

Monitoring Ultrafast Lattice Dynamics in 2D NbTe₂

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

In my thesis, I present my work investigating the ultrafast, photoinduced dynamics of NbTe₂ using time-resolved transient reflectivity, ultrafast electron diffraction, transmission electron microscopy, Raman spectroscopy and DFT calculations. Transient reflectivity and ultrafast electron diffraction measurements were setup and performed primarily by me with assistance from Ruofei Zheng and Sam Netzke, while all the data analysis was done solely by me. Transmission electron microscopy images were taken by Dr. Tyler Lott. Raman measurements were done by Leon Daniel using setups housed at the University of Duisburg-Essen in Prof. Marika Schleberger's group. DFT calculations were performed by Dedi Sutarma in Prof. Peter Kratzer's group.

Additional work was done over the course of my Master degree on developing the novel UED setup designed by Sam Netzke. Upon arrival to the lab, the high vacuum chamber was assembled and the electron gun was conditioned voltages up to ~ 120 KeV. I assisted Sam Netzke to: obtain and image, for the first time, the electron beam, image the first diffraction pattern of polycrystalline Al and perform the first time-resolved experiment on a blank copper mesh. Between each of these milestones, countless hours were spent troubleshooting and aligning.

More work was done with a visiting professor, Watheq Al-Basheer, from King Fahd University of Petroleum and Minerals. Here, he carried out transient reflectivity measurements on GeS and GaS to characterize their elastic properties. The data analysis was performed solely by me and has lead to two publications:

- W. Al-Basheer, C. Viernes, M. Cheng, R. Zheng, S. Netzke, K. Pichugin, and G. Sci-

aini. Determining the Out-of-Plane Longitudinal Sound Speed in GeS by Broadband Time-Domain Brillouin Scattering. ACS Omega 9, 15463–15467 (2024).

- W. Al-Basheer, C. Viernes, R. Zheng, S. Netzke, K. Pichugin, and G. Sciaini. Out-of-Plane Longitudinal Sound Speed Determination in GaS by Broadband Time-Domain Brillouin Scattering. ACS Omega 9, 47475–47479 (2024).

Abstract

The discovery and control of emergent phenomena in strongly-correlated materials is a cornerstone of modern condensed matter physics and materials science. Among these phenomena, charge density waves (CDWs) represent a striking example of how the coupling between electrons and the atomic lattice can give rise to new properties. Understanding the microscopic mechanisms behind CDW formation and their dynamical evolution is crucial not only for fundamental science, but also for the development of ultrafast, energy-efficient electronic and quantum devices. The idea behind controlling such phenomena has been propelled by the advent of ultrafast lasers which enables investigation of electron-lattice interactions and has lead to the realization of many phase transitions [1–4].

In this thesis, the ultrafast lattice dynamics of the layered quasi-two-dimensional material niobium ditelluride (NbTe_2) are explored, a system known to host a robust CDW phase. By employing both time-resolved transient reflectivity (TR) and ultrafast electron diffraction (UED), the femtosecond response is revealed from two different perspectives. These techniques enable direct observations of the dynamical structural distortion and coherent phonon generation with sub-picosecond temporal resolution. These findings reveal a rapid, photoinduced suppression of the CDW order within 200 femtoseconds, followed by coherent lattice oscillations that reflect the material’s transient structural state. UED measurements quantify a transient 1.3% CDW order suppression, while TR data show fluence-dependent modulations of phonon frequencies and lifetimes, highlighting the complex nature of the lattice response. At high fluence, the CDW order of NbTe_2 approaches a complete melting along with an irreversible tellurium crystallization on the sample surface—a phenomenon characterized by Raman spectroscopy and interpreted through density functional theory (DFT)-based calculations.

Beyond characterizing the behavior of NbTe₂, this thesis establishes a broader experimental framework for investigating symmetry-breaking transitions and metastable states in low-dimensional quantum materials. The work highlights the power of ultrafast techniques for unveiling non-equilibrium phenomena and offers insights into how light can be used to engineer and manipulate material properties on demand.

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Firstly, I would like to express my deepest gratitude towards my supervisor, Prof. German Sciaini, for his unwavering support, guidance and mentorship. His optimism and encouragement have been invaluable to both my academic and personal growth.

Next, I am thankful for all the group members who I've worked alongside with for the last two years, especially Dr. Kostyantyn Pichugin, Dr. Tyler Lott, Sam Netzke and Ruofei Zheng. Specifically, I would like to thank Sam Netzke. His expertise, both scientific and technical, has been essential. The countless late nights spent disassembling and reassembling the electron diffractometer have greatly accelerated this work.

I would also like to express further thanks to Ruofei Zheng. Without her, I would never have developed the patience required to align optics. I am especially grateful for her organizational skills which have kept me on top of the mountain of paperwork needed for our research stay in Germany. Beyond the lab, I'm thankful for our shared moments that have made this journey unforgettable.

I would also like to extend my sincere thanks to everyone at the University of Duisburg-Essen with whom I had the pleasure of collaborating. I am particularly grateful to Leon Daniel for his Raman spectroscopy knowledge and to Dedi Sutarma for his proficiency with DFT calculations. Thank you both for not only supporting this work, but also introducing me to German culture and making my stay in Duisburg truly enjoyable.

Finally, I thank my friends and family for their unwavering love and support.

Dedication

This is dedicated to the one I love.

Table of Contents

Author's Declaration	ii
Statement of Contributions	iii
Abstract	v
Acknowledgements	vii
Dedication	viii
List of Figures	xii
List of Tables	xvi
List of Abbreviations	xvii
1 Introduction	1
1.1 Ultrafast Processes	3

1.1.1	Carrier Excitation	3
1.1.2	Coherent Phonon Generation	5
1.2	Charge Density Wave Theory	7
1.2.1	The 1-D Crystal	8
1.2.2	The Periodic Lattice Distortion	9
1.2.3	The Electronic Gap	11
1.2.4	The Periodic Charge Density	13
1.2.5	Collective Excitations	15
2	Methodology	19
2.1	Reflectivity Theory	20
2.1.1	Reflectivity	20
2.1.2	The Dielectric Response	21
2.2	Diffraction Theory	25
2.2.1	Scattering Theory	26
2.2.2	Scattering from a Crystal	27
2.2.3	Diffraction Condition	30
2.3	Experimental Setups	32
2.3.1	Transient Reflectivity	32
2.3.2	Ultrafast Electron Diffraction	33
2.4	Charge Density Wave Observables	38
2.5	Data Collection and Analysis	41

3	Ultrafast Dynamics of a Charge Density Wave	47
3.1	NbTe ₂	47
3.2	Sample Characterization	49
3.3	Ultrafast Electron Diffraction	51
3.3.1	Static Electron Diffraction	51
3.3.2	Ultrafast Electron Diffraction	53
3.3.3	Structure Factor Calculations	55
3.4	Transient Reflectivity	58
3.5	Recomposition	62
4	Conclusion and Outlook	67
4.1	Conclusion	67
4.2	Outlook	68
	References	70
	APPENDICES	82
A	PDF Plots From Matlab	83
A.1	Functions used to fit traces	83
A.2	Functions used to analyze UED data	85
A.3	Example script used to extract intensities from a set of diffraction data . .	98

List of Figures

1.1	a) Timescale of the carrier dynamics following excitation. b) Illustration of coherent optical phonon generation mechanisms. In the ISRS case, the pump acts as an impulsive force on the atoms. In the DECP case, the pump changes the equilibrium position of the atoms	4
1.2	a) shows the divergent response function leading to the Kohn Anomaly and periodic lattice distortion in b) and c).	12
1.3	The periodic lattice distortion opens a gap in the quasiparticle spectrum shown in a) leading to the formation of electron hole pairs shown in b). . .	14
1.4	a) The mexican-hat shape of the free energy surface corresponding to order parameter fluctuations. b) The dispersion relations for collective excitations of the amplitude and phase of the order parameter. c) and d) The atomic motions and electron density modulations associated with the amplitudon and phason.	17
2.1	Illustration of the pump-probe scheme and the probes relevant to this thesis.	20
2.2	Illustration of the Lorentz model, the real and imaginary dielectric response and the reflectivity at normal incidence due to an incident plane-wave. . .	22

2.3	Forms of the shape factor in 1 dimension for different crystal sizes.	29
2.4	a) Construction of an Ewald sphere in reciprocal space. b) Bragg condition shown in real-space.	31
2.5	Layout of the experimental setups at UeIL. OPA = optical parametric amplifier, BS = beamsplitter, M = mirror, G = grating, BBO = barium borate crystal, HVC = high voltage cable, HVF = high voltage feedthrough, PC = photocathode, ML = magnetic lens, YAG = yttrium aluminum garnet. . .	33
2.6	a) The electric fields of our electron gun with an applied voltage of 100 kV calculated using POISSON. b) The pulse durations at the sample which is located 3.6 cm from the photocathode.	36
2.7	a) and c) show the diffraction patterns above and below the transition temperature. The satellite and Bragg peaks are labelled in c). The backfolding is shown in b) and the collective excitations of the order parameter is illustrated in d and e).	39
2.8	a) Example of one diffraction image of NbTe ₂ . b) Region of interest to perform fitting. c) Slice of ROI showing 2D Gaussian fitting of all the peaks. d) Peaks are isolated by subtracting fits of other peaks. The intensities are found by integrating over a specified region.	43
3.1	Top and side views of the structure of 1T'' NbTe ₂ . The unit cell of the undistorted and distorted phases are shown in blue and black respectively. The double zig-zag bonding is drawn with dashed lines which causes a formation of niobium trimers. The undistorted positions of the Niobium atoms are shown in the blurred in the top view.	48

3.2	Samples used in this experiment. a) Bulk crystal used for transient reflectivity. b) Low magnification TEM image of the microtomed samples used for UED. c) Exfoliated samples used for Raman spectroscopy. d) 1T phonon band calculations. e) 1T'' phonon band calculations. f) Experimental Raman spectra using 532 nm excitation.	49
3.3	(a) TEM image of a single NbTe ₂ domain. The reciprocal lattice unit cells of the undistorted and the distorted phases are drawn in blue and black respectively. The calculated reciprocal lattice is overlaid on the right half of the image with red dots denoting Bragg peaks and black dots denoting superlattice peaks. (b) Indexed UED pattern. Anomalous peaks are circled in purple. (c) Simulated diffraction patterns of different domain orientations, rotated by 60° and 120°, replicating the observed domain structure.	52
3.4	(a) Differential diffraction pattern at 300 fs post-excitation. (b) Temporal evolution of select diffraction peaks and background intensity, fitted using exponential decays. The arrows indicate the selected peaks. (c) Proposed stages of the system following photoexcitation.	54
3.5	Experimentally observed and simulated intensity variations, revealing a 1.3% structural distortion. Inset: atomic displacements used in the undistorted structure model.	56
3.6	a) Representative differential reflectivity data. b) Fourier transform of a). c) Select transient reflectivity traces at 600 nm for varying fluences. Inset: Fourier transforms of the TR signals, comparing the 1T'' and HF phases at 1.1 mJ/cm ² after background subtraction. (d–f) Extracted fitting parameters for the oscillatory term, highlighting fluence-dependent phonon dynamics.	59

3.7	a) Superlet transform of the TR signal at 600 nm with a pump fluence of 3.7 mJ/cm ² . The solid vertical line shows the slice taken for b. b) Time-resolved spectral slice at 1 ps fitted with a Lorentzian to track the peak position. c) Temporal evolution of the phonon mode frequency.	62
3.8	a) Raman spectra before and after laser irradiation with the frequencies of each peak labelled. b) Microscope images before (bottom) and after (top) irradiation. c) and d) Zoomed in spectra at higher spectra showing additional, less intense modes.	63
3.9	a) Peak temperatures as a function of excitation fluence. The decomposition temperature threshold is shown with a red dotted line. b) Changes in reflectivity before and after complete Te crystallization as a function of number of shots at a fluence of 11.2 mJ/cm ² . c) Fourier transforms of TR data using a fluence of 3.7 mJ/cm ² after exposing the sample to different levels of high fluence.	66

List of Tables

2.1	UeIL UED instrument parameters used in this thesis.	38
3.1	Change in phonon amplitudes from the Fourier transform after exposure to a different number of total 14 mJ/cm ² shots. The phonon amplitudes are taken from data obtained with a pump fluence of 3 mJ/cm ² . The A _g ¹ amplitudes after more than 30000 shots is below the noise.	65

List of Abbreviations

ASTRA A Space Charge Tracking Algorithm

BBO Barium Borate

CDW Charge Density Wave

CWT Continuous Wavelet Transform

DECP Displacive Excitation of Coherent Phonons

DFT Density Functional Theory

EELS Electron Energy Loss Spectroscopy

FFT Fast Fourier Transform

FHG Fourth Harmonic Generation

FT Fourier Transform

FWHM Full Width at Half Maximum

IRF Instrument Response Function

ISRS Impulsive Stimulated Raman Scattering

LEED Low Energy Electron Diffraction

OPA Optical Parametric Amplification

PLD Periodic Lattice Distortion

RMS Root Mean Square

ROI Region of Interest

SLT Superlet Transform

STFT Short Time Fourier Transform

STM Scanning Tunelling Microscopy

TEM Transmission Electron Microscopy

TMDC Transition Metal Dichalcogenide

TR Transient Reflectivity

UED Ultrafast Electron Diffraction

UeIL Ultrafast electron Imaging Lab

YAG Yttrium Aluminum Garnet

Chapter 1

Introduction

The properties of solid-state materials are often understood by considering their fundamental subsystems: charge, lattice, orbital, and spin degrees of freedom. In many cases, these subsystems can be treated as largely independent, allowing for simplified models of electronic and structural behaviour [5, 6]. However, in strongly correlated materials, interactions between these subsystems give rise to emergent phenomena, such as ferromagnetism, superconductivity and charge density waves (CDWs), which cannot be explained through independent electron approximations. Understanding these interactions is essential for the development of next-generation quantum materials.

Ultrafast lasers have revolutionized the study of correlated materials by enabling the selective excitation of specific subsystems while monitoring the dynamical response of other subsystems on femtosecond timescales. This capability allows researchers to probe non-equilibrium states and transient interactions that are otherwise inaccessible in steady-state measurements. A particularly intriguing aspect of ultrafast dynamics is the possibility of inducing metastable, hidden states, commonly referred to as photoinduced phase transi-

tions. Such phases, with distinct properties, which may be accessed with such precise control has started this idea of “properties on demand” [7] and offers new pathways for material engineering and device applications. Some examples of famous photoinduced phase transitions are: the topological phase transition in WTe_2 [1], the insulator to metal transition in VO_2 [4, 8, 9] and a plethora of charge density wave transitions in various 2D materials (TaS_2 [10, 11], TaTe_2 [?], VTe_2 [12], etc.).

