone-boundary phonon mode that is folded to the zone center due to the quadrupling of the unit cell by the magnetic sublattice in the field-induced C phase of TbMnO$_3$ [62]. This identification is supported by several features of the data: First, this mode appears near the IC-C critical field at 10 K,
i.e., $H_c \sim 5.5 \text{T}$, for $H \parallel b$. Second, a similar mode is not observed at $H = 8 \text{T}$ in the $H \parallel a$ spectra (see bottom spectrum, Fig. 4.3(c)), in which field orientation the field-induced C phase occurs outside the magnetic field range of this study, $H^e_c > 9 \text{T}$ [62]. Finally, the evolution of the field-induced “C-phase” mode in TbMnO$_3$ is similar to that theoretically predicted for magnetic-order-induced folded phonons [73, 74] and experimentally observed in the Raman spectra of magnetic systems such as RuSr$_2$GdCu$_2$O$_8$ [75], CuO [76], and VI$_2$ [77]. In particular, magnetic-order-induced folded Raman modes in these systems are associated with a strong modulation of the exchange coupling constants by specific normal mode vibrations of the lattice, which contributes a spin-dependence to the mode intensity [73, 74, 75, 76, 77]: $I_{sd} \sim |M\langle S_i \cdot S_j \rangle|^2$, where $S_i$ and $S_j$ are the spins on sites i and j, respectively, $M$ is the spin-dependent Raman tensor [74], and $\langle \ldots \rangle$ represents a statistical average over all lattice sites. Therefore, the presence of these magnetic-order-induced zone-folded modes not only directly illustrates the strong spin-lattice coupling in these materials, but the temperature- and field-dependent changes of their intensity directly reflect changes in the sublattice magnetization of the materials. In the specific case of TbMnO$_3$, the rapid growth of the C mode shown in Fig. 4.5(a) is consistent with that predicted for phonon modes that strongly modulate the exchange coupling of magnetic materials [74, 78, 77, 79]. This folded mode may involve longitudinal vibrations of the O ions, as these are expected to strongly modulate ferromagnetic (FM) and antiferromagnetic (AFM) exchange coupling in TbMnO$_3$ by modifying the Mn-O-Mn angle [62].

Because of its sensitivity to the sublattice magnetization of TbMnO$_3$, the field- and temperature-dependent linewidth and intensity of the C mode provides us an opportunity to identify several interesting properties of the IC-C transition in TbMnO$_3$. Fig. 4.5 presents the detailed field-dependence ($H \parallel b$) of the IC and C modes at two temperatures, (a) $T = 10 \text{K}$ and (b) $T = 25 \text{K}$. The intensities of the various modes in this frequency range are summarized as a contour plot in Fig. 4.5(c) and their energies as a function of field are represented by solid diamonds. It is evident from this plot that, with increasing magnetic field, the 125 cm$^{-1}$ IC mode is suppressed, while the 137 cm$^{-1}$ C mode appears near the IC/C phase boundary ($H_c$...
The C mode exhibits a systematic decrease in linewidth and increase in intensity with increasing field. Additionally, there is a dramatic softening in the $A_g$-symmetry Tb mode with increasing magnetic field from $\sim 147$ cm$^{-1}$ in the low-field IC phase to $\sim 144$ cm$^{-1}$ in the high-field C phase; there is also evidence for two-mode behavior associated with this Tb phonon in the intermediate field regime, which will be discussed in further detail later. The softening of the $147$ cm$^{-1}$ Tb mode with increasing field indicates that there is a structural change, likely involving the Tb$^{3+}$ ions, through the field-tuned IC-C phase transition. The exact nature of this structural transition is not clear from our data, but it may reflect an abrupt change in the lattice modulation associated with the Tb ions through the field-induced IC-C transition. Interestingly, x-ray scattering provides evidence for a strong coupling between the Tb- and Mn-sublattices below $T_c$ [80], so it is likely that this change in modulation though the IC-C transition in TbMnO$_3$ affects the Mn-ions as well.

Notably, the field-dependence of the C mode intensity and linewidth also provides strong evidence for fluctuating C phase domain regions that appear at magnetic fields and temperatures well outside the established IC-C phase boundary, $H_c \sim 5.5$ T (at 10 K). This is seen in Fig. 4.5(a) for $T = 10$ K, where, for $H > H_c$, the C mode is strong, with a resolution-limited linewidth, indicative of a long-lived excitation and the presence of long-range commensurate order. However, in the vicinity of the field-induced IC/C phase boundary, the C mode has a weak intensity and is broad, with a linewidth 3–4 times its resolution-limited value. Taken together, these results suggest that the onset of long-range commensurate order at the critical field, $H_c$, in TbMnO$_3$ is preceded at lower fields by fluctuations of commensurate domains that coexist with incommensurate domain regions near the IC/C phase boundary of TbMnO$_3$. A similar dynamical coexistence of phases has also been observed using Raman scattering near the quantum neutral-ionic phase transition of isostructural charge-transfer complexes [81] and near the $x$-dependent quantum ($T \sim 0$) charge-density-wave/superconductor transition of Cu$_x$TiSe$_2$ [15].