The **CDW** is an example of a phenomena arising from interactions between the charge and lattice systems. Instabilities in the electronic system make the lattice susceptible to a periodic lattice distortion (**PLD**). The elastic energy cost in creating this distortion is offset by a gap opening in the single-particle dispersion, creating sinusoidally modulated electron densities. Then, by optically exciting the electronic system, these instabilities relax and potentially destroys the **CDW** order. As a result, a plethora of ultrafast experiments have been performed on various **CDW** materials in an attempt to reveal this phase transition and understand the corresponding mechanism [3, 10, 13–15].

In this thesis, I aim to elucidate the charge-lattice interactions which lead to the formation of **CDWs** in NbTe_2 . In chapter 1, I will first introduce typical responses to ultrafast photoexcitation and then outline Peierls’ theory of **CDWs** by considering the simple 1D monoatomic crystal. Here, the derivation begins with the Hamiltonian of the system and expressions for the **PLD**, electronic gap and modulated electron density are obtained using mean-field approximations.

In chapter 2, I present the techniques used in this thesis: Transient reflectivity (**TR**) and ultrafast electron diffraction (**UED**). Reflectivity will be described using the Drude and Lorentz models as a way to understand how photoexcitation may create observable changes. With electron diffraction, I will begin with discussing the problem of a single electron scattering from some potential and then generalize it to periodic potentials, as in

the case of crystals. I will then show the experimental setups with more detail provided about the [UED](#) setup which has been in development over the whole course of this thesis. This is followed by two brief sections providing an overview of how these techniques can be used to monitor [CDWs](#) and how the data obtained from these techniques are analyzed. Chapter [3](#) showcases NbTe_2 , a [CDW](#) system which was theoretically predicted to align well with Peierls' theory described in chapter [1](#). The structural dynamics, as seen using [UED](#), following photoexcitation report an ultrafast suppression of the [CDW](#) order within 200 fs, while [TR](#) is able to indirectly reveal non-thermal melting of the [CDW](#). At extreme excitation conditions, I show an irreversible, crystallization of tellurium on the sample characterized by Raman spectroscopy measurements. Further investigation is done to unravel the nature of this Te growth via all the aforementioned techniques and density functional ([DFT](#)) calculations.

The final chapter of the thesis, chapter [4](#), summarizes the results and provides different avenues to continue this research such as additional experiments on NbTe_2 which give deeper understanding into both the non-thermal melting and Te growth mechanisms.

1.1 Ultrafast Processes

1.1.1 Carrier Excitation

When an ultrafast laser pulse is incident on a material, the initial absorption of photons by charge carriers leads to a highly non-equilibrium electronic distribution [[16](#)]. In semiconductors and insulators, this absorption results in the promotion of electrons across the bandgap via single-photon or multi-photon absorption, depending on the excitation energy. Immediately after excitation, the electronic system deviates significantly from

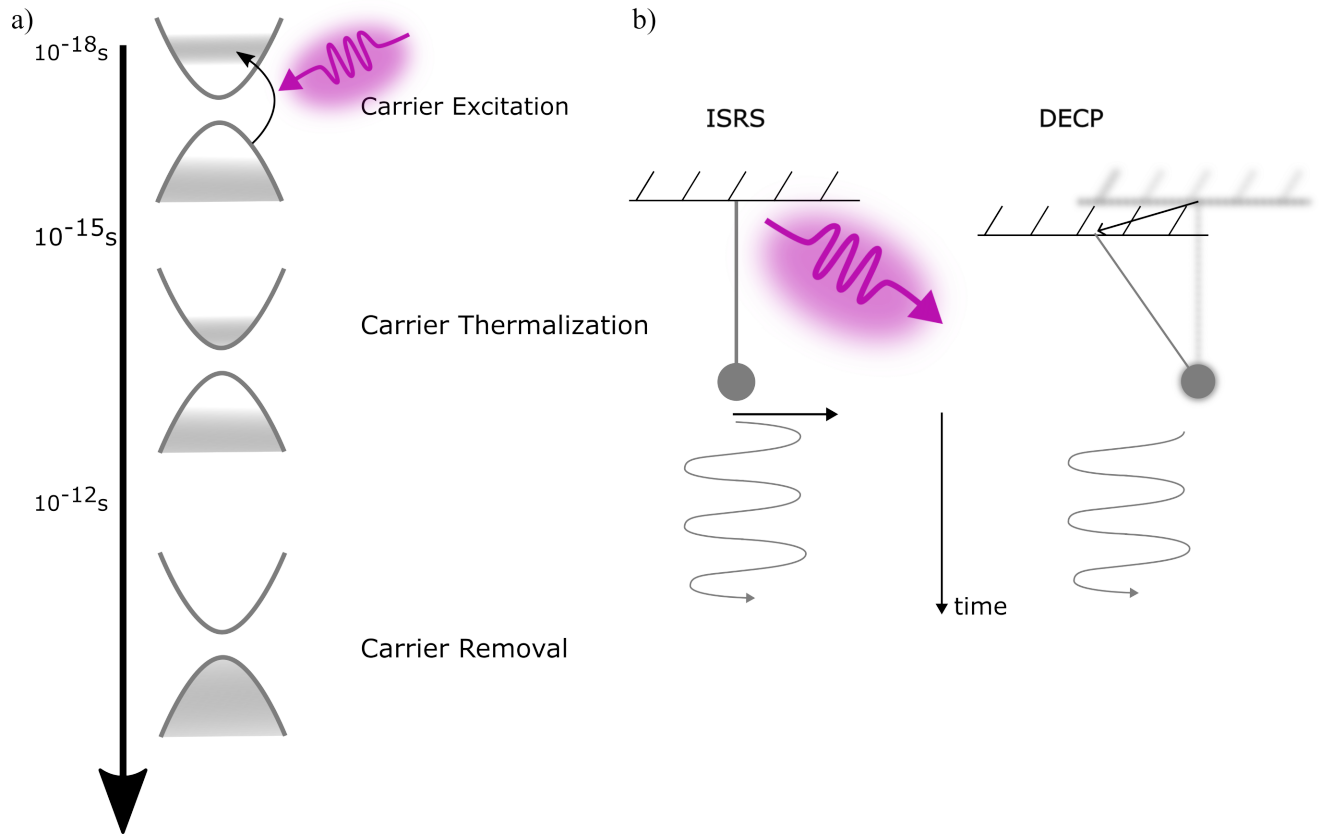


Figure 1.1: a) Timescale of the carrier dynamics following excitation. b) Illustration of coherent optical phonon generation mechanisms. In the [ISRS](#) case, the pump acts as an impulsive force on the atoms. In the [DECP](#) case, the pump changes the equilibrium position of the atoms

thermal equilibrium, rendering conventional statistical descriptions such as Fermi-Dirac or Boltzmann distributions inapplicable [17].

Following excitation, the high-energy carriers undergo rapid relaxation through various scattering mechanisms. Carrier-carrier scattering, occurring within tens of femtoseconds, facilitates energy redistribution among charge carriers. The eventual thermalization and recovery of the Fermi-Dirac distribution of the electronic system primarily occurs through electron-phonon scattering, wherein excess energy is transferred from the electronic subsystem to the lattice. Due to the relatively low energy of phonons, achieving complete thermal equilibrium between these subsystems requires multiple scattering events over picosecond timescales. Finally, in semiconductors and insulators, excited carriers may undergo radiative recombination (via photon emission) or non-radiative recombination mechanisms such as Auger processes, leading to the decay of the excited state. Beyond this eventual thermalization of charge carriers, this impulsive excitation can generate coherent lattice vibrational modes. The following section discusses some of the proposed mechanisms

1.1.2 Coherent Phonon Generation

The equation of motion for any vibrational mode in a solid may be described by a phenomenological second-order differential equation with the excitation pulse acting as the driving force:

$$\frac{d}{dt^2}Q + \omega^2 Q = F(\mathbf{r}, t) \quad (1.1)$$

Many theories have been put forward to explain the origins of this driving force [18–21]. In all these mechanisms, it is necessary that the photoexcitation is much shorter than

the period of the phonon of interest for coherent generation. With regards to coherent optical phonons, one well-established mechanism is impulsive stimulated Raman scattering (ISRS) [19,20]. Here, the driving force is the electric field itself. Raman scattering is a phenomenon which describes incident light inelastically scattering with the vibrational modes of the crystal, producing light which is frequency shifted negatively (Stokes shifted) or positively (Anti-Stokes shifted) by the vibrational frequency. Working backwards, the vibrational mode may be excited with a combination of light waves, one which is already Stokes/Anti-Stokes shifted from the other, “stimulating” the vibrational mode. Instead if we have a single pulse which is sufficiently short, then the spectral bandwidth of the pulse must also contain components which satisfy this stimulation condition. Since the modes are excited on a timescale much shorter than their period, they are coherent.

An alternative mechanism has been proposed which considers materials that absorb instead of scatter called the displacive excitation of coherent phonons (DECP) [18,20]. The absorbed pulse excites the carriers which quickly scatter and thermalize faster than the atoms’ response, resulting in a sudden change in the electronic potential, driving the vibrational mode by essentially shifting the atoms’ equilibrium position. While both of these mechanisms only excite Raman-active modes, one of the differences is the nature of the two driving forces. With ISRS, the modes are driven by an impulsive “delta force” stemming from the ultrashort electric field pulse, while with DECP, the new electronic potential of the excited state acts as a step-wise force. The observable difference, shown in figure 1.1b, is a phase difference between the two exciting schemes.

These theories are limited to Raman-active, optical phonon modes with zero momentum. Typically, UV-Vis light is used for photoexcitation and therefore wavelengths on the order of 10^2 nm. Consider phonons which involve oscillations over multiple unit cells (finite momenta) and therefore have wavelengths on the order of 1 nm. Then, since the momenta,

which is inversely proportional to the wavelength, must be conserved, it is impossible to directly excite these phonons. However, many studies have been conducted which use pump-probe techniques to monitor coherent acoustic phonons, with non-zero momenta, to measure elastic constants in many different materials [22–25]. Here, the acoustic phonon is generated as a consequence of the impulsive, sharp, temperature gradient [26]. The excitation pulse is absorbed in a very confined region causing a local expansion in the lattice. This starts a strain-wave propagating parallel to this temperature gradient.

Together, these mechanisms illustrate how coherent acoustic and optical phonons can be generated, offering precise control of a material’s structure. In the next section, I will introduce the CDW phase, which causes a spontaneous breaking of the lattice symmetry. Here, it will be shown that a single phonon mode connects the two structures, whereby sufficiently exciting this particular phonon opens up the possibility of optically controlling the CDW phase.

1.2 Charge Density Wave Theory

CDWs arise as a result of spontaneous symmetry breaking arising from charge-lattice interactions and is characterized by a periodic modulation of the electronic density accompanied by a structural distortion of the lattice. The modulation is associated with a specific wavevector and leads to a gapped fermi surface and periodic lattice distortion (PLD). In this section, I introduce the theory behind CDW formation [27].

1.2.1 The 1-D Crystal

CDW theory is introduced by considering the simplest model system: the 1-D monoatomic crystal. Following the derivations in [27], consider a monatomic lattice and a free electron gas. The hamiltonian can be described by the sum of the hamiltonians for the electron and lattice system as well as an interaction hamiltonian:

$$\begin{aligned}
H &= H_{el} + H_{ph} + H_{el-ph} \\
&= \sum_k \varepsilon_k a_k^\dagger a_k + \sum_q \hbar \omega_q (b_q^\dagger b_q + \frac{1}{2}) + \sum_{k,q} g (b_{-q}^\dagger + b_q) a_{k+q}^\dagger a_k
\end{aligned} \tag{1.2}$$

Where k indicate electronic wavevectors, $a^\dagger$ and a are the electronic raising and lowering operators, q indicates phonon wavevectors, ω_q is the frequency of the phonon, $b^\dagger$ and b are the phonon raising and lowering operators and g is an electron-phonon coupling constant, which, for simplicity, does not depend on q . Here, the interaction term assumes that only the relative positions between the electron and ions matter and that the displacement of the ions from equilibrium is small. With this, the equation of motion of the ionic normal mode position operator is:

$$\begin{aligned}
\frac{d^2}{dt^2} Q_q &= -\frac{1}{\hbar^2} [[Q_q, H], H] \\
&= -\omega_q^2 Q_q - g \sqrt{\frac{2\omega_q}{M\hbar}} \rho_q
\end{aligned} \tag{1.3}$$

Here $Q_q = \frac{1}{\sqrt{2\omega_q}} (b_q + b_{-q}^\dagger)$ is the normal mode coordinate, M is the ion mass and $\rho_q = \sum_k a_{k+q}^\dagger a_k$ is the electronic density fluctuation operator which gives the charge density. The charge density includes the induced charge density from the movement of the posi-

tively ionic potential, $\phi(q) = g(b_{-q}^\dagger + b_q) = g\sqrt{\frac{\hbar}{2M\omega_q}}Q_q$, attracting the negatively charged electrons. Assuming that this induced charge is proportional to the ionic potential, i.e. linear response, then the normal mode behaves as the same harmonic oscillator, but with a renormalized frequency. This renormalization is known as the Kohn anomaly [27]:

$$\omega_{ren,k}^2 = \omega_q^2 - \frac{2g^2\omega_q}{\hbar}\chi(q) \quad (1.4)$$

Where $\omega_{ren,k}$ is the renormalized frequency and $\chi(q)$ is the proportionality constant called the electric susceptibility. Then, with a sufficiently strong electron-phonon coupling constant and/or electric susceptibility, the frequencies of some modes may be softened completely to zero, creating a “frozen-in” distortion. In the next section, the conditions for strong susceptibilities will be detailed.

1.2.2 The Periodic Lattice Distortion

The electric susceptibility may be derived using the Drude model, introduced in chapter 2, and assumes the electrons are free electrons and do not interact with each other. However, to accurately describe the CDW phenomenon, this model must be extended to include Pauli exclusion effects (the Sommerfeld model) and electron-ion interactions beyond the mean-field Hartree Fock approximation, leading to the Lindhard susceptibility [5]:

$$\chi(\mathbf{q}) = \frac{1}{(2\pi)^d} \int \frac{f_k - f_{k-q}}{\epsilon_k - \epsilon_{k-q}} d^3k \quad (1.5)$$

Where d is the number of dimensions, $f_k = f(\epsilon_k)$ is the fermi distribution and ϵ_k is the electronic energy. From equation 1.5, the contributions to the response are primarily due to

a large number of electron-hole pairs (opposite fermi occupations maximizes the numerator) which are separated by some momentum $\mathbf{q}_{FSN}$ and have a similar energy (minimizes the denominator). Then, the states which satisfy these conditions must be near the fermi-level and this momentum which connects the fermi-surface is the nesting vector. States from below (electrons) the fermi-level are paired with states above (holes) the fermi-level.

For the free-electron gas, the fermi surface is a ball with radius k_F and the strongest response would have magnitude $2k_F$ which pairs electrons and holes from across this surface, creating a singularity in the response. In one dimension, the fermi surface is a 1-d ball, i.e. 2 points, and there is only 1 possible nesting vector resulting in the divergent response at 0 K shown in figure 1.2. With increasing temperature, the differences between the occupation below and above the fermi-level decreases, decreasing the response. Quantitatively, integrating at $2k_F$ yields a temperature dependence of the material's susceptibility:

$$\chi(2k_F, T) = -e^2 n(\epsilon_F) \ln \frac{1.14\epsilon_F}{k_B T} \quad (1.6)$$

Where $n(\epsilon_F)$ is the density of states at the fermi-level. Subbing this into equation 1.4 allows a mean-field transition temperature to be defined where the frequency renormalizes to zero:

$$k_B T_{CDW}^{MF} = 1.14\epsilon_F e^{\frac{-1}{\lambda}} \quad (1.7)$$

where $\lambda = \frac{g^2 n(\epsilon_F)}{\hbar \omega_{2k_F}}$ is the non-dimensional electron-phonon coupling constant. A temperature dependence close to the transition temperature is obtained by Taylor expanding:

$$\omega_{ren, 2k_F} = \omega_{2k_F} \sqrt{\frac{T - T_{CDW}^{MF}}{T_{CDW}^{MF}}} \quad (1.8)$$

In principle, the softened phonon mode can induce a distortion which does not have long-range order, i.e. spatial fluctuations. Fluctuations are discussed in the last section, but for now, the distortion is assumed to be coherent. This can be interpreted as a non-zero expectation value of the softened phonon mode and therefore $\langle b_{2k_F} \rangle$ and $\langle b_{-2k_F}^\dagger \rangle$ are non zero. The magnitude of the lattice distortion can be found by subbing in the expectation values into the normal mode coordinate, Q_q and:

$$\langle u(x) \rangle = \Delta u \cos(2k_F x + \phi) \quad (1.9)$$

$$(1.10)$$

and

$$\Delta u = \sqrt{\frac{\hbar}{2NM\omega_{2k_F}}} \frac{|\Delta|}{g} \quad (1.11)$$

Here, the order parameter is defined as, $\Delta = |\Delta|e^{i\phi} = \langle b_{2k_F} \rangle + \langle b_{-2k_F}^\dagger \rangle$. In addition to describing the [PLD](#), we will see in the following sections that it also describes the formation of a gap in the fermi-surface and the periodically modulated electron density.

1.2.3 The Electronic Gap

To understand the effect of this distortion on the electronic states, a mean-field approximation is employed and the expectation value, $\langle b_q \rangle$, is substituted for the respective operator. Then, the hamiltonian for the electronic part is:

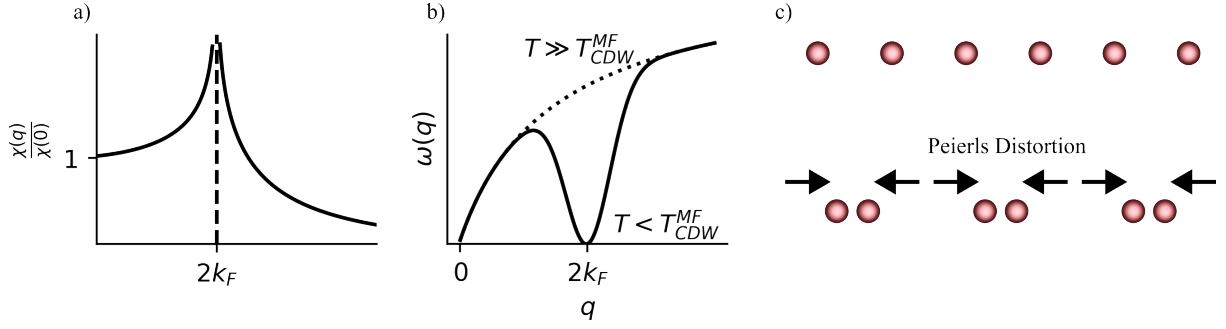


Figure 1.2: a) shows the divergent response function leading to the Kohn Anomaly and periodic lattice distortion in b) and c).

$$H = \sum_k \epsilon_k (a_{1,k}^\dagger a_{1,k} - a_{2,k}^\dagger a_{2,k}) + |\Delta| e^{i\phi} a_{1,k}^\dagger a_{2,k} + |\Delta| e^{-i\phi} a_{2,k}^\dagger a_{1,k} \quad (1.12)$$

Here, only states near the Fermi surface are considered and a linear dispersion relation is assumed. The indices 1 and 2 refer to $+k_F$ and $-k_F$ respectively and k relative to 1 and 2. For a monatomic 1-D crystal, this linear dispersion assumption holds since the Fermi level is far from the Brillouin zone boundary. This Hamiltonian is diagonalizable using the following transformation:

$$\gamma_{-,k} = U_k e^{-i\frac{\phi}{2}} a_{1,k} - V_k e^{i\frac{\phi}{2}} a_{2,k} \quad (1.13a)$$

$$\gamma_{+,k} = V_k e^{-i\frac{\phi}{2}} a_{1,k} + U_k e^{i\frac{\phi}{2}} a_{2,k} \quad (1.13b)$$

where

$$V_k^2 = \frac{1}{2} \left(1 + \frac{\epsilon_k}{E_k} \right) \quad (1.14a)$$

$$U_k^2 = \frac{1}{2} \left(1 - \frac{\epsilon_k}{E_k} \right) \quad (1.14b)$$

and:

$$E_{\pm,k} = \pm \sqrt{\epsilon_k^2 + \Delta^2} \quad (1.15)$$

is the dispersion relation at $\pm k_F$ relative to the fermi energy, resulting in the diagonalized hamiltonian:

$$H = \sum_k E_{-,k} \gamma_{-,k}^\dagger \gamma_{-,k} + E_{-,k} \gamma_{+,k}^\dagger \gamma_{+,k} \quad (1.16)$$

The new dispersion relation is plotted in figure 1.3 and we can see that a gap has opened at the fermi-level with magnitude 2Δ . The magnitude of the gap is determined by optimizing the elastic energy gained from the lattice distortion and the electronic energy lost from the opening of this gap and [27]:

$$\Delta = 2\epsilon_F e^{-1/\lambda} \quad (1.17)$$

Having established how the PLD opens a gap in the fermi-surface, in the next section, it will be shown how the periodic charge density is derived.

1.2.4 The Periodic Charge Density

To see the periodic charge density, the form of the CDW state must be found first. To construct the ground state, $|\phi_0\rangle$, start by filling up the states with lowest energies up to the fermi-level, i.e. all of the $\gamma_{-,k}$ states:

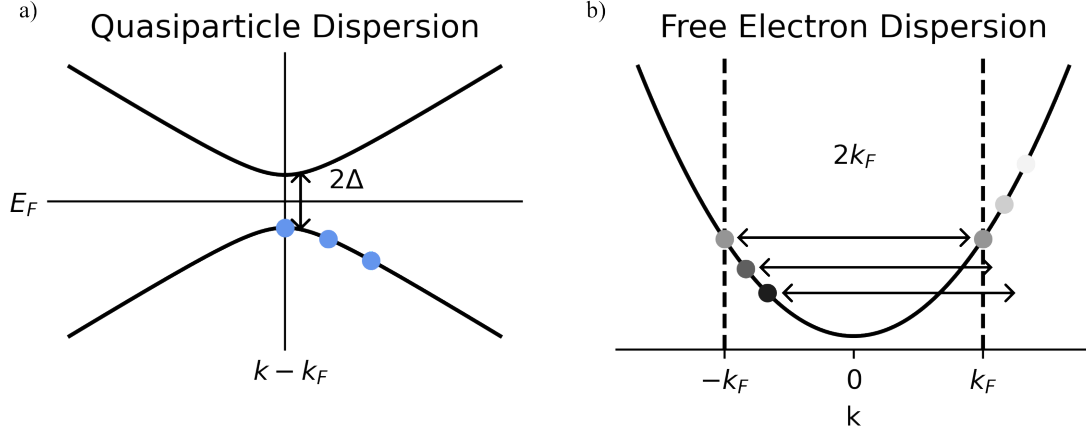


Figure 1.3: The periodic lattice distortion opens a gap in the quasiparticle spectrum shown in a) leading to the formation of electron hole pairs shown in b).

$$|\phi_0\rangle = \prod_{|k| < k_F} \gamma_{-,k} |0\rangle \quad (1.18)$$

Here, $|0\rangle$ is the vacuum state. Then, the ground state consists of a pairing of electronic states which are separated by $2k_F$. For states deep within the fermi-level, the dispersion is approximately the same as in the free electron gas, indicated by $V_k^2 \sim 1$ and $U_k^2 \sim 0$ and the quasiparticles are essentially electrons. Near the fermi-level, the quasiparticles are an equal superposition of an electron and a hole. This pairing is illustrated in figure 1.3. Assuming that the gap is much smaller than the fermi energy, then the charge density can be found by finding the expectation value of the density operator, $\Psi = \sum_k (a_{1,k} e^{ik_1 x} + a_{2,k} e^{ik_2 x})$ [27]:

$$\begin{aligned}
\rho(x) &= \langle \phi_0 | \Psi^*(x) \Psi(x) | \phi_0 \rangle \\
&= \rho_0 \left[1 + \frac{\Delta}{\hbar v_f k_f \lambda} \cos(2k_f x + \phi) \right]
\end{aligned} \tag{1.19}$$

Therefore, the charge density wave phase is completely defined by the complex parameter $\Delta e^{i\phi}$ and relates to the amplitude and phase of the [PLD](#), the modulated electron density and the magnitude of the electronic gap. In section [1.2.2](#), it is assumed that the distortion occurs coherently across the whole crystal, however, it is important to consider the effects of both spatial and temporal fluctuations in the amplitude and phase that occur due to thermal excitations across the gap. These fluctuations are considered in this final section.

1.2.5 Collective Excitations

With any phase transition, an order parameter is associated which vanishes above the phase transition temperature. Commonly, the temperature dependence of the free energy is approximated using Ginzburg-Landau theory [\[28\]](#). For the [CDW](#) transition, the order parameter is Δ and the free energy is approximated as:

$$F = a|\Delta|^2 + b|\Delta|^4 + c\left|\frac{d}{dx}\Delta\right|^2 + d\left|\frac{d}{dt}\Delta\right|^2 \tag{1.20}$$

Where the first two terms on the right side describe the potential energy of the [CDW](#) whose coefficients may be determined using the mean-field solutions from the previous sections, the third term describes additional potential energy due to spatial fluctuations and the last term describes the kinetic energy associated with any temporal fluctuations.

The temperature dependence is contained in the first term with $a = a_1(T - T_{CDW})$. The equilibrium order parameter which minimizes the energy is then $\Delta_0 = \sqrt{\frac{a_1(T - T_{CDW})}{2b}}$. This “mexican hat” shaped free energy is illustrated in figure 1.4 at some temperature below T_{CDW}

Then, consider a small fluctuation near equilibrium in the order parameter by $\Delta = [|\Delta_0| + \delta(x, t)]e^{i\phi(x, t)}$. Subbing this back into the free energy and ignoring terms with a higher order than 2:

$$F = a|\Delta_0|^2 + a\delta^2 + c\left(\frac{d\delta}{dx}\right)^2 + d\left(\frac{d\delta}{dt}\right)^2 + |\Delta|^2\left[c\left(\frac{d\phi}{dx}\right)^2 + d\left(\frac{d\phi}{dt}\right)^2\right] \quad (1.21)$$

$$(1.22)$$

Now, the kinetic and potential energy terms can be collected to construct the Lagrangian and the equations of motions for each fluctuation:

$$L = (\delta_t)^2 - c(\delta_x)^2 - a\delta^2 + |\Delta|^2[d(\phi_t)^2 - c(\phi_x)^2] \quad (1.23)$$

$$\implies c\frac{d^2\delta}{dx^2} = d\frac{d^2\delta}{dt^2} + a\delta, \text{ and} \quad (1.24)$$

$$c\frac{d^2\phi}{dx^2} = d\frac{d^2\phi}{dt^2} \quad (1.25)$$

The equations of motions here have yielded two separate wave equations for amplitude and phase fluctuations allowing collective excitations called amplitudons and phasons respectively. Assuming wave solutions, $Ae^{i(\omega t - kx)}$, then we get the following dispersion relations:

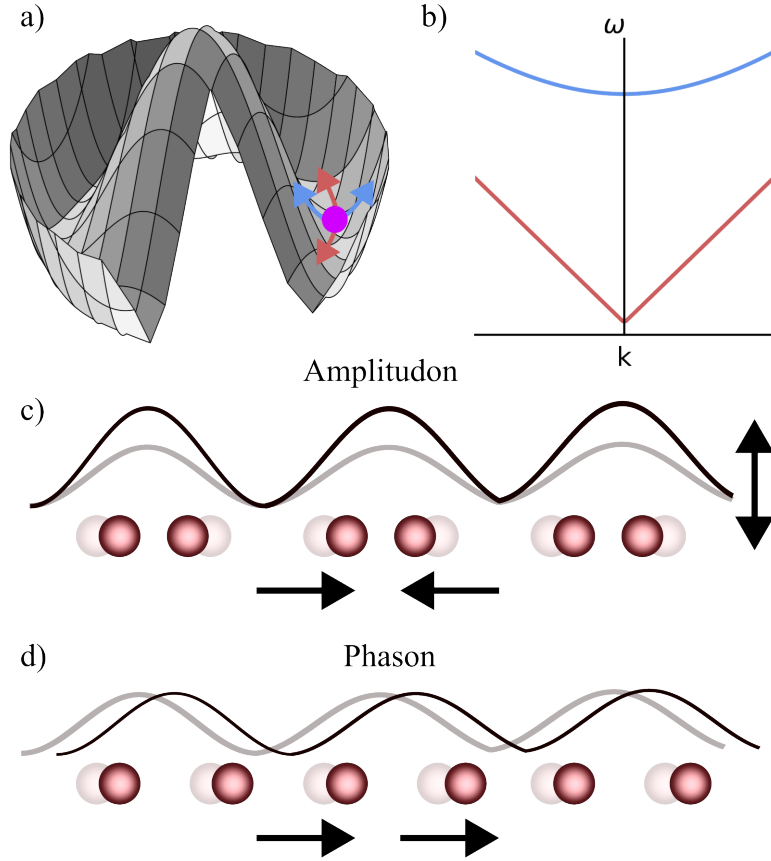


Figure 1.4: a) The mexican-hat shape of the free energy surface corresponding to order parameter fluctuations. b) The dispersion relations for collective excitations of the amplitude and phase of the order parameter. c) and d) The atomic motions and electron density modulations associated with the amplitudon and phason.

$$\omega_\delta = \frac{a}{d} + \frac{c}{d}k^2 \quad (1.26)$$

$$\omega_\phi^2 = \frac{c}{d}k^2 \quad (1.27)$$

.