Fig. 4.6 also illustrates the wide range of the phase diagram over which dynamical fluctuations of domains are evident in TbMnO$_3$. Specifically, Fig. 4.6 shows
Figure 4.5: Field-dependence of TbMnO$_3$ at (a) 10 K and (b) 25 K. Dashed lines illustrate Lorentzian fits to the C and 147 cm$^{-1}$ modes, used to extract intensity and linewidth parameters for the C mode [10]. (c) Contour plot of the intensities of the various modes at 10 K.

contour plots of the $\sim$137 cm$^{-1}$ C-mode (a) linewidth and (b) integrated intensity as functions of both magnetic field and temperature. Also shown for comparison are
the established phase boundary lines for the TbMnO$_3$ system (dashed lines) from Ref. [11]. The noteworthy features of Fig. 4.6 are the following: first, the C mode attains its maximum value, and has a resolution-limited linewidth, inside the established C phase boundary line, again indicating the presence of long-range commensurate order. However, a fluctuational C mode contribution—characterized by an enhanced linewidth (red regions) and weakened intensity (lighter green regions)—is clearly evident outside the established IC/C phase boundary line, suggesting the presence of fluctuating C domains over a wide range of the phase diagram. These results suggest that, with increasing magnetic field, the C phase nucleates as small fluctuating domains well before the thermodynamic phase transition, and that these C-phase domains become more long-lived and prevalent as $H \rightarrow H_c$, the field at which long-range commensurate magnetic order develops. Significantly, this evidence for field-induced domain formation in TbMnO$_3$ is supported by recent field-dependent
neutron scattering results on TbMnO$_3$, in which an observed memory effect has been attributed to the formation of commensurate domains [82]. These neutron results further suggest that the C-phase domains are associated with a field-induced flop of the spiral plane from the $bc$-plane in the IC phase to the $ab$-plane. In combination with our evidence for fluctuating domains, these results suggest that strong polarization fluctuations likely accompany the magnetic fluctuations as precursors to the IC-C phase boundary.

We note, finally, that the presence of coexisting IC- and C-phase regions in the intermediate field range $H_c \sim 4T \leq H \leq 7T$ (near $T \ll T_c$) is also supported by the field-dependence of the $A_g$ symmetry Tb phonon mode. Specifically, this mode exhibits in the intermediate field range a significant linewidth broadening, eventually leading to two-mode behavior—i.e., the presence of distinct peaks at 144 cm$^{-1}$ and 147 cm$^{-1}$ associated with the same vibrational mode (see inset in Fig. 4.7)—consistent with the coexistence of IC- and C-phase regions. The intensity and frequency of the $A_g$-symmetry Tb mode is summarized as a function of field in Fig. 4.7(a) and (b) respectively. That these two peaks are indeed associated with the same phonon mode is supported by the observation that increasing magnetic field leads to a gradual transfer of spectral weight from the 147 cm$^{-1}$ peak, which is associated with the IC phase, to the 144 cm$^{-1}$ peak, which is associated with the C phase. The appearance of both these peaks in the field range $H_c \sim 4T \leq H \leq 6T$ of TbMnO$_3$ corroborates our other evidence that dynamically fluctuating domains of IC and C phases are present in the intermediate field regime even for $T \ll T_c$.

In summary, our Raman scattering measurements on TbMnO$_3$ offer evidence that dynamic fluctuations of the field-induced commensurate phase are present outside the established C-phase boundary, both for fields $H<H_c$ and temperatures $T>T_c$. These results suggest that the field-induced destabilization of the atomic and magnetic lattices through the IC-C transition in TbMnO$_3$ is associated with the development of fluctuating IC and C domains, which may be instrumental to the field-induced polarization flop from the $c$-axis to the $a$-axis. We suggest that these magnetic fluctuations are also accompanied by strong polarization fluctuations that should also be observable as precursors to the field-induced IC-C phase.
Figure 4.7: Field dependence (at T=10 K) of the (a) integrated intensity and (b) frequency of the $A_g$ symmetry Tb- phonon mode associated with the IC phase (blue squares), where the phonon frequency is $\sim 147$ cm$^{-1}$, and with the C phase (red circles), where the phonon frequency is $\sim 144$ cm$^{-1}$. The gray shaded area highlights a region of coexistence of the 144 cm$^{-1}$ and 147 cm$^{-1}$ Tb modes, indicating a coexistence of IC- and C-phases in this intermediate field region. The inset illustrates Lorentzian fits to the raw 10 K spectrum in the intermediate field regime (H=6 T), showing the coexistence of 144 cm$^{-1}$ and 147 cm$^{-1}$ Tb modes in this region [10].

boundary. Our results also reveal the appearance of additional temperature- and field-dependent modes in the different magnetic phases of in TbMnO$_3$ that reflect strong spin-phonon coupling effects, which likely arise from the strong modulation of the exchange interaction by zone-boundary phonon modes. This coupling results in additional modes whose intensities reflect the temperature- and field-dependent sublattice magnetization of TbMnO$_3$. Finally, our data provides evidence for a
structural change that accompanies the field-induced IC-C transition. This structural change is likely associated with an abrupt change in the modulation wavevector of the Tb and Mn ions, but x-ray and neutron scattering experiments would help elucidate the exact nature of this field-induced structural modification.
Chapter 5

Quantum Phase Transitions in Titanium Diselenide: The Effects of Cu-intercalation

In this chapter, I will discuss the results of temperature- and $x$-dependent Raman scattering studies of the charge-density-wave (CDW) amplitude modes in Cu-intercalated TiSe$_2$ (Cu$_x$TiSe$_2$). Undoped ($x = 0$) TiSe$_2$ is a layered dichalcogenide, which undergoes a transition from a semimetal to a CDW phase at $T_{CDW} \sim 200$ K [29, 30]. While TiSe$_2$ has a simple, commensurate CDW structure, the mechanism driving the transition is believed to be unconventional – it cannot be explained by Fermi surface nesting unlike most other dichalcogenides that transition to a CDW phase [83, 84]. This fueled extensive research interest aiming to clarify the nature of the CDW transition in $1T$-TiSe$_2$ [85, 86, 87, 88, 89]. Recently, further interest in the study of this material was sparked by the discovery that intercalation of TiSe$_2$ with Cu drives Cu$_x$TiSe$_2$ to a superconducting (SC) state for $x > 0.04$ [16]. Cu$_x$TiSe$_2$ is therefore an ideal system to investigate the microscopic details of quantum phase transitions between CDW order and SC. The CDW amplitude mode – which is associated with the collective transverse fluctuations of the CDW order parameter – offers detailed information regarding the evolution and stability of the CDW state and the CDW soft mode [90] and has been shown to be extremely sensitive to temperature and pressure [14, 91]. It is of particular interest to clarify the nature of this “soft mode” in CDW-SC transitions.