The dispersion relations and atomic motions are shown in figure 1.4. These temporal fluctuations of the order parameter cause the atoms to move out-of-phase (amplitudon) and in-phase (phason) and therefore appear as optical and acoustic phonon modes, which from the first section, are able to be excited coherently by an ultrafast laser. The ability to essentially control the order parameter opens up the possibility of complete order suppression, driving the system to the higher symmetry phase. The next chapter introduces the probes used in this thesis to track the dynamics of the order parameter.

Chapter 2

Methodology

To monitor the sub-picosecond changes following photoexcitation, I utilize the pump-probe technique (2.1): A single laser pulse is split into two pulses. One is used to excite the sample while the other probes some kind of information. The timing between the two pulses are precisely controlled by modifying the path lengths allowing us to collect the information at any point before or after excitation. By combining these measurements, we obtain a full “movie” of information. In my thesis, I utilize [TR](#) and [UED](#) which monitor changes in the sample’s reflectivity and structure respectively. Below, I outline the theory of these two techniques and introduce the experimental setups.

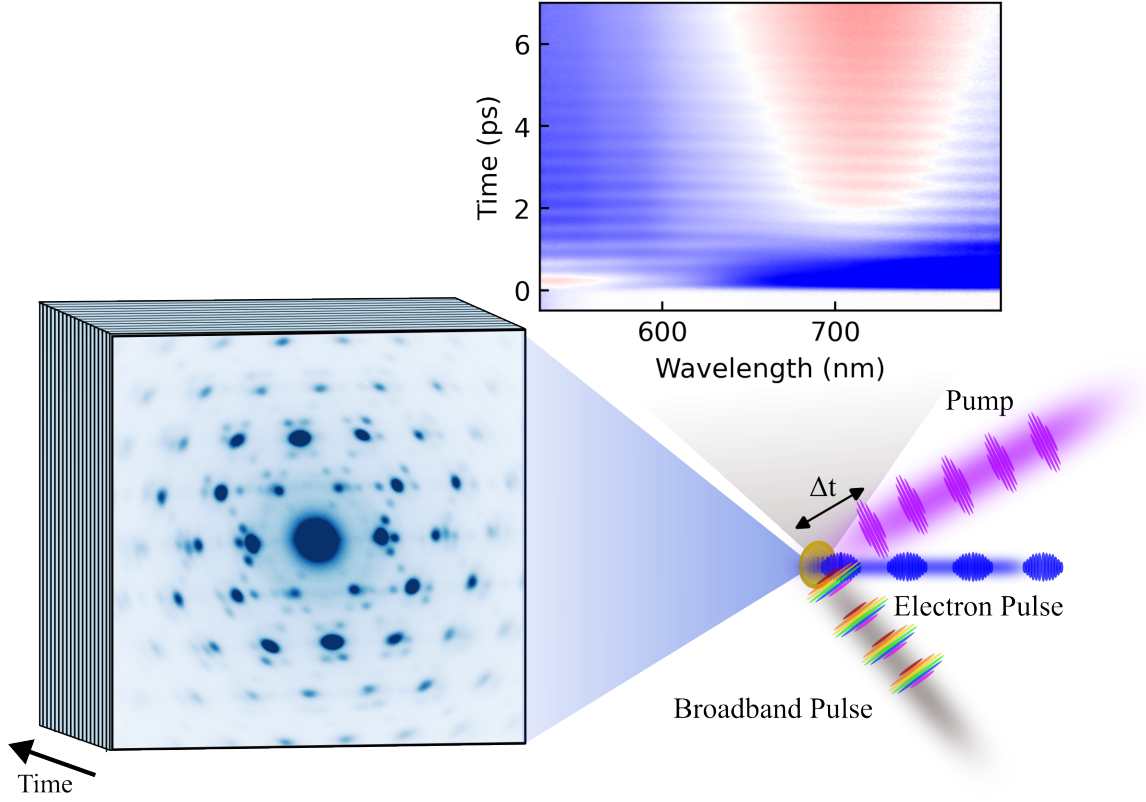


Figure 2.1: Illustration of the pump-probe scheme and the probes relevant to this thesis.

2.1 Reflectivity Theory

2.1.1 Reflectivity

When light is incident on the interface between two media, some of the light will reflect away and some will refract into the material. The amplitude and angles of both beams may be solved starting from Maxwell's equations while considering a conservation of energy and momentum and the appropriate boundary conditions. The equations which describe this relation are the Fresnel equations:

$$R_s = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \right|^2 \quad (2.1)$$

$$R_p = \left| \frac{n_1 \cos \theta_t - n_2 \cos \theta_i}{n_1 \cos \theta_t + n_2 \cos \theta_i} \right|^2 \quad (2.2)$$

Where R_s and R_p are the fractions of intensity reflected with s and p polarizations, n_1 and n_2 are the refractive indices of the two media and θ_i and θ_t are the angles of incidence and refraction given by Snell's law. Here the incident light is assumed to be a plane-wave and the media are isotropic. The refractive index is a property of the material and is related to its response, χ , to an applied electric field. In the following sections, I outline how this response is affected by the incoming pump pulse which then creates changes in the reflectivity.

2.1.2 The Dielectric Response

Electronic Contribution

An external field applied onto matter can polarize positive and negative charges within the material, inducing another electric field [29]. The polarization in general can depend on the applied electric field:

$$\mathbf{P} = \int_{-\infty}^{\infty} \chi(t - t') \mathbf{E}(\mathbf{t}) dt \quad (2.3)$$

Where χ is the response function called the electric susceptibility. Here, it is assumed that the response of the material is linear, but may be expanded to include higher orders of $\mathbf{E}$

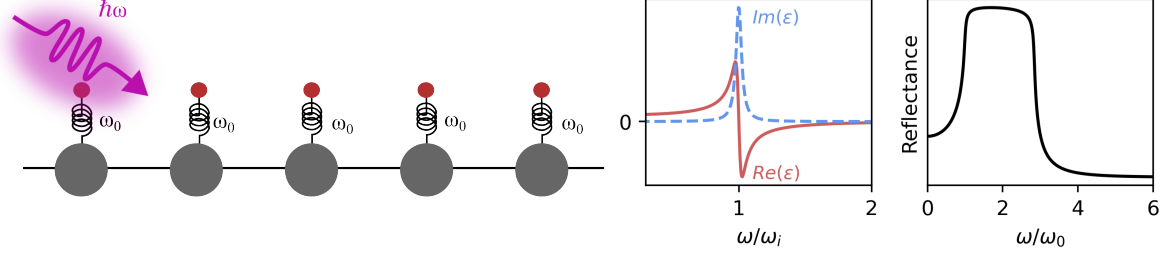


Figure 2.2: Illustration of the Lorentz model, the real and imaginary dielectric response and the reflectivity at normal incidence due to an incident plane-wave.

as well as the anisotropic tensor χ . By recognizing this is the convolution of two functions, it can be simplified by taking the Fourier transform:

$$\mathbf{P}(\omega) = \chi(\omega)\mathbf{E}(\omega) \quad (2.4)$$

After transforming, the response is a complex function and because of causality, the real and imaginary parts must be related by the Kramers-Kronig relations. With the susceptibility, the dielectric constant, ϵ , and the complex index of refraction, $\tilde{n}$ is defined as:

$$\begin{aligned} \epsilon &= \epsilon_0(1 + \chi) \\ &= \tilde{n}^2 \end{aligned} \quad (2.5)$$

Therefore, we may interpret transient reflectivity as probing the changes in this dielectric function. To obtain a quantitative form of the dielectric function, I will present the simple Lorentz model in 1D by assuming that there are N electrons in a material which are tightly bounded to the much heavier nuclei, such as in dielectric materials. Then, for small

displacements away from equilibrium, the electrostatic energy of the i -th electron may be approximated up to second order and the electrons follow this equation of motion:

$$m\left(\frac{d^2}{dt^2} + 2\gamma_i \frac{d}{dt} + \omega_i^2\right)x_i = F \quad (2.6)$$

Then, in the presence of a monochromatic electric plane-wave field, $E = E_0 e^{i(kx - \omega t)}$, the result is an oscillating net polarization:

$$\begin{aligned} P(t) &= q \sum_i x_i(t) \\ &= \sum_i^n \frac{q^2/m}{\omega_i^2 - \omega^2 - i\gamma_i\omega} E \\ &= \chi_{Lorentz} E \end{aligned} \quad (2.7)$$

Figure 2.2 shows the dielectric response for a system with N equal Lorentz oscillators around resonance and their corresponding reflectance. For frequencies lower than resonance, there is less reflectivity and less absorption corresponding to excitations below the bandgap. Near resonance, there is a large imaginary component leading to large reflectivity and absorption. As the frequency goes much larger, the material behaves similarly to a metal. In the case of metals, where electrons are mostly unbounded, the Lorentz model can be extended to the Drude model by setting the frequency of the restoring force to zero. Finally, combining both models yields an expression for the dielectric response of electrons in a general material:

$$\begin{aligned}
\epsilon &= \epsilon_0(1 + \chi) \\
&= \epsilon_0\left(1 + \chi_{Lorentz} - \frac{nq^2/m}{\omega^2 + i\omega/\mu}\right)
\end{aligned} \tag{2.8}$$

where n is the number of free electrons and μ is the electron mobility. Such a primitive model can be further generalized to consider the fermionic nature and electron-ion interactions [5], as well as material-dependent properties like band transitions and effective masses [30], however, this description is enough to qualitatively describe transient reflectivity data in terms of excited charge carriers.

We have now seen how the transient free carrier population induced by photoexcitation can be tracked by monitoring the changes in reflectivity. In the next section, the effects of coherently generated phonons on the reflectivity will be investigated.

Ionic Contribution

In addition to electrons, the ions also oscillate in response to the electric field according to the phonon modes of the crystal whose generation mechanisms were briefly discussed in section 1. Although these processes are nonlinear, assume that a coherent phonon mode has already been excited without assuming any specific mechanism. Then, each mode may be approximated as a Lorentz oscillator with resonant frequencies much smaller due to the higher masses of the ions. Then, similar dispersion curves shown in figure 2.2 appear at new resonant frequencies.

Additionally, the electronic susceptibility is, in general, a function of the instantaneous atomic positions [31]. Expanding around equilibrium atomic positions yields:

$$\chi \approx \chi_0 + \frac{d\chi}{dQ_k} Q_k + \dots \quad (2.9)$$

Where χ_0 is the susceptibility in equilibrium and the second term leads to the Raman susceptibility, where $Q_k = A_k \cos(k_k x - \omega_k t)$ is a normal mode. If an electric field plane wave is applied on this system, then the first term gives the Lorentz susceptibility derived in the previous section, while the second term gives us an oscillating time dependence on our susceptibility with the same frequency as the phonon mode.

Therefore, putting this together with the ultrafast responses discussed in chapter 1: photoexcitation causes charge carriers to be excited, freeing them from the valence band into the conduction band. As a result, some Lorentz contribution to the dielectric function is transferred into the Drude contribution resulting in a change in the reflectivity. As the carriers relax, the dielectric function returns back to the ground state. If a phonon is also coherently excited, the dielectric function and therefore the reflectivity oscillates at the phonon frequency.

2.2 Diffraction Theory

The other probe involved in this thesis is an electron pulse. While TR is an excellent tool to observe changes in the dielectric, it is hard to quantitatively monitor the amplitude of the atomic motions. Here I outline the theory of electron diffraction.

2.2.1 Scattering Theory

Following the derivations performed in [32], consider the problem of an electron incident on some localized potential, $V(\mathbf{r})$ at the origin, such as the coulomb potential of an atom. If the electrons are measured far from the potential, then only the asymptotic solutions to the scattering wavefunction φ should be of concern. Initially, assume that the particle is a plane wave heading towards the atom from the z-direction with wavevector k . Then, they interact and the result is a scattered wave as well as a transmitted wave. Then, far from the origin, ignoring the evolution during the interaction:

$$\varphi_k|_{r \rightarrow \infty} = e^{ik_i z} + f_k(\theta, \phi) \frac{e^{ikr}}{r} \quad (2.10)$$

The coefficient of the scattered term is called the scattering amplitude and determines the probability of detecting the particle at an angle θ and ϕ . To find the scattering amplitude, the time-independent Schrodinger equation should be solved:

$$(\Delta + k^2)\varphi(\mathbf{r}) = U(r)\varphi(\mathbf{r}) \quad (2.11)$$

which is equivalent to the integral equation [32]:

$$\varphi(\mathbf{r}) = \varphi_0(\mathbf{r}) + \int G(\mathbf{r} - \mathbf{r}')U(\mathbf{r}')\varphi(\mathbf{r}')d^3r' \quad (2.12)$$

Here, $V(\mathbf{r}) = \frac{\hbar^2}{2m}U(\mathbf{r})$, $\varphi_0 = e^{i\mathbf{k} \cdot \mathbf{r}}$ solves the homogeneous differential equation and $G(\mathbf{r})$ is the Green's function of the operator $\Delta + k^2$. To find a solution, it can be solved iteratively using a Born expansion by changing variables of equation 2.12 and substituting it back

into itself. By taking the first order term in $U(\mathbf{r})$, the first-order Born approximation to the scattering amplitude is:

$$f(\mathbf{K}) = -\frac{1}{4\pi} \int e^{-i\mathbf{K}\cdot\mathbf{r}'} U(\mathbf{r}') d^3r' \quad (2.13)$$

Where $\mathbf{K} = \mathbf{k} - \mathbf{k}_i$ is the scattering vector. Notice that the angular dependence is contained in the scattering vector. This approximation remains valid so long that the scattering potential is much smaller than the incident particle's kinetic energy, such as in the case of [UED](#). Additionally, it is important to notice that equation [2.13](#) looks like a Fourier transform of the scattering potential. Then, if the potential was periodic, this Fourier transform gives only non-zero scattering amplitude according to the periodicity as we will see in the following section.

2.2.2 Scattering from a Crystal

The results derived in the previous section can be extended to scattering from a crystal. A crystal is a periodic arrangement of atoms and therefore has a periodic coulomb potential which can interact with an incident electron. Mathematically, the periodicity is represented as “lattice points” which are points, $\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ constructed by integer multiples, n_i , of the set of lattice vectors, $\mathbf{a}_i$. Each atom j is represented as a point, $\mathbf{r}_{n,j} = \mathbf{R}_n + x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3$ around each lattice point forming a “basis”, where x_j, y_j , and z_j are between 0 and 1. Then, the total scattering potential is the sum of the potentials of each individual atom:

$$V(\mathbf{r}) = \sum_{\mathbf{n}} \sum_j^J V_j(\mathbf{r} - \mathbf{r}_{n,j}) \quad (2.14)$$

Where the first summation is over the N total lattice points and the second sum is over the J atoms around each lattice point. Then, this can be inserted into equation 2.13 to get the scattering amplitude:

$$\begin{aligned}
f(\mathbf{K}) &= -\frac{m}{2\pi\hbar^2} \int e^{-i\mathbf{K}\cdot\mathbf{r}} \sum_{\mathbf{n}}^N \sum_j^J U_j(\mathbf{r} - \mathbf{r}_{\mathbf{n},j}) d^3r \\
&= \sum_{\mathbf{n}}^N e^{-i\mathbf{K}\cdot\mathbf{R}_{\mathbf{n}}} \sum_j^J e^{-i\mathbf{K}\cdot\mathbf{r}_j} \left[\int -\frac{m}{2\pi\hbar^2} e^{-i\mathbf{K}\cdot(\mathbf{r}-\mathbf{R}_{\mathbf{n}})} U_j(\mathbf{r} - \mathbf{r}_j) d^3r \right] \\
&= S(\mathbf{K}) \sum_j^J e^{-i\mathbf{K}\cdot\mathbf{r}_j} f_j \\
&= S(\mathbf{K}) F(\mathbf{K})
\end{aligned} \tag{2.15}$$

Where in the second line, the crystal potential, U , is independent of $\mathbf{n}$ because of translational symmetry. In the third line, the atomic scattering amplitude or atomic form factor, f_j , is defined in the square brackets and the shape factor is $S(\mathbf{K}) = \sum_{\mathbf{n}}^N e^{-i\mathbf{K}\cdot\mathbf{R}_{\mathbf{n}}}$. Finally, $F(\mathbf{K})$ is the structure factor. It is important to realize that the macroscopic information such as the size and symmetry of the crystal is contained in the shape factor, while the microscopic information about the individual atoms is contained in f_j and their positions relative to the lattice points are contained in the structure factor.

First consider the shape factor, which may be broken up into the product of three sums, one for each lattice vector $\mathbf{a}_i$, where N_i is the number of lattice points in that direction. Each sum may be simplified as:

$$\left| \sum_{n_1}^{N_1-1} e^{-i\mathbf{K}\cdot n_1 \mathbf{a}_1} \right|^2 = \frac{\sin^2(\frac{1}{2}N_1\mathbf{K} \cdot \mathbf{a}_1)}{\sin^2(\frac{1}{2}\mathbf{K} \cdot \mathbf{a}_1)} \tag{2.16}$$

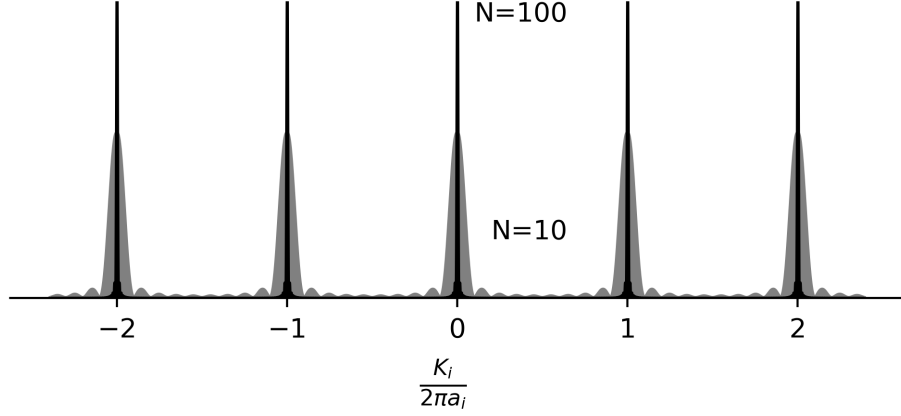


Figure 2.3: Forms of the shape factor in 1 dimension for different crystal sizes.

Here, the square is taken since this is what is actually measured.

Figure 2.3 shows the effect of the shape factor for different crystal sizes. Firstly, we can see that the intensities are essentially zero everywhere except at integer multiples of $2\pi\mathbf{a}_i$. With larger crystals, the widths of these peaks decrease and the heights increase.

Now consider the effect of the structure factor by taking its square:

$$\begin{aligned}
 |F(\mathbf{K})|^2 &= \left| \sum_j^J e^{-i\mathbf{K} \cdot \mathbf{r}_j} f_j \right|^2 \\
 &= \left[\sum_j^J |f_j|^2 + 2 \sum_{j,i < j}^J f_j f_i \cos(\mathbf{K} \cdot (\mathbf{r}_i - \mathbf{r}_j)) \right] e^{-2W} \quad (2.17)
 \end{aligned}$$

The first term shows a contribution which is solely determined by the type of atoms. The second term has a dependence on the type of atoms as well, but also on the relative positions between the atoms. I have also inserted an exponential term, called the Debye-Waller factor where $W = \frac{k_b T K^2}{2m\omega^2}$, that accounts for random thermal motion by assuming

the atoms are oscillators with frequency ω .

With an understanding of the factors contributing to the intensities observed in diffraction images, I now divert more attention to the shape factor, which plays a key role in determining the distribution of scattered intensity. Due to this factor, significant diffraction intensities appear only at specific angles, giving rise to the characteristic pattern of Bragg peaks. The positions of these peaks reflect the underlying symmetry of the crystal lattice and consequently, in studies of symmetry breaking phenomena, such as [CDWs](#), a precise understanding of the diffraction condition becomes essential for interpreting structural changes.

2.2.3 Diffraction Condition

From the shape factor, $S(\mathbf{K})$ defined in the previous section, the diffraction intensities are only non zero when $\mathbf{K} \cdot \mathbf{a}_i$ is close to an integer multiple of 2π . With this, define the reciprocal lattice which is constructed by reciprocal lattice vectors, $\mathbf{b}_i$, defined as:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad (2.18)$$

With this definition, $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$ and therefore, the exact diffraction condition (Laue Condition) can be written as:

$$\mathbf{K} = \mathbf{G}_{hkl} \quad (2.19)$$

Where $\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ with h, k, l integers which are called the Miller indices. This

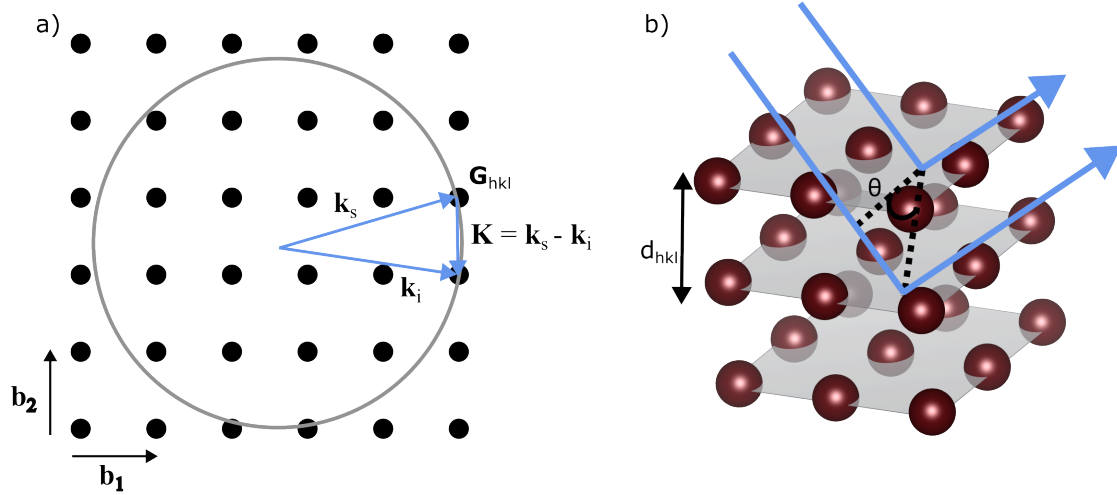


Figure 2.4: a) Construction of an Ewald sphere in reciprocal space. b) Bragg condition shown in real-space.

can be visualized easily with the Ewald sphere which is constructed as following: First, draw the reciprocal lattice. Then, draw the incident wavevector, $\mathbf{k}_i$, such that its tip aligns with one of the reciprocal lattice points. Next, draw a sphere around the origin of the incident wavevector with radius k_i . Then, any reciprocal lattice points on the sphere fulfill the diffraction condition. This construction is demonstrated in figure 2.4.

An equivalent condition can be formulated in real space. Geometrically, reciprocal lattice points represent planes of real space lattice points, where the corresponding reciprocal lattice vector is perpendicular to this plane and the magnitude determines the spacing, $d_{hkl} = \frac{2\pi}{|\mathbf{G}_{hkl}|}$ between parallel planes. Then, consider a wave incident onto some set of planes. Some of the wave reflects off the first plane, and the rest penetrate and reflect off the subsequent planes and depending on the path difference between the waves which reflect off different planes, they may constructively or destructively interfere. This condition (Bragg's law) is:

$$m\lambda = 2d_{hkl}\sin\theta \quad (2.20)$$

where m is an integer and θ is the scattering angle shown in figure 2.4.

2.3 Experimental Setups

The layout of the experimental setup for TR and UED are shown in figure 2.5 and are centered around our femtosecond laser from Light Conversion which outputs 170 fs pulses at a repetition rate of 6 kHz centered around a wavelength of 1030 nm. The laser is split into two beams. One beam goes through an optical parametric amplifier (OPA), allowing the wavelength to be varied, and is used to excite the sample in both setups. The other beam is again split into two, one for TR and one for UED.

2.3.1 Transient Reflectivity

The beam for TR is focused into a yttrium aluminum garnet (YAG) to undergo supercontinuum generation, producing a broadband pulse containing wavelengths 500-900 nm. The white light is focused onto the sample and the reflected beam is guided towards a spectrometer. The pump beam passes through a mechanical chopper, blocking every other pulse, allowing two different spectra to be recorded. One spectrum after the sample is excited and one spectrum when the mechanical chopper blocked excitation. The two spectra are subtracted in to obtain a differential signal.

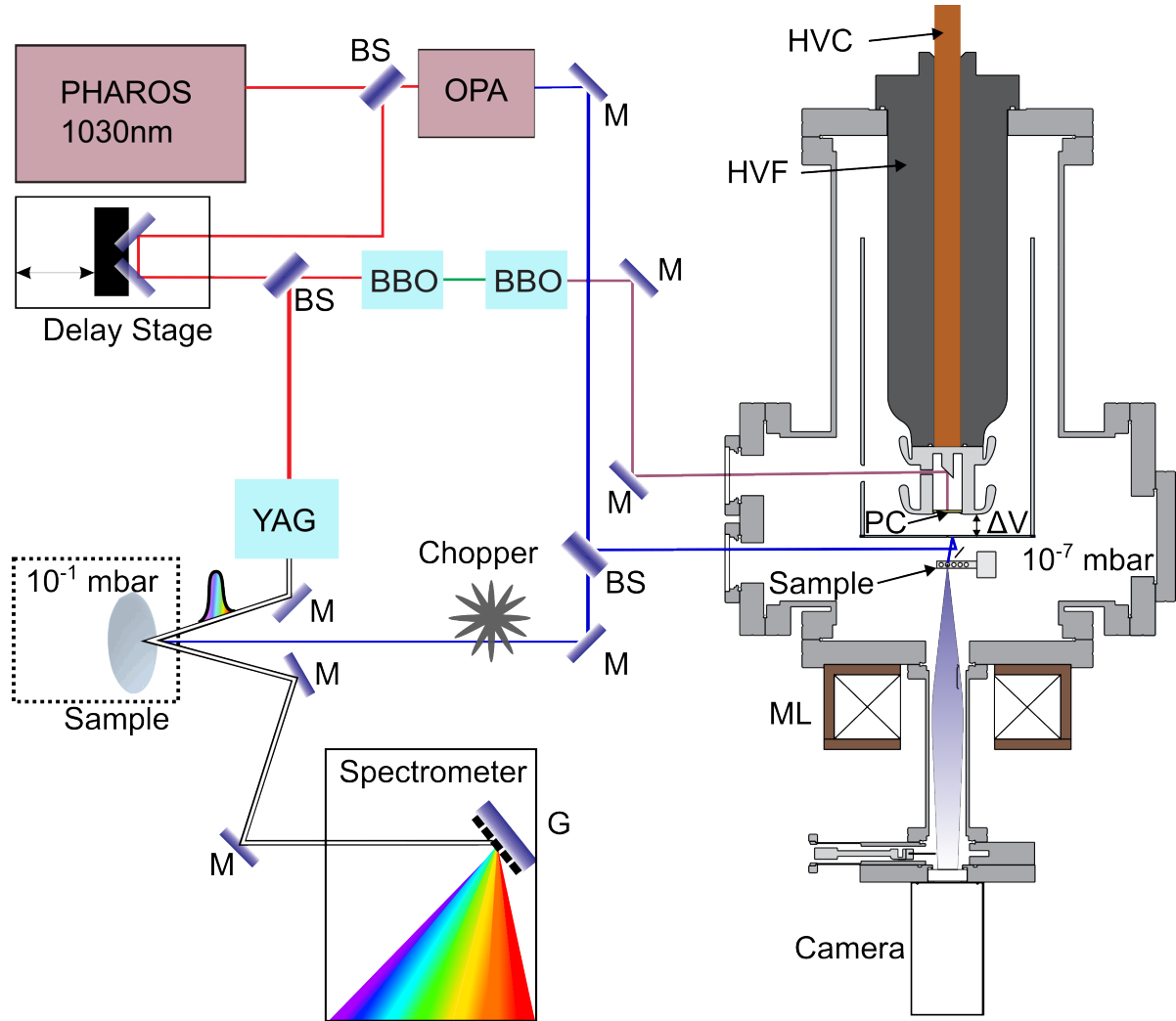


Figure 2.5: Layout of the experimental setups at UeIL. OPA = optical parametric amplifier, BS = beamsplitter, M = mirror, G = grating, BBO = barium borate crystal, HVC = high voltage cable, HVF = high voltage feedthrough, PC = photocathode, ML = magnetic lens, YAG = yttrium aluminum garnet.