5.1 Raman Scattering Studies of $1T$-TiSe$_2$

The structure of $1T$-TiSe$_2$ is shown in Fig. 5.1(a). It has a layered structure with strong, covalent bonding between the hexagonally packed planes of Ti and
Figure 5.1: (a) Structure of $1T$-TiSe$_2$. The closed circles represent Ti atoms, while the open circles represent Se atoms. (b) The Brillouin zone of $1T$-TiSe$_2$ showing the wave vectors of the three CDWs. (c) The atomic displacements that "freeze in" to form the superlattice structure (large gray circles) in the CDW phase of $1T$-TiSe$_2$. Blue circles are Ti atoms. Light red circles represent Se atoms in a layer above the Ti layer and dark red circles represent Se atoms in the layer below the Ti layer. The primitive and Wigner-Seitz cells are denoted by the dashed lines.

Se atoms within a layer, and weak Van der Waals bonding between the layers. This two-dimensional character explains many of the interesting and highly anisotropic physical properties observed in this material. Additionally, the layered nature makes it easier to cleave samples to obtain a fresh exposed surface for our experiments.

Below $T_c \sim 200$ K, TiSe$_2$ undergoes a second-order phase transition to a CDW
phase, as discussed previously in Section 2.4. In the CDW phase, there is a spontaneous distortion of the atomic lattice that results in a periodic modulation of the charge density [92]. This ordering is the result of a strong coupling between electronic and lattice degrees of freedom and consequently, is accompanied by a lattice distortion, shown in Fig. 5.1(c), to a $2a_o \times 2a_o \times 2c_o$ superlattice of different symmetry ($D_{3d}^3$ to $D_{3d}^4$) [29, 30]. The CDW in TiSe$_2$ is commensurate, which means that the periodicity of the CDW is an integer multiple of the lattice periodicity. The direct transition to a commensurate CDW phase as a function of temperature sets it apart from most other dichalcogenide CDW systems, which typically have an intermediate incommensurate CDW phase.

$1T$-TiSe$_2$ is also unique in that the mechanism driving the CDW transition is not conventional Fermi surface nesting [84]. After much debate, it was concluded that either a variant of the Jahn-Teller (JT) effect or exciton formation is responsible for the structural instability that drives the CDW transition. In the former scenario, the energy of the valence and conduction bands is believed to be lowered by a lattice distortion [85, 86]. By contrast, in the latter scenario, electron-hole coupling between the valence and conduction bands makes the system unstable to the formation of bound electron-hole pairs (excitons), which consequently drives a transition to a condensed excitonic ground state that is accompanied by a doubling of the lattice in $1T$-TiSe$_2$ [87, 88]. More recent high-resolution ARPES measurements of TiSe$_2$ suggest that both these competing mechanisms contribute to CDW formation [89]. An indirect JT effect causes the lattice distortion to split the unoccupied conduction band and lower its energy. This, in turn, flattens the valence band, since the electron-hole coupling prevents an overlap between the conduction and valence bands. The net effect is a reduction of the system’s energy and the formation of a small gap CDW state.

The temperature dependence of the Raman spectrum of TiSe$_2$ is plotted in Fig. 5.2(a). The room temperature spectrum, shown in Fig. 5.2(b), is dominated by two phonon modes – the $E_g$ symmetry mode at 134 cm$^{-1}$ and the $A_{1g}$ symmetry mode at 203 cm$^{-1}$. The normal mode displacement patterns for these modes are shown in the inset to Fig. 5.2(b). Below $T_c \sim 200$ K, several new modes are seen
Figure 5.2: (a) Temperature dependence of the Raman spectra of $1T$-TiSe$_2$ [14]. (b) The room temperature spectrum of $1T$-TiSe$_2$, with the insets showing the normal mode displacement patterns for the two phonon modes. (c) Summary of the $x = 0$ $A_{1g}$ symmetry CDW mode frequency ($\omega_o$) vs temperature (filled squares) and the $x = 0$ $A_{1g}$ symmetry CDW mode linewidth (FWHM) vs temperature (filled circles) for TiSe$_2$. The solid line is a fit to the frequency data with $\omega_o/\omega_o(0) = (1 - x/x_c)^\beta$ with $\beta \sim 0.15$. The dashed line illustrates the contribution to the linewidth expected from two-phonon damping [15].

to appear in the Raman spectrum – an $E_g$ symmetry mode at 74 cm$^{-1}$ and an $A_{1g}$ symmetry mode at 116 cm$^{-1}$. These modes are the CDW amplitude modes, which are excitations of the CDW ground state, involving fluctuations of the CDW
state that modulate the amplitude of the charge density wave. The $A_{1g}$ amplitude mode is an “in-phase” mode and involves fluctuations that preserve the symmetry of the CDW ground state (Fig. 5.1(c)), while the $E_g$ amplitude mode is an “out-of-phase” mode that involves fluctuations of the CDW amplitude away from the ground state symmetry. [91, 93] Fig. 5.1(c) shows the atomic distortions that “freeze in” and the $2a_o \times 2a_o \times 2c_o$ superlattice that forms, resulting in a doubling of the lattice periodicity below $T_c \sim 200$ K [30]. This “folds” the Brillouin zone (Fig. 5.1(b)) that, in turn, folds the soft zone boundary TA phonon at the L-point to the zone center and causes these CDW amplitude modes to appear in the Raman spectrum below $T_c$.

As illustrated in Fig. 5.2(c), the CDW amplitude modes exhibit soft-mode behavior typical of amplitude modes observed in other CDW systems including (i) a temperature-dependent frequency [filled squares, Fig. 5.2(c)] given by the power-law form $\omega_o(T) \sim (1 - T/T_{CDW})^\beta$ with $\beta \sim 0.15$ [solid line, Fig. 5.2(c)], (ii) a weakening of the amplitude mode intensity as the CDW lattice loses coherence as $T \to T_{CDW}$, and (iii) a dramatic increase in linewidth with increasing temperature [filled circles, Fig. 5.2(c)]; the latter mainly reflects overdamping of the amplitude mode due to an increase in CDW fluctuations, as it is in substantial excess of the broadening expected from anharmonic (i.e., two-phonon) contributions [dashed line, Fig. 5.2(c)].

The anomalous temperature dependence of the 116 cm$^{-1}$ $A_{1g}$ amplitude mode in TiSe$_2$ confirms that the eigenvector couples strongly to the lattice distortion responsible for the CDW transition at $T_{CDW}$, and thus mimics the collapse of the soft mode and the CDW gap as $T \to T_{CDW}$. The intensity of the CDW modes serve as good order parameters for the CDW state.

The use of CDW amplitude modes as a sensitive probe of the stability and elasticity of the CDW phase is well illustrated by Raman studies of the pressure tuned “quantum melting” of the CDW phase [14]. Fig. 5.3(a) shows the pressure dependence of the $A_{1g}$ symmetry mode at 116 cm$^{-1}$. The hardening of the $E_g$ phonon mode, shown in Fig. 5.3(a), confirms the crystalline nature of the lattice. On the other hand, the 116 cm$^{-1}$ $A_{1g}$ CDW amplitude mode, also shown in Fig. 5.3(a), has an intensity that decreases with increasing pressure, disappearing for $P > 25$ kbar;
Figure 5.3: (a) Pressure-dependence of the 116 cm$^{-1}$ $A_{1g}$ amplitude mode and the 135 cm$^{-1}$ $E_g$ phonon mode at $T = 3$ K in TiSe$_2$. (b) Summary of the pressure-dependence of the $A_{1g}$ amplitude mode frequency, $\omega_o$ (red circles), and normalized intensity, $I(P)/I(P = 0)$ (blue squares) at $T = 3$ K. Also shown is the pressure-dependence of the normalized intensity of the $E_g$ amplitude mode (red squares), which loses intensity more rapidly than the $A_{1g}$ amplitude mode. The pressure dependence is divided into three regimes: the “crystalline” region below 5 kbar, the “soft” CDW regime between 5–25 kbar and the “melted” CDW region for pressures above 25 kbar [Reprinted figure with permission from [14] ©(2003) by the American Physical Society].

this intensity dependence suggests that the CDW state collapses above this critical pressure. Additionally, the pressure-dependence of the frequency of this amplitude mode suggests that the CDW in 1T-TiSe$_2$ exhibits three regimes of behavior as a function of pressure, which are summarized in Fig. 5.3(b): (i) A “crystalline” region below 5 kbar, where, like the phonon mode, the frequency increases linearly with
increasing pressure. This stiffening of the CDW mode frequency can be explained as an enhancement of the JT interaction as a result of applying pressure, which would cause further lowering of the conduction and valence bands. (ii) A ‘soft’ CDW phase regime for pressures between $5 \leq P \leq 25$ kbar, in which the energy of the $A_{1g}$ CDW mode remains roughly constant with increasing pressure and the intensity decreases systematically with pressure. Additionally, the out-of-phase $E_g$ mode disappears in this regime, indicating the loss of long-range CDW order. In this regime, it is likely that the electron-hole coupling is overwhelmed by the increased JT interaction and the CDW gap collapses, leading to the loss of long-range CDW order. (iii) As pressure is increased further, the CDW melts into a disordered metallic phase in which the CDW order is completely suppressed.

While applying pressure compresses the lattice, Cu intercalation has the effect of expanding the lattice. The following section examines the results of our Raman scattering studies on Cu-intercalated TiSe$_2$ and contrasts it with the effects of lattice compression via application of pressure. In order to present a more complete picture, we also summarize, in detail, the results of more recent high-pressure studies by A. F. Kusmartseva et al., which provide evidence for a new pressure-induced superconducting phase in 1$T$-TiSe$_2$ [31].

### 5.2 Effects of Cu-intercalation

Increasing Cu intercalation in TiSe$_2$ (increasing $x$ in Cu$_x$TiSe$_2$) results in:

- **Lattice expansion:** Upon controlled intercalation of TiSe$_2$ with copper, it is seen that Cu atoms occupy the spaces between the TiSe$_2$ layers, as shown in the inset to Fig. 5.4. Morosan et al. [16] showed that the lattice parameters $a$ and $c$ increase systematically with increasing Cu content up to $x = 0.1$. Above this doping, they no longer increase, implying that $x = 0.11$ is the solubility limit for Cu intercalation in TiSe$_2$.

- **Suppression of the CDW transition temperature:**

The phase diagram Fig. 5.4 summarizes the effect of Cu intercalation on the CDW transition temperature, $T_{CDW}$. Specific heat measurements on undoped
Figure 5.4: Electronic phase diagram of Cu-intercalated TiSe$_2$ from Ref. [16]. The inset shows the crystal structure of Cu$_x$TiSe$_2$ with the Cu atoms occupying the positions between the TiSe$_2$ layers.

TiSe$_2$ have shown that the onset of the CDW transition is marked by a drop in the susceptibility, consistent with the decrease in electronic density of states that occurs when a gap is opened at the Fermi level [16]. Similar measurements have been used to determine the values of $T_{CDW}$ in Cu$_x$TiSe$_2$ as a function of $x$ up to $x = 0.06$. For higher Cu content, the susceptibility drop is no longer clearly visible. These values have also been confirmed via x-ray and electron diffraction measurements for $x = 0.03$ and $x = 0.08$ and transport measurements of resistivity and the Seebeck co-efficient. High resolution angle resolved photoemission spectroscopy measurements have shown that Cu intercalation enhances the den-
sity of states around the Fermi energy, $E_F$. In addition, Cu intercalation slightly raises the chemical potential, which suppresses the CDW transition temperature; it has been suggested that this suppression results from the suppression of exciton formation [94].