2.3.2 Ultrafast Electron Diffraction

For **UED**, the probe beam undergoes fourth harmonic generation (**FHG**) by passing through two beta barium borate (**BBO**) crystals to produce UV pulses centered around 257 nm.

The UV pulses are sent into a high vacuum ($\sim 10^{-7}$ mbar) chamber and photoexcites an electron pulse by striking the back of a thin gold photocathode. A high voltage power supply applies a voltage difference between the photocathode the anode, accelerating the electron pulse towards the anode. An aperture on the anode crops the transverse width of the pulse. The electron pulse then diffracts through the sample, passes a solenoid magnetic lens and the image is recorded on a CMOS camera. A cross section of the chamber with some of the components labelled is shown in figure 2.5.

Electron Beam Characterization

Temporal Resolution

Section 2.2 describes the scattering of a single electron, but experimentally, the diffraction images are taken using pulses containing up to $\sim 10^4$ electrons which are closely bunched and therefore, we must consider electron-electron interactions. Here lies the challenge of ultrafast electron diffraction. We require the bunches to be shorter than the timescale of the dynamics of interest. In our case, phonon vibrations with periods as short as 200 fs. Additionally, the electrons must be coherent enough to form sharp diffraction images with resolvable peaks with sufficient density to obtain sufficient signal [33]. Fortunately, for solid state crystals whose dynamics are reversible, i.e. relax completely back down to the groundstate following photoexcitation and with small unit cells, less than a nm, flux and coherence length are generally not a limiting factor. With reversible systems, a low flux may be compensated for by averaging over many diffraction images at each time point. The coherence length which depends on the angular spread of the beam, is typically on the order of a few nanometers and is sufficient for most unit cell lengths. Therefore, the focus is on maintaining short pulses.

In the limit of no coulomb repulsion (low electron densities), the root mean square (RMS)

duration of the electron pulse, σ_t is mainly determined by the laser pulse length, σ_l and the initial energy spread of the electron pulse [34], σ_i . :

$$\begin{aligned}\sigma_t &= \sqrt{\sigma_i^2 + \sigma_l^2} \\ \sigma_t &= \sqrt{\left(k \frac{\sqrt{\Delta\varepsilon_0}}{|E|}\right)^2 + \sigma_l^2}\end{aligned}\tag{2.21}$$

Here $\Delta\varepsilon_0$ is the initial energy spread, E is the acceleration field and $k = 991 \frac{\text{fs}\cdot\text{MV}}{\text{m}\cdot\text{eV}^{0.5}}$. Using a typical energy spread of 0.2 eV, an applied voltage of 100 kV over a distance of 1 cm and a laser pulse duration of 40 fs, we estimate a pulse length of ~ 60 fs. In order to confirm that we are indeed in this low density regime, we employ A Space Charge Tracking Algorithm (ASTRA) [35] to simulate coulomb broadening for various number of electrons. The acceleration fields are first calculated by extracting the geometry of the electron gun and inputting it into POISSON [36]. The calculated fields are inputted into ASTRA and the beam properties are extracted at the sample position, ~ 3.6 cm from the photocathode.

Figure 2.6 shows the results of POISSON and ASTRA calculations. The initial electron distribution is assumed Gaussian with $\sigma_x = \sigma_y = 300 \mu\text{m}$. The initial temporal spread is $\sigma_l = 40$ fs and the initial energy distribution is assumed isotropic with $\Delta\varepsilon_0 = 0.2$ eV. We can see that for 10^3 electrons, the duration agrees with the estimated 60 fs. Although the experiments in this thesis were performed with an applied voltage difference of 60 kV and a laser pulse duration of 170 fs (FWHM), as long as we stay inside this low density regime, we can use equation 2.21 to estimate the pulse duration, which turns out to be 230 fs (FWHM).

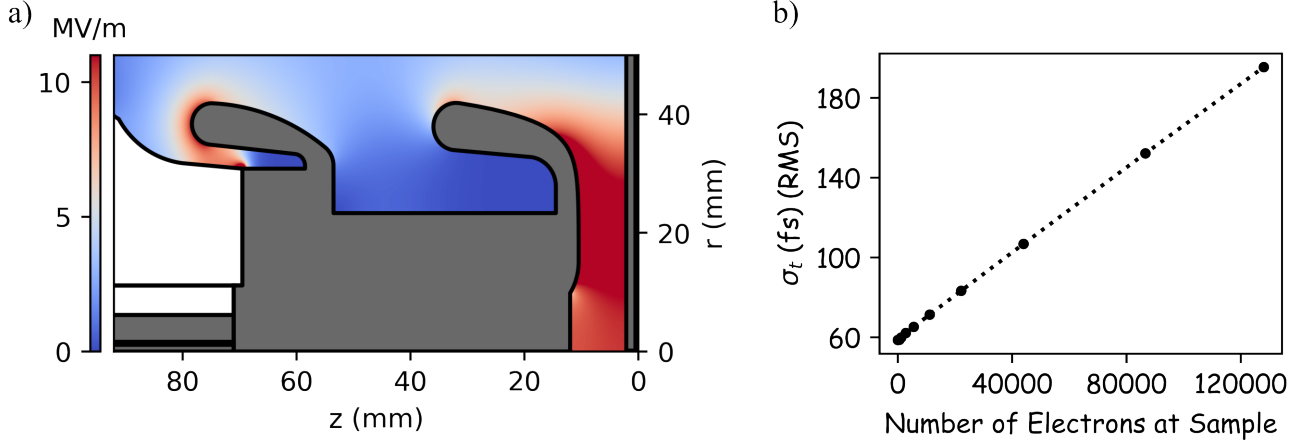


Figure 2.6: a) The electric fields of our electron gun with an applied voltage of 100 kV calculated using POISSON. b) The pulse durations at the sample which is located 3.6 cm from the photocathode.

Spatial Resolution

When discussing the spatial resolution of [UED](#), we must first distinguish between the real-space and reciprocal-space resolution. In reciprocal-space, the parameter to consider is the beam's divergence, σ_θ . The divergence or angular spread affects the path lengths which alters the Bragg condition and results in a blurred diffraction image. With this, the coherence length of our pulse is defined as $l_c = \frac{\lambda}{2\pi\sigma_\theta}$, which establishes approximate maximum unit cell dimensions resolvable by the [UED](#) setup [[33](#), [37](#)]. From the [ASTRA](#) simulations, our coherence length is on the scale of a few nanometers, which is larger than most unit cells. Additionally, we may use either smaller apertures on the anode plate or reduce the photoemission spot size and reduce the divergence, increasing the coherence length. Of course, this will reduce the signal, but can be compensated for by integrating for a longer period of time.

In real-space, we are mainly concerned with the transverse size of the beam at the sample.

If this is too large, then the diffracted beams may overlap without a sufficient sample to detector distance. This is addressed in our setup by modifying the distance between the sample and the detector as well as by reducing the spot size at the sample using an aperture. By increasing this distance, either by moving the detector or by using a magnetic lens, the diffraction peaks can separate allowing us to resolve them. Additionally, the signal is averaged over the probed region. Then, larger beams neglect any heterogeneities within the sample.

Electron Energy

The energy of the electrons is controlled by the applied potential difference between the photocathode and the anode and in general, the higher the better. Higher energies increase the Ewald sphere radius, the mean free path, temporal and spatial resolution. Firstly, this larger Ewald sphere is one of the primary reasons that electron pulses are chosen instead of X-rays. Consider the best X-ray facilities which produce $\sim 1 \text{ \AA}$ X-rays [38–40]. The de Broglie wavelength corresponding to 100 KeV electrons, which is easily feasible on table-top instruments, is 3.7 pm. This is almost 30 times smaller, resulting in Ewald spheres which intersect many more reciprocal lattice points. Another advantage of electrons is the higher scattering cross-section. The probability of detecting a scattered electron is much higher than X-rays, allowing much better signal-to-noise ratios. Consequently, the samples must be ultrathin to avoid having to analyze complicated multiple scattering effects, but at the same time, thinner samples are homogeneously excited. With increasing energy, the total scattering cross section decreases, increasing the mean free path, which allows thicker samples to be used [41]. Finally, higher electron energies increase the spatial and temporal resolution. Higher energy electrons reach the sample faster, reducing the amount of time that the pulse can expand due to coulomb repulsion. At even higher energies, relativistic

Parameter	Value
Acceleration Voltage	60 kV
Field Strength	6 MV/m
Number of Electrons	10^3
Pulse Duration	230 fs (FWHM)
Transverse Beam Size	160 μm (FWHM)
Aperture Size	115 μm
Coherence Length	$\sim\text{nm}$

Table 2.1: [UeIL UED](#) instrument parameters used in this thesis.

effects suppress these space-charge forces [42, 43]. Here, we use 60 KeV electrons, limited by electrical discharges, but work is currently being done to improve stability at voltages up to 150 KeV. All of the parameters used in this thesis are given in table 2.1.

Now that the information collected by each probe is defined, in the next section, I explain how the [CDW](#) phase specifically is monitored.

2.4 Charge Density Wave Observables

The periodic lattice distortion derived in section 1 causes some of the scattering intensity of the diffraction peaks to redistribute and create new “superlattice peaks” at $\mathbf{k}_{CDW}$ relative to the main Bragg peak [44]. Starting from the structure factor derived in section 1, we can use the results of equation 1.10 and displace each atom in the unit cell by a [PLD](#), $\Delta u \cos(\mathbf{k}_{CDW} \cdot \mathbf{R}_n)$, where $\mathbf{k}_{CDW}$ is the nesting vector. Following the same derivation, we obtain the same structure factor, however we get a modified shape factor, $S'(\mathbf{K})$:

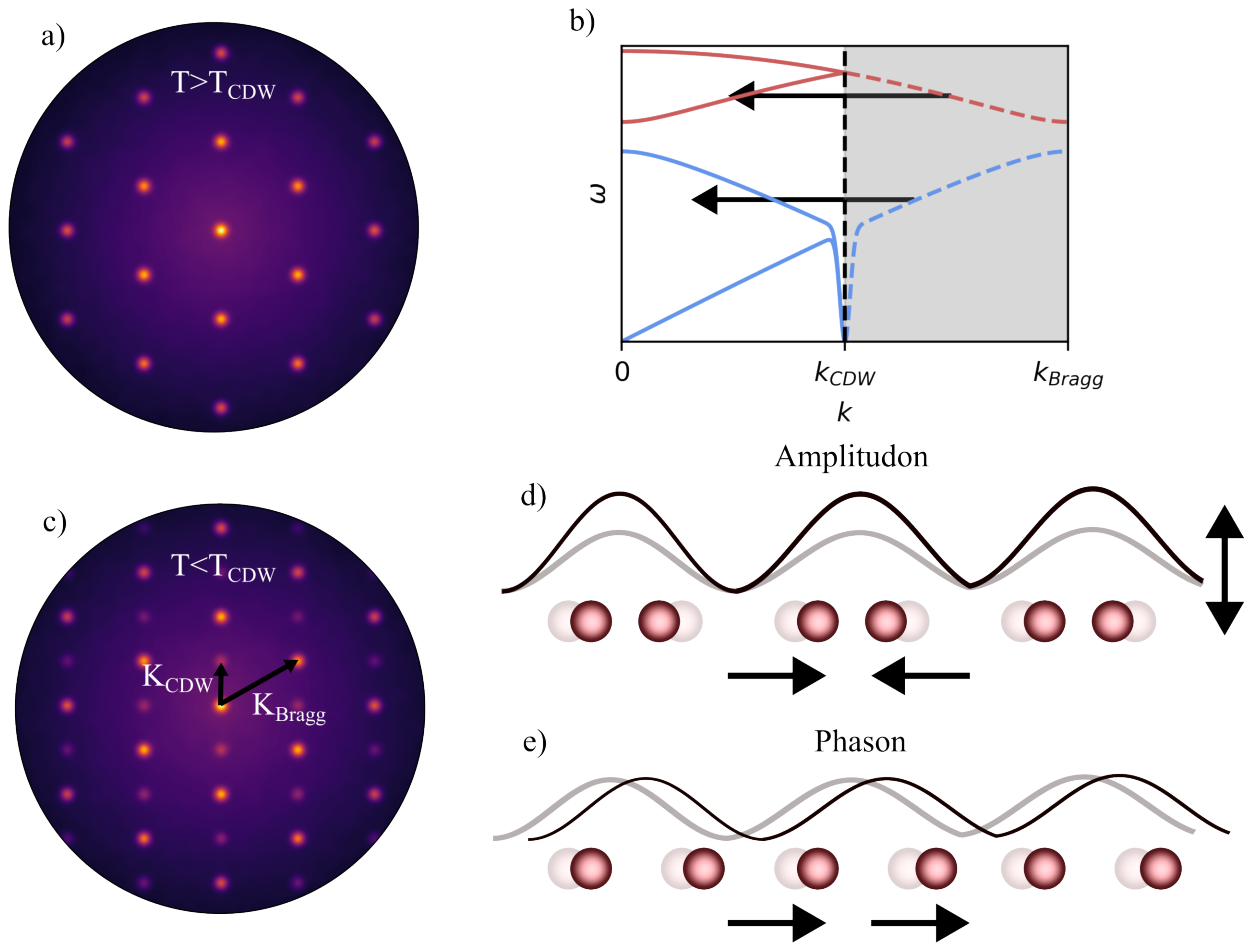


Figure 2.7: a) and c) show the diffraction patterns above and below the transition temperature. The satellite and Bragg peaks are labelled in c). The backfolding is shown in b) and the collective excitations of the order parameter is illustrated in d and e).

$$\begin{aligned}
S'(\mathbf{K}) &= \sum_n^N e^{-i\mathbf{K} \cdot [\mathbf{R}_n + \Delta \mathbf{u} \cos(\mathbf{k}_{CDW} \cdot \mathbf{R}_n)]} \\
&\sim \sum_n^N \left[e^{-i\mathbf{K} \cdot \mathbf{R}_n} - i \frac{\mathbf{K} \cdot \Delta \mathbf{u}}{2} (e^{-i(\mathbf{K} - \mathbf{k}_{CDW}) \cdot \mathbf{R}_n} + e^{-i(\mathbf{K} + \mathbf{k}_{CDW}) \cdot \mathbf{R}_n}) \right] \\
&= S_{bragg}(\mathbf{K}) - i \frac{\mathbf{K} \cdot \Delta \mathbf{u}}{2} S_{CDW}(\mathbf{K})
\end{aligned} \tag{2.22}$$

In the second line, I assume that the distortion is small and expanded around the equilibrium atomic positions, keeping only the first term. The first term is the same shape factor of the undistorted lattice which gives rise to the diffraction peaks at the reciprocal lattice points. The second term produces addition peaks at $\pm \mathbf{k}_{CDW}$, called superlattice peaks, around each reciprocal lattice point which are proportional to $\Delta \mathbf{u}$ and are illustrated in [2.7](#). From this, we can find the scattering intensity:

$$|S'(\mathbf{K})|^2 = |S_{Bragg}(\mathbf{K})|^2 + (\mathbf{K} \cdot \Delta \mathbf{u})^2 |S_{CDW}(\mathbf{K})|^2 \tag{2.23}$$

Since this is a result of simply displacing the atoms, the total scattering intensity does not change according to Plancherel's theorem. Then:

$$\begin{aligned}
\int |S(\mathbf{K})|^2 d^3k &= \int |S'(\mathbf{K})|^2 d^3k \\
\Rightarrow \int |S_{bragg}(\mathbf{K})|^2 d^3k &= \int [|S(\mathbf{K})|^2 - (\mathbf{K} \cdot \Delta \mathbf{u})^2 |S_{CDW}(\mathbf{K})|^2] d^3k
\end{aligned} \tag{2.24}$$

and we can see that the intensities at the original peaks have decreased and is related to the magnitude of the lattice distortion, $\Delta \mathbf{u}$.