- Emergence of a superconducting phase: At low temperatures, for $x > 0.04$, resistivity and magnetization measurements show the emergence of a superconducting state in Cu$_x$TiSe$_2$. The superconducting transition temperature, $T_c$, reaches a maximum of 4.15 K for $x = 0.08$ and decreases for higher Cu content. In-plane thermal conductivity measurements performed on $x = 0.07$ samples provide strong evidence that the superconducting gap most likely has an s-wave symmetry [95]. While it is agreed that the enhancement of the density of states around the Fermi energy, evidenced by high resolution ARPES measurements, favors the emergence of a superconducting (SC) state, the microscopic mechanism driving this transition remains controversial [94, 95].

### 5.3 Results and Discussion of Raman Scattering Measurements on Cu$_x$TiSe$_2$

The behavior of the soft mode – i.e., the phonon mode whose eigenvector mimics the CDW lattice distortion, and hence whose frequency tends towards zero at the second-order phase transition – is one of the most fundamental and well-studied phenomena associated with classical (thermally driven) displacive phase transitions [92, 96, 97]; on the other hand, soft mode behavior associated with quantum transitions is not well understood. In our investigations, we studied in detail, the doping-dependent evolution of the CDW amplitude modes in Cu$_x$TiSe$_2$ through the CDW-SC quantum phase transition.

The $T = 6$ K Raman spectra of Cu$_x$TiSe$_2$ for various values of $x$ are shown in Fig. 5.5(a). One can readily identify the phonon and CDW modes that are similar to those of the undoped system. Figs. 5.5(b-d) show the temperature dependence of the $A_{1g}$-symmetry CDW mode for $x = 0, 0.02, 0.03$. As expected, the CDW mode
is suppressed at lower temperatures for higher \( x \) values, reflecting the suppression of the CDW transition temperature by Cu-intercalation. The mode frequency and intensity at \( T=6 \) K, extracted through Lorentzian fits to the data (as illustrated in select spectra in Fig. 5.5), are summarized in Fig. 5.6(a) as a function of Cu concentrations, \( x \). Because the \( A_{1g} \) amplitude mode (dashed lines, Fig. 5.5(a) and (c)) is in most cases well-separated from, or much broader and stronger than, nearby optical modes (dotted lines, Fig. 5.5(a) and (c)), estimated errors in the amplitude mode frequency obtained in this manner were \( \leq 1\% \).

From a comparison of Fig. 5.6(a) and Fig. 5.6(b) it is apparent that the \( x \)-dependent mode softening exhibits identical characteristics to temperature-dependent mode softening in \( \text{Cu}_x\text{TiSe}_2 \). For example, Fig. 5.6(a) shows that the \( A_{1g} \) amplitude mode softens by \( \sim 18\% \) between \( x = 0 \) and \( x = 0.05 \) at \( T = 6 \) K (solid squares), and exhibits a 400\% increase in linewidth between \( x = 0 \) and \( x = 0.04 \) at \( T = 6 \) K (solid circles). Note that the dramatic \( x \)-dependent increase in the \( T = 6 \) K amplitude modes linewidths [filled circles, Fig. 5.6(a)] cannot be attributed to the effects of disorder (e.g., inhomogeneous broadening caused by Cu substitution), as there is not a comparably large increase in the other phonon linewidths with increasing \( x \). Rather, the \( x \)-dependent damping of the CDW amplitude modes in \( \text{Cu}_x\text{TiSe}_2 \) reflects a dramatic enhancement of CDW fluctuations — and a loss of CDW coherence — with increasing \( x \).

A microscopic analysis of the nature and origin of \( x \)-dependent mode softening in \( \text{Cu}_x\text{TiSe}_2 \) [see Fig. 5.6(a)] can be made using Rice and collaborators’ mean-field result for the frequency of a CDW amplitude mode \([98, 99]\),

\[
\omega_0 = 1.4\lambda^{1/2}\tilde{\omega}t^{1/2},
\]

which has been successfully applied to the analysis of CDW soft mode behavior in other dichalcogenides \([100, 101, 102]\). In Eq. 5.1, \( \tilde{\omega} \) is the unscreened (high temperature) phonon frequency, \( t = (T_{CDW} - T)/T_{CDW} \) is the reduced temperature, \( \lambda = N(0)g^2(0)/\tilde{\omega} \) is the electron-phonon coupling constant associated with the CDW, where \( g(0) \) is the electron-phonon coupling matrix element between the soft phonon mode and the electronic states at the Fermi surface involved in the CDW.
Figure 5.5: (a) Doping \(x\) dependence of the Raman spectrum of \(Cu_xTiSe_2\) at \(T=6\,\text{K}\), illustrating the \(E_g\) and \(A_{1g}\) symmetry CDW amplitude modes (arrows) as a function of \(x\). (b)-(d) Temperature dependence of the \(A_{1g}\) symmetry CDW mode spectra at (b) \(x=0\), (c) \(x=0.02\), and (d) \(x=0.03\) in \(Cu_xTiSe_2\) [15]. Also shown are example Lorentzian fits to the \(A_{1g}\) amplitude mode (dashed line) and nearby optical modes (dotted line).

duction, and \(N(0)\) is the joint density of states of the electrons and holes involved in the CDW transition [100, 101, 102]. Note that the unscreened frequency
Figure 5.6: Summary of the $T = 6$ K $A_{1g}$ symmetry CDW mode frequency ($\omega_o$) vs $x$ (filled squares) and the $T = 6$ K $A_{1g}$ symmetry CDW mode linewidth (FWHM) vs $x$ (filled circles) for Cu$_x$TiSe$_2$. The solid line is a fit to the doping dependence of the $T = 6$ K frequency data using $\omega_o/\omega_o(0) = (1 - x/x_c)^{\beta}$ with $\beta \sim 0.15$ and $x_c \sim 0.07$, and the dashed line is a fit to $\Gamma \sim (x_c/x)^{-2}$ with $x_c \sim 0.07$ [15]. For convenient comparison, we reproduce in the (b) summary of the $x = 0$ $A_{1g}$ symmetry CDW mode frequency ($\omega_o$) vs temperature (filled squares) and the $x = 0$ $A_{1g}$ symmetry CDW mode linewidth (FWHM) vs temperature (filled circles) for TiSe$_2$, also shown in Fig. 5.2(c).

\(\tilde{\omega}\) in Eq. 5.1 is not expected to have a significant doping dependence between $x = 0$ and $x = 0.06$ in Cu$_x$TiSe$_2$, which is supported by the fact that the optical phonon frequencies exhibit a negligible change with $x$ (e.g., see 137 cm$^{-1}$ mode in Fig. 5.5). Consequently, Eq. 5.1 suggests that the $x$-dependent softening of the $A_{1g}$ amplitude mode in Cu$_x$TiSe$_2$ is associated with a substantial reduction in the
electron-phonon coupling constant $\lambda$ with Cu-intercalation. One possible source of this reduction is a decrease in the density of electrons/holes, $N(0)$, participating in the CDW transition between $x = 0$ and $x = 0.05$ in Cu$_x$TiSe$_2$. Indeed, Morosan et al. observed a $\sim$50% decrease in the size of the magnetic susceptibility drop below $T_{CDW}$ between $x = 0$ and $x = 0.05$, indicating that fewer electronic states are gapped at the CDW transition with increasing $x$ [16]. Importantly, however, this reduction in $N(0)$ is not likely associated with a loss of Fermi surface nesting with increasing $x$, because ARPES studies of Cu$_x$TiSe$_2$ have shown that nesting actually increases with $x$ [103]. Another possibility is that the primary effect of Cu intercalation on the CDW phase is caused by the linear expansion of the $a$-axis parameter with Cu intercalation in Cu$_x$TiSe$_2$ [16], which leads to a reduction in $\lambda$ by expanding the Ti-Se bond length primarily responsible for the CDW instability in 1T-TiSe$_2$ [30, 104, 105, 106]. Notably, this alternative is consistent with Castro Neto's proposal that the layered dichalcogenides have a critical lattice spacing above which CDW order is suppressed [107].

Remarkably, Fig. 5.7 shows that, in spite of the different microscopic effects of Cu-intercalation and temperature on the lattice, $x$-dependent and thermal mode softening in Cu$_x$TiSe$_2$ exhibit essentially identical scaling behavior. In particular, Fig. 5.7 compares the following data sets: (i) the normalized $A_{1g}$ amplitude mode frequency $\omega_o/\omega_o(0)$ vs. the reduced doping $x/x_c$ for $T = 60$ K (using $x_c$ from [16]) (filled squares); and (ii) the normalized $A_{1g}$ amplitude mode frequency vs. the reduced temperature $T/T_{CDW}$ for $x = 0$ (using $T_{CDW} = 218$ K from Ref. [16])(filled circle), $x = 0.02$ ($T_{CDW} = 180$ K [16])(open triangles), and $x = 0.03$ ($T_{CDW} = 140$ K [16])(open diamonds). The solid line in Fig. 5.7 shows that all these data sets collapse onto the same curve given by $\omega_o/\omega_o(0) = (1 - p)^\beta$, with $p = x/x_c$ or $T/T_{CDW}$ and $\beta \sim 0.15$. An estimated uncertainty of $\Delta \beta = \pm 0.05$ in the “best fit” value of $\beta \sim 0.15$ is suggested by the gray lines in Fig. 5.7, which show the functional form $\omega_o/\omega_o(0) = (1 - p)^\beta$ for both $\beta = 0.20$ (bottom gray line) and $\beta = 0.10$ (top gray line).

Two key points should be made regarding Fig. 5.7: First, although we cannot measure the amplitude mode frequency with temperature (doping) all the way to the
Figure 5.7: Plots of $\omega_0/\omega_o(0)$ vs $x/x_c$ for $T = 60$ K ($x_c = 0.06$ [16]) (filled squares), and $\omega_0/\omega_o(0)$ vs $T/T_{CDW}$ for $x = 0$ ($T_{CDW} = 218$ K [16]) (filled circles), $x = 0.02$ ($T_{CDW} = 180$ K [16]) (open triangles), and $x = 0.03$ ($T_{CDW} = 140$ K [16]) (open diamonds). The solid line shows that all these data sets collapse onto the same curve given by $\omega_0/\omega_o(0) = (1-p)^\beta$, where $\beta = 0.15$ and $p = x/x_c$ or $T/T_{CDW}$. The gray lines provide an estimate of the uncertainty in $\beta$ by comparing fits with $\beta = 0.2$ (bottom) and $\beta = 0.10$ (top) [15].

critical point $T_{CDW}$ ($x_c$), for reasons described above, we can nevertheless extract a reliable value for the scaling parameter $\beta$ from fits to these data in Fig. 5.7, because we know the values of $T_{CDW}$ (for all $x$) and $x_c$ (at $T = 60$ K) from Ref. [16]. Second, we note that that the scaling parameter $\beta \sim 0.15$ obtained from our amplitude
mode data is substantially smaller than the value of 1/2 suggested by the mean-field model of Eq. 5.1 [98, 99]. However, the scaling parameter of $\beta \sim 0.15$ in Cu$_x$TiSe$_2$ is consistent with the critical exponent for the order parameter in the 2D three-state Potts model, $\beta = 0.133$ [108]: this model is appropriate for the CDW in layered Cu$_x$TiSe$_2$ because of the three-fold degenerate ground state that arises from the three commensurate CDWs in this material [30, 92, 96, 97].