This new set of superlattice peaks may be also thought of by considering the unit-cell expansion due to the distortion. In the simple half-filled 1-D model, the distortion doubles the lattice constant and therefore, halves the reciprocal lattice vectors and produces additional peaks between the main peaks.

Because the unit cell is doubled, the Brillouin zone is halved, causing the phonon modes which cross this edge to be backfolded. This produces additional phonon bands called zone-folded phonons, some of which may be Raman-active and therefore triggered by photoexcitation (Figure 2.7c) [45–47]. Finally, the raman-active amplitudon mode, derived in section 1, can also be triggered by photoexcitation and the oscillations of the atoms are monitored in the same fashion as regular phonons.

2.5 Data Collection and Analysis

TR data collection is done as followed: First, the sample is scanned using the probe beam until a region which reflects the beam nicely is found. This may be time-consuming depending on how relatively flat the sample is. Then, the pump is overlapped spatially with the probe beam visually. Because the pump passes through a chopper which blocks every other pump pulse, we can subtract the spectra in pairs to see the differential spectra. Using this differential spectra, the length of the probe beam is altered using the delay stage until the probe and pump pulses overlap temporally and a non-zero differential spectra may be seen due to the pump. Then, we can maximize this signal, by optimizing the spatial overlap. Finally, the data is ready to be obtained by averaging these differential spectra at specified delay stage positions.

UED data collection is done in a similar manner, but orders of magnitude harder since the sample is kept inside a vacuum chamber and cannot be seen unless the chamber is vented,

however, then the electron beam cannot be used. First, under vacuum, an aperture is used in place of the sample and then aligned into position so that the electron beam goes straight through the aperture. Then, the chamber is vented and the pump beam is aligned to pass through the same aperture to ensure spatial overlap. Under vacuum again, the sample is moved in place of the aperture and then the delay stage is scanned until the pulses temporally overlap. Similarly, the signal is maximized by optimizing spatial overlap and then data is ready to be taken. Unlike in [TR](#), the camera is not synchronized to a chopper and differential images cannot be taken. Therefore, we simply take images at each time point and obtain a differential image by subtracting data from before time-zero and after time-zero. Each image is taken by integrating over some time and care is taken so that the camera never acquires for so long that the relevant diffraction peaks saturate.

The data obtained in pump probe measurements typically consist of “scans” which contain data at each time point. Subsequent scans can then be averaged to improve signal-to-noise. In [TR](#), the data at each time point is a spectra and therefore, each scan is a simple 2D ($\sim 100 \times 500$) array. With [UED](#), the data at each time point is a 2D (1280×1080 array) diffraction image and therefore, the scan is an extremely large 3D array. With multiple UED scans, we easily get thousands of images. Here I outline the procedure I use to extract relevant information from [UED](#).

First, the total intensity of each image is plotted in chronological order. There may be a trend over time due to a fluctuating number of electrons in each pulse owing to the UV beam drifting slowly, however, the idea here is to remove any outliers which may be caused spontaneous fluctuations such as during electrical discharges. Then, each image is normalized to the same total intensity to remove the beam-drift fluctuation and images at the same time delay are averaged to obtain a single scan. To monitor the changes in individual diffraction peaks, a region of interest ([ROI](#)) is selected and all the peaks within

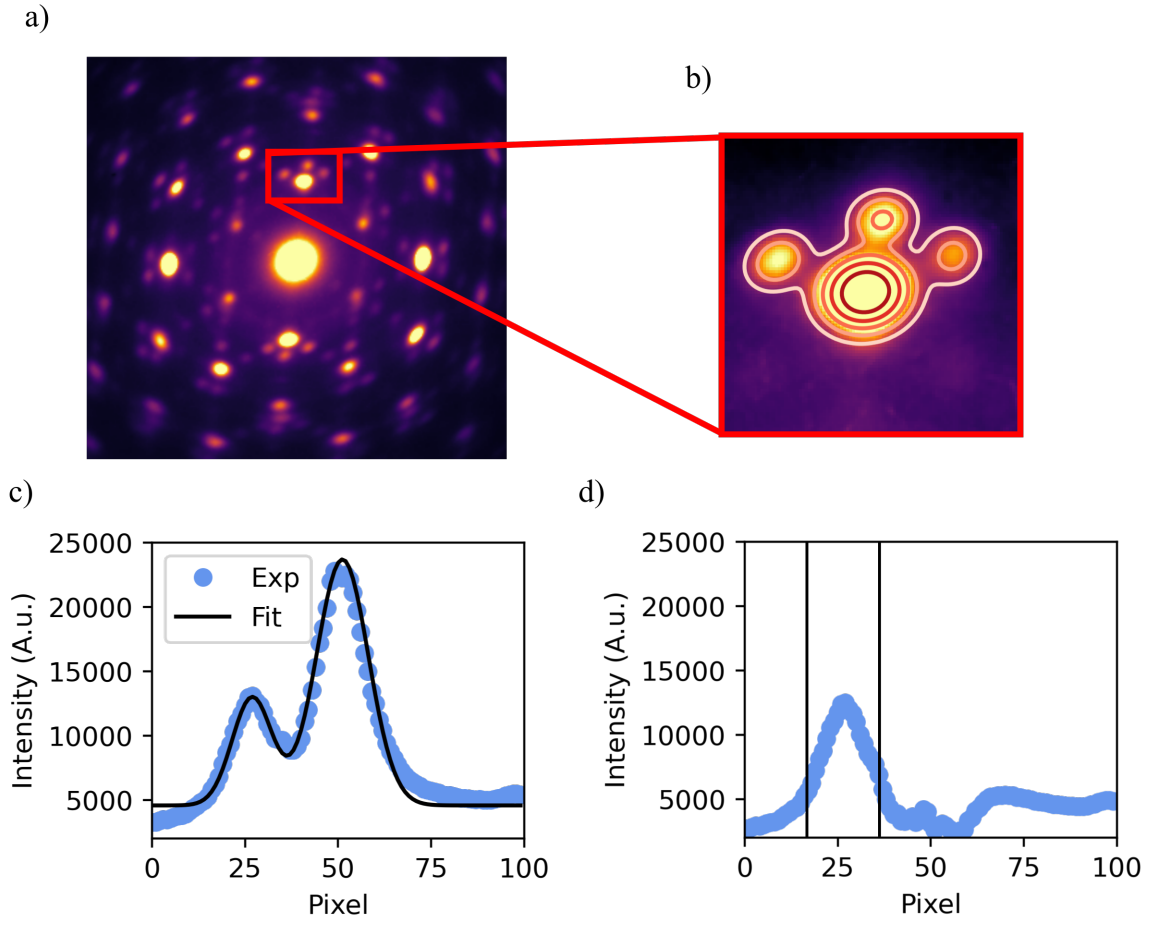


Figure 2.8: a) Example of one diffraction image of NbTe_2 . b) Region of interest to perform fitting. c) Slice of [ROI](#) showing 2D Gaussian fitting of all the peaks. d) Peaks are isolated by subtracting fits of other peaks. The intensities are found by integrating over a specified region.

the region are fit with a 2D Gaussian. In some patterns, the peaks are so close that they overlap and all the peaks must be fit simultaneously. Then, to get the intensities of a particular peak, all of the other fitted peaks are first subtracted and a region around the peak of interest is integrated. Finally, this is done for the same peak at every time-point and then these diffraction peak intensities are subtracted and divided by the average peak intensity of all the images taken pre-time-zero to get a differential peak intensity. Additional parameters can be included in this Gaussian fit to monitor changes in the peak position and peak size. The procedure is shown in figure 2.8.

Once the UED data is shrunk to several traces of diffraction peak intensity over time, the analysis is the same as with TR data. Each time-trace of interest is fit to a phenomenological function to extract information. Here, we use a sum of exponential decays and exponentially decaying sine functions to obtain amplitudes, time-constants, and frequencies:

$$S(t) = \left[H(t-t_0) \left[\sum_i A_i e^{k_i(t-t_0)} + \sum_j B_j e^{k'_j(t-t_0)} \sin(2\pi f_j(t-t_0) + \phi_j) \right] \right] * \text{IRF}(t-t_0) \quad (2.25)$$

Where H is the heaviside function and IRF is the instrument response function. Here, the IRF represents the finite temporal resolution of the setup and is approximated as a Gaussian. The interpretation of these parameters varies from system to system.

Time-Frequency Analysis

As I will show in chapter 3, our transient reflectivity setup has a sufficient temporal resolution to resolve phonon modes with frequencies as high as $\sim 150 \text{ cm}^{-1}$ and for this reason,

it is sometimes referred to as time-resolved Raman spectroscopy. [TR](#) has the advantage of probing the temporal evolution of coherently excited phonon modes. In the time-domain, we can clearly see when phonons are excited and their decay, but we do not know the frequencies of these modes. Then, we can take Fourier transforms of the signal and accurately determine which modes are present, but then we lose any dynamical information about the modes. To characterize the time-dependence of each individual mode's frequency, damping rate and amplitude, time-frequency representations are necessary. A popular technique used to tackle this is called short-time Fourier transforms ([STFTs](#)). Simply, the signal is divided into windows and the Fourier transforms of each window is taken. Here lies the weakness of the [STFT](#). For higher temporal resolution, smaller windows are necessary, but with smaller windows, we lose information about the lower frequency modes. Such is the effect of the Heisenberg-Gabor uncertainty principle [\[48\]](#).

The continuous wavelet transform ([CWT](#)) overcomes this limit by scaling the windows for different frequencies. Whereas the [FT](#) essentially convolutes the signal with plane-waves, the [CWT](#) convolutes the signal with localized wave packets. First, a mother wavelet and the number of cycles is chosen. Commonly chosen is the Morlet wavelet which is a plane wave with a Gaussian envelope:

$$\psi_{f,c} = \frac{1}{B_c \sqrt{2\pi}} e^{\frac{t^2}{2B_c^2}} e^{i2\pi f t} \quad (2.26)$$

Where c is the number of cycles and $B_c = \frac{c}{k_{sd}f}$ contained within k_{sd} number of standard deviations of the Gaussian envelope, thereby providing larger windows for smaller frequencies. Then, by convoluting the signal, g , with wavelets of different frequencies, we can get a time-frequency representation:

$$W_\psi[g(t)] = \int_{-\infty}^{\infty} g(t)\psi_{f,c}(t - \tau)dt \quad (2.27)$$

The limits here lies at higher frequencies, which it can be shown that the wavelets become indistinguishable from neighboring frequencies at higher frequencies. More cycles are necessary to separate the two, but then the temporal resolution declines.

Finally, Moca et. al. introduced the superlet transform where the superlet is a set of identical wavelets containing a different number of cycles [49]. Superlets improve the resolution by taking advantage of the high temporal resolution of the low cycle wavelets and the high frequency resolution of the many cycle wavelets. The superlet of order o is defined as:

$$SL = \{\psi_{f,c} : c = c_1, c_2, \dots, c_o\} \quad (2.28)$$

Here, c_i may be defined arbitrarily, but for this thesis, $c_i = c_1 * i$. Then the superlet transform (SLT) of g is computed by taking the geometrical mean of the individual continuous wavelet transforms of each wavelet in the set:

$$SLT[g(t)] = \left(\prod_i^o W_{\psi_{f,c_i}}[g(t)] \right)^{1/o} \quad (2.29)$$

With all the tools presented, I investigate the charge density wave material, NbTe₂ and show the results in the next chapter.

Chapter 3

Ultrafast Dynamics of a Charge Density Wave

3.1 NbTe₂

NbTe₂ is a layered material belonging to the family of transition-metal dichalcogenides (TMDCs) and its structure is shown in figure 3.1. This material crystallizes into a trigonal lattice, where in a unit-cell, the tellurium atoms are octahedrally coordinated around a central niobium atom. This structure is laterally repeated, forming layers. The layers are stacked on top of each other in an AA fashion and held together via van der Waal forces. This is a typical structure occurring in TMDCs and is called the 1T structure. However, NbTe₂ undergoes a charge density wave phase transition to the 1T' phase, where a double zig-zag bonding causes niobium atoms to clump together and form trimers while the tellurium atoms buckle out-of-plane [50]. The successive layers shift and the result is a $(3 \times 1 \times 3)$ unit cell corresponding to $\mathbf{q}_{CDW} = 1/3\mathbf{a}^*$. This phase is thermodynamically

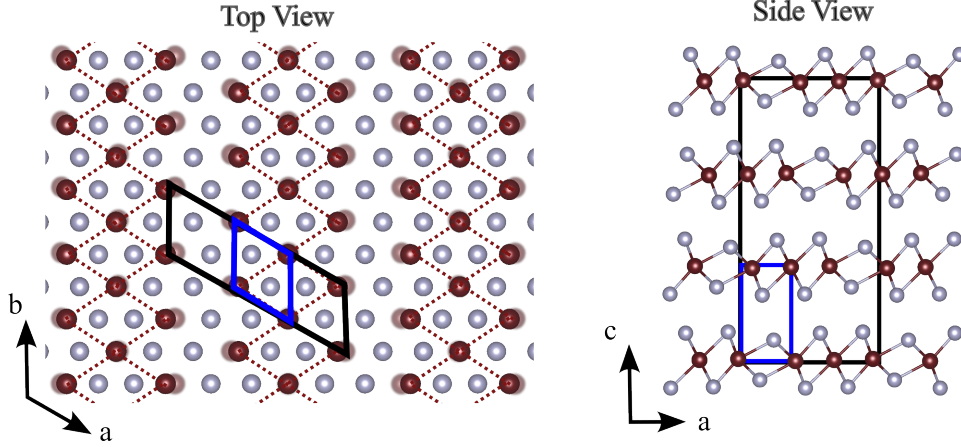


Figure 3.1: Top and side views of the structure of 1T'' NbTe₂. The unit cell of the undistorted and distorted phases are shown in blue and black respectively. The double zig-zag bonding is drawn with dashed lines which causes a formation of niobium trimers. The undistorted positions of the Niobium atoms are shown in the blurred in the top view.

stable down to 0.7 K, where it transitions to a superconducting phase [51], and up to 800 K, where the material decomposes [52]. Although some have reported a phase transition to occur at 550 K, no such structure was seen in TEM [53] measurements. Instead, a $(\sqrt{19} \times \sqrt{19})$ CDW phase has been accessed via impulsive heating [54, 55]. Both of these CDW phases have been theoretically investigated and aligns well with calculated susceptibility instabilities [56] which suggest a Peierls mechanism described in section 1. In contrast to the 1-D model, here the instability at $\mathbf{q}_{CDW}$ gaps the 2D fermi-surface only at this single point which leaves the system metallic in the CDW phase.