The “universal” scaling of the Cu$_x$TiSe$_2$ amplitude mode as functions of both $T/T_{CDW}$ and $x/x_c$ in Fig. 5.7 emphasizes that $x$-dependent mode softening – like more conventional thermal mode softening – is associated with a critical point at $x_c$ that drives both critical softening behavior ($\omega_o \to 0$) and overdamping of the amplitude mode as $x \to x_c$. Indeed the $x$-dependent amplitude mode softening data between $0 < T \leq 100$ K, which are summarized in Fig. 5.8, suggest the presence of a CDW phase boundary line $x_c(T)$ in Cu$_x$TiSe$_2$ that extends – from the phase boundary line established by Morosan et al. [16] – down to a quantum ($T \sim 0$) critical point. To obtain quantitative estimates of $x_c(T)$ in Cu$_x$TiSe$_2$ from our data, the $\omega_o$ vs. $x$ curves in Fig. 5.8 were fit using the same functional form as that used to fit the $x$-dependent data at $T = 60$ K in Fig. 5.7, i.e., $\omega_o(x) = \omega_o(0)(1 - x/x_c)^\beta$ with $\beta \sim 0.15$, where $\omega_o(0)$ is the $x = 0$ value of the A$_{1g}$ amplitude mode frequency at a particular temperature. Note that the quantities contributing to the prefactor, $\omega_o(0)$, should not have a significant $x$-dependence: the reduced temperature factor in Eq. 5.1 varies less than 5% between $x = 0$ and $x = 0.06$, and the unscreened frequency $\tilde{\omega}$ in Eq. 5.1 is not expected to have a significant doping dependence in Cu$_x$TiSe$_2$ for reasons described above. Additionally, in obtaining estimates of $x_c(T)$ from our data, we assume that the scaling parameter $\beta \sim 0.15$ obtained from fits to the $T = 60$ K data in Fig. 5.7 does not vary significant for the $\omega_o$ vs. $x$ curves at the other temperatures shown in Fig. 5.8 – this assumption is justified by the wide range of $\omega_o$ vs $T$ and $\omega_o$ vs. $x$ curves that scale according to the power-law form $\omega_o \sim (1 - p)^{0.15}$ in Fig. 5.7 ($p = T/T_{CDW}$ or $x/x_c$), and by theoretical predictions for the critical exponent expected for the order parameter in a 2D system with a threefold degenerate ground state, $\beta \sim 0.133$ [92, 96, 97, 108]. Thus, the resulting fits of the data in Fig. 5.8 (solid lines) have only $x_c(T)$ as an unconstrained
Figure 5.8: Summary of the $A_{1g}$ amplitude mode frequency ($\omega_o$) vs $x$ for different temperatures. The solid lines are fits using $\omega_o/\omega_o(0) = (1 - x/x_c(T))^\beta$, with $\beta = 0.15$–0.16. The inset shows estimated values of $T(x_c)$ from the fits (filled circles); $T_{CDW}$ data from Ref. [16] (open circles) are shown for comparison. The inset also shows a contour plot of the temperature an $x$-dependent linewidth $\Gamma$ data, which ranges from light red ($\Gamma \sim 3\text{cm}^{-1}$) to dark red ($\Gamma \sim 17\text{cm}^{-1}$). The solid line denotes the superconductor (SC) phase boundary line [15].

parameter. The estimates of $T(x_c)$ obtained from the fits in Fig. 5.8 are represented by the filled circles in the inset of Fig. 5.8; also shown for comparison are previous measurements of $T(x_c)$ (open circles) by Morosan et al. [16]. The reasonableness of our $T(x_c)$ estimates is supported by two self-consistency checks: First, our estimates
of $T(x_c)$ provide good fits of the $x$-dependent $A_{1g}$ amplitude mode linewidths using the functional form, $\Gamma(T) \sim (x_c(T) - x)^{-\gamma}$, as illustrated by the dashed line in Fig. 5.6(a) for $\gamma \sim 2$, and second, our estimated value for $x_c$ ($T = 80$ K) overlaps with the known phase boundary line from Morosan et al. [16].

The values of $T(x_c)$ estimated from our $x$-dependent mode softening results in Fig. 5.8 are consistent with a low temperature CDW phase boundary in $\text{Cu}_x\text{TiSe}_2$ that extends from the phase boundary line measured by Morosan et al. [16] down to a quantum critical point at roughly $x_c(T = 0) \sim 0.07$. This suggests that SC and fluctuating CDW order coexist in the doping range $x \sim 0.04$–0.07 of $\text{Cu}_x\text{TiSe}_2$. We note, however, that because the amplitude mode becomes overdamped and unobservable very close to the transition region – due to the breakdown of long-range CDW order and zone-folding [100, 101, 102] – we cannot rule out the possibility that other effects, e.g., disorder from Cu intercalation, may lead to different quantum critical behavior (i.e., for $T \sim 0$ and near $x \sim 0.07$) than that implied by the $x$-dependent scaling behavior we observe up to $x = 0.05$ in Fig. 5.8. Consequently, it would be useful to study the putative transition region $x_c(T = 0) \sim 0.07$ with methods more sensitive to short-range fluctuating CDW order, such as inelastic x-ray or neutron scattering. It is nevertheless interesting that the value of the quantum critical point $x_c(T = 0) \sim 0.07$ estimated from our $x$-dependent mode softening data is close to the peak in $T(x_c)$, suggesting a possible connection between SC and the presence of fluctuating CDW order in $\text{Cu}_x\text{TiSe}_2$. Indeed, the inset of Fig. 5.8 also shows a contour plot of the temperature and $x$-dependent $A_{1g}$ amplitude mode linewidth, $\Gamma$, which ranges from light red ($\Gamma \sim 3$ cm$^{-1}$) to dark red ($\Gamma \sim 17$ cm$^{-1}$), illustrating the dramatic increase of CDW fluctuations as the phase boundary is approached with increasing $x$ and/or temperature.

This enhancement of CDW fluctuations and the loss of CDW coherence – evidenced by the dramatic increase in the amplitude mode linewidths – as a function of increasing $x$, is strikingly similar to the effect of pressure on the CDW, even though pressure and intercalation melt the CDW state via very different mechanisms. Remarkably, recent pressure-dependent transport measurements show that the collapse of the CDW with increasing pressure also leads to a SC phase [31].
The phase diagrams of TiSe$_2$ as functions of applied pressure and Cu-intercalation – which are summarized in Fig. 5.9 – have striking similarities. The onset of SC occurs at a pressure of about 2 GPa (20 kbar), close to the value of the critical pressure of “CDW melting”, $P \geq 25$ kbar. The SC transition temperature in the pressure-induced SC phase increases with increasing pressure, reaches a maximum value of $T_c=1.8$ K at $\sim 3$ GPa (30 kbar), and decreases upon application of higher pressures [31].

The phases along the $x$ and $P$ axes differ in some details – they have different electronic states [109, 110], and the SC phases have vastly different sensitivities to an applied magnetic field [16, 31]. However, both the intercalated and pressure-tuned phase diagrams resemble the proposed phase diagram for the layered dichalcogenides, in which there are two quantum critical points as a function of increasing lattice parameter: superconductivity (SC) and CDW order coexist above the lower of the two critical lattice parameters, while SC is present, but CDW order is not, above the higher of the two critical parameters [111]. Also, in both cases, there are strong CDW fluctuations in the vicinity of the peak of the SC phase. The evolution
of superconductivity upon the suppression of the CDW also raises the interesting possibility that the superconductivity could be the unusual exciton-mediated SC phase that was proposed by W. A. Little in 1964, but that has never been observed experimentally [112, 113]. Normally, the formation of a CDW precludes the evolution of an excitonic SC phase. However, when the CDW is suppressed via doping or pressure, it is possible that the system supports an unusual form of SC mediated by excitonic fluctuations. This possibility has been explored further, for the specific case of pressure-induced SC in 1$T$-TiSe$_2$, by van Wezel et al. who have proposed a theoretical model to explain how the interplay between phonons and excitons in 1$T$-TiSe$_2$ is shown to be responsible for its CDW phase and how the melting of CDW order gives rise to excitonic fluctuations that can drive the system to a SC state [114]. The Cu$_x$TiSe$_2$ system could well be the first system where we can experimentally study this hitherto unobserved, unique form of SC. Even if future experiments refute these claims, a careful investigation of the short-range fluctuating CDW order with more sensitive experimental techniques will provide a deeper understanding of the connection between fluctuating CDW order and superconductivity. Wagner et al. have also performed preliminary measurements of Cu$_x$TaS$_2$, which indicate that intercalation enhances the SC transition temperature, $T_c$, in this material and the SC phase has a dome shape similar to that in Cu$_x$TiSe$_2$ as a function of $x$ [115]. While the chemistry and structure of Cu$_x$TaS$_2$ is very similar to Cu$_x$TiSe$_2$, the microscopic mechanism of CDW formation in Cu$_x$TaS$_2$ is more conventional. Experimental comparison of these chemically similar systems would help clarify the universality of this behavior [115].
Chapter 6
Conclusions

In this thesis, I have described the results of our Raman scattering studies on two diverse strongly correlated systems – TbMnO$_3$ and Cu-intercalated TiSe$_2$ – as a function of temperature, magnetic field and doping. The main focus of our measurements was the study of quantum phase transitions – transitions that are driven, not by thermal fluctuations, but by quantum mechanical interactions at $T \sim 0$. In both cases, we find that critical fluctuations play a crucial role in driving the system through the quantum phase transition.

In TbMnO$_3$, we mapped out the detailed temperature and magnetic-field dependent phase diagram. Below a Néel temperature of 41 K, TbMnO$_3$ transitions to a sinusoidally modulated, incommensurate anti-ferromagnetic phase. We observe the appearance of a new soft mode in the incommensurate phase, and we attribute this “incommensurate phase” (IC) mode to the magnetoelastically induced lattice modulation that accompanies IC magnetic ordering. A second magnetic transition in TbMnO$_3$ occurs below $T_c \leq 28$ K; in this phase the Mn$^{3+}$ ions have an incommensurate spiral magnetic ordering that breaks inversion symmetry and induces an electric polarization along the $c$-axis. The application of a magnetic field along the $b$-axis direction causes a phase transition to a commensurate, magnetic spiral phase, in which the electric polarization flops to the $a$-axis direction. Our magnetic field-tuned measurements show evidence for field-induced quantum fluctuations of commensurate domains near the field-induced incommensurate-commensurate phase transition; we speculate that these domain fluctuations – which should be associated with strong quantum fluctuations of the polarization – help drive the field-induced polarization flop in this material.

In TiSe$_2$, we compare the “melting” of the charge order in the charge density
wave (CDW) phase as a function of temperature and Cu-intercalation. The CDW amplitude modes that appear in the Raman spectra below the CDW transition temperature, $T_{CDW} = 200$ K, are soft modes that serve as order parameters of the CDW state. Studying the evolution of these modes as a function of temperature and Cu-intercalation gives information about the long-range correlations and elastic properties of the CDW ground state. Our studies show that both temperature and Cu-intercalation cause a suppression of the transition temperature $T_{CDW}$ and a “melting” of long-range CDW order. Remarkably, the frequency dependence of the soft mode shows identical scaling behavior both as a function of temperature and Cu-intercalation. In addition, Morosan et al. showed that Cu$_x$TiSe$_2$ has an emergent superconducting (SC) phase for $x \geq 0.04$, with a maximum SC transition temperature of $T_c \sim 4.15$ K at $x=0.08$. The softening and significant linewidth broadening of the CDW amplitude modes indicates strong fluctuations of the CDW near the quantum phase boundary between CDW and superconductor phases. This suggests a possible coexistence of fluctuating CDW and SC phases in this regime. A strikingly similar phase diagram has also observed for pressure-tuned TiSe$_2$ by Kusmartseva et al., with a fluctuating CDW order transitioning to a SC phase, leading to speculation that the emergent phase is an excitonic superconductor that evolves upon suppression of the CDW order.
References


[10] Barath, H., Kim, M., Cooper, S. L., Abbamonte, P., Fradkin, E., Mahns, I., Rübhausen, M., Aliouane, N. & Argyriou, D. N. Domain fluctuations near the


We note also that the expected coupling of $\mathbf{q} = 0$ optical phonons to finite-$\mathbf{q}$ spin waves due to zone folding—which is an alternative description of the 125 cm$^{-1}$ IC-mode shown in Fig. 3—has also been recently discussed by de Sousa and Moore in the specific case of incommensurate magnetic phases in multiferroic materials; see R. de Sousa and J.E. Moore, phys. rev. b 77, 012406 (2008).