In addition to these bulk phases, even more have been reported from scanning tunneling microscopy (STM) [50, 57] and low-energy electron diffraction (LEED) [58] measurements which are surface sensitive, revealing an undistorted 1T and a $(1 \times \frac{9}{2})$ CDW phase. In monolayers, (4×4) , (4×1) , $(\sqrt{19} \times \sqrt{19})$ and $(\sqrt{28} \times \sqrt{28})$ CDW phases have been realized depending on growth temperatures [59] and may potentially belong to the 1H

polytype instead of the 1T [60]. Given the plethora of phases, I have decided to study NbTe₂. But, before studying the excited state dynamics of the system, it is important to understand the system in its ground state.

3.2 Sample Characterization

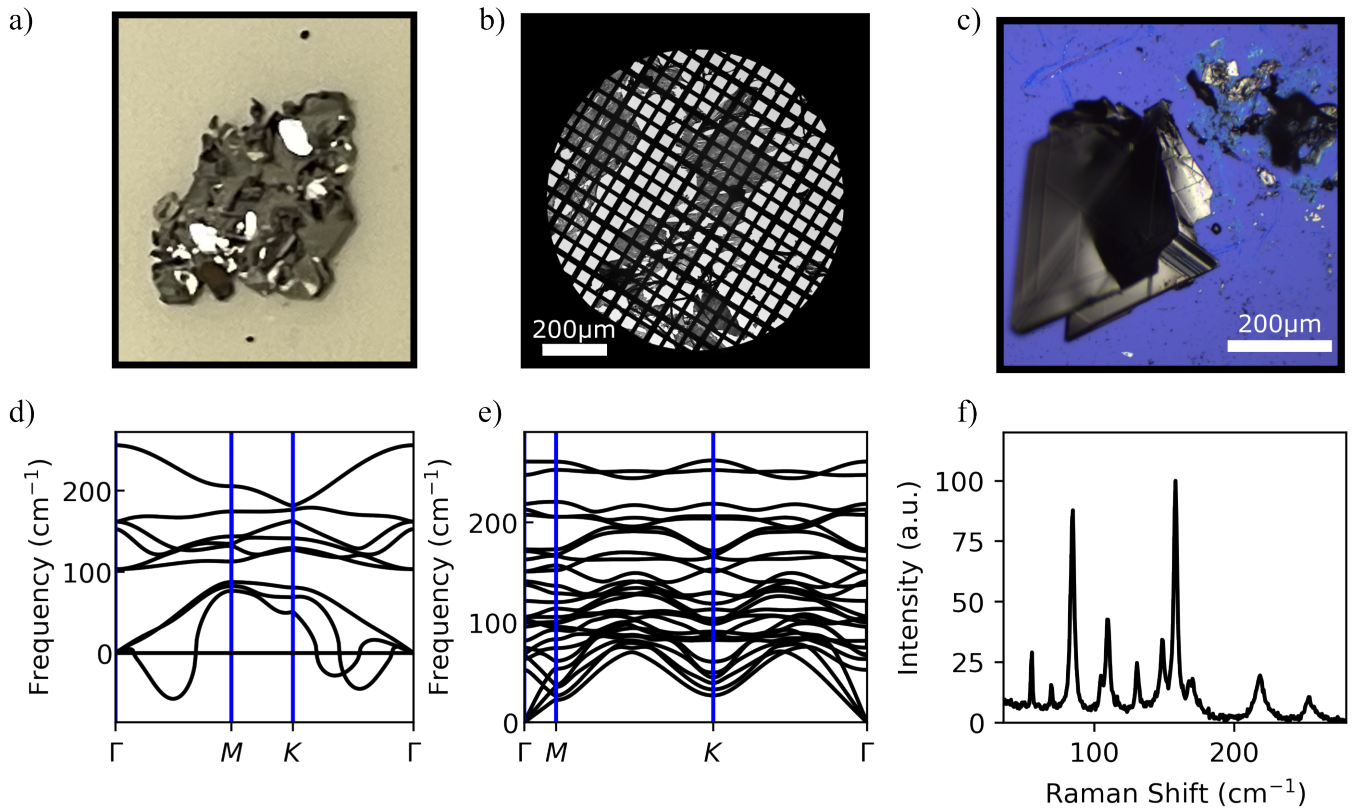


Figure 3.2: Samples used in this experiment. a) Bulk crystal used for transient reflectivity. b) Low magnification TEM image of the microtomed samples used for UED. c) Exfoliated samples used for Raman spectroscopy. d) 1T phonon band calculations. e) 1T'' phonon band calculations. f) Experimental Raman spectra using 532 nm excitation.

Firstly, phonon band calculations were performed on both 1T and 1T'' NbTe₂ using the

structures found by Brown et al. [61] and are shown in figures 3.2d and 3.2e respectively which qualitatively agree with previous calculations [56, 62]. In the 1T calculations (figure 3.2d), we see there are negative frequencies due to instabilities in the lattice since the calculations were performed assuming 0 K and therefore, this structure is not the ground state structure. Additionally, it is important to notice that the most negative band occurs in the Γ -M direction, corresponding to the wavevectors pointing in the $\mathbf{a}^*$ direction associated with $\mathbf{q}_{CDW}$ and shows the important Kohn anomaly leading to the lattice distortion. After performing the same calculations using the stable 1T'' structure, we can see that the negative, unstable bands have been removed. Also, we can see that the number of bands increased in the 1T'' calculations (figure 3.2e) due to CDW unit-cell tripling, creating zone-folded phonon modes and increasing the number of Raman-active modes from 2 to 12. I highlight one mode in particular: the A_g^2 , centered around 81 cm^{-1} , mode whose eigenvector has a clear component in the direction of this distortion. In other words, it involves a stretching of Nb-Nb atoms as well as out-of-plane buckling of Te atoms and is therefore the amplitudon mode which directly modulates the amplitude of the CDW order parameter.

After theoretical characterization, bulk NbTe₂ samples were obtained from 2DSemiconductors. Raman spectroscopy was performed on exfoliated crystals, which are shown in figure 3.2c, using an excitation wavelength of 532 nm and is shown in figure 3.2f. The spectrum reveals 11 modes centered around 55, 70, 85, 105, 109, 130, 149, 158, 168, 218 and 253 cm^{-1} and are assigned to the A_g^1 , B_g^1 , A_g^2 , A_g^3 , B_g^3 , A_g^4 , A_g^5 , A_g^6 , B_g^4 , A_g^7 and A_g^8 modes respectively, which agrees with previous experiments [62–64].

3.3 Ultrafast Electron Diffraction

Further groundstate characterization of the structure using electron diffraction is done. The sample used in the [TEM](#) and for [UED](#) is shown in figure [3.2b](#) which was prepared using a microtome. Bulk crystals ($\sim 0.5 \times 0.5$ mm) large and several mm thick are fixed on top of the sample holder. A diamond knife is held at a fixed distance away from the sample holder which can be brought towards the knife very precisely in steps of as low as 1 nm using piezoelectrics. Then, once the sample is very close, the sample arm begins to swing across the knife. After every swing, the sample approaches the knife by some set step. This swinging continues until the knife slices the sample. Therefore, the thickness of the sample is determined by this step size. The thickness of the sample shown in figure [3.2b](#) is measured using [EELS](#) to be approximately 20 nm [\[65\]](#).

3.3.1 Static Electron Diffraction

Figure [3.3](#) shows static electron diffraction images taken in a [TEM](#) and in our [UED](#) setup with the beam in the $[001]$ direction, perpendicular to the layers. The [TEM](#) image reveals the expected monoclinic structure with satellite peaks appearing along the a -axis. Red dots highlight the Bragg peaks associated with the 1T phase and black dots highlight the [CDW](#) peaks. Clear differences can be seen between the diffraction image taken in the [TEM](#) and in our [UED](#) setup. Firstly, the b -axis is not perpendicular to the a -axis as it should be in monoclinic crystals due to the sample not being perfectly perpendicular to the beam. Here lies another limitation of the [UED](#) setup which may only rotate the sample in the x - z plane. Secondly, we can see that the peaks are much larger and is partly due to the divergence of the [UED](#) electron beam which is less coherent than the [TEM](#) and partly due to the domain structure. The appearance of satellite peaks along three axes rather than

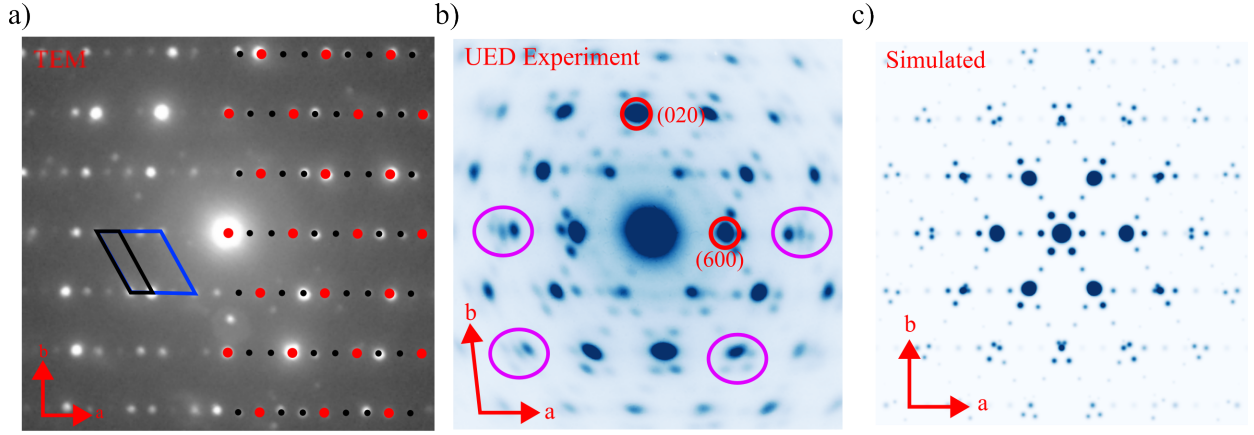


Figure 3.3: (a) **TEM** image of a single NbTe₂ domain. The reciprocal lattice unit cells of the undistorted and the distorted phases are drawn in blue and black respectively. The calculated reciprocal lattice is overlayed on the right half of the image with red dots denoting Bragg peaks and black dots denoting superlattice peaks. (b) Indexed **UED** pattern. Anomalous peaks are circled in purple. (c) Simulated diffraction patterns of different domain orientations, rotated by 60° and 120°, replicating the observed domain structure.

just the a-axis indicates the existence of domains which are rotated 60 and 120 degrees with respect to each other. Previous studies have shown that these domains are at least several nm large, causing our **UED** setup to image every domain simultaneously [54]. Finally, we can also notice some "smearing" of peaks closer to the edge of the image and these mystery peaks which do not look like **CDW** peaks (appearing 1/3 between Bragg peaks) circled in purple. Here, we have a mix of contributions from distortions due to our magnetic lens between the sample and the detector, as well as the domain structure. Magnetic lenses are well-known to produce all types of distortions (barrel, pincushion, astigmatism, etc.) and will be strongest near the edge, where the magnetic field applies the most force [66]. With the domain structure, the **CDW** distortion causes that axis to shrink slightly which causes the Bragg peaks to deviate from a trigonal symmetry. The result is the diffraction peaks from rotated domains do not overlap perfectly and cause elongations closer to the center,

but may separate entirely further from the center. Therefore, analysis is limited to peaks closer to the center.

To properly identify the peaks in our [UED](#) diffraction patterns considering this divergence, domain structure and distortion, I first index the [TEM](#) image. Since the beam is almost perfectly along [001], we can recreate the monoclinic lattice and modify the lattice vectors to overlap, by eye, with all the [TEM](#) peaks. With the lattice vectors and equation 2.15 we can simulate the pattern. The atomic positions are taken from [61] and atomic form factors calculated from this table [67]. The simulated pattern is rotated 60 and 120 degrees and shown in figure 3.3c. A remarkable similarity can be seen between simulation and our [UED](#) image. With this, we can match the peaks from [UED](#) to our simulation.

3.3.2 Ultrafast Electron Diffraction

Finally, after thorough characterization of the sample, time-resolved data was taken using a pump fluence of 3.7 mJ/cm^2 . Figure 3.4b shows the changes in the peak intensities for the (910) Bragg and (800) satellite peak which demonstrates the lattice response and is schematically illustrated in figure 3.4c. Initially, we observe a rapid increase in the Bragg peak intensity and a decrease in the satellite peak intensity. Then, both peaks reach an extremum and the Bragg peak intensity starts to decrease while the satellite peak intensity recovers. This is a typical response observed in [CDWs](#) [10, 15, 68]. Firstly, the ultrafast laser excites charge carriers which disrupts and weakens the modulated charge order. The weakened charge order then disrupts and weakens the [PLD](#) and causes the intensity of the satellite peaks to reduce and redistribute back to the Bragg peaks as observed. Then, the excited carriers transfer energy to the lattice which causes the modulated charge order to recover and simultaneously increases the lattice temperature, which suppresses the Bragg

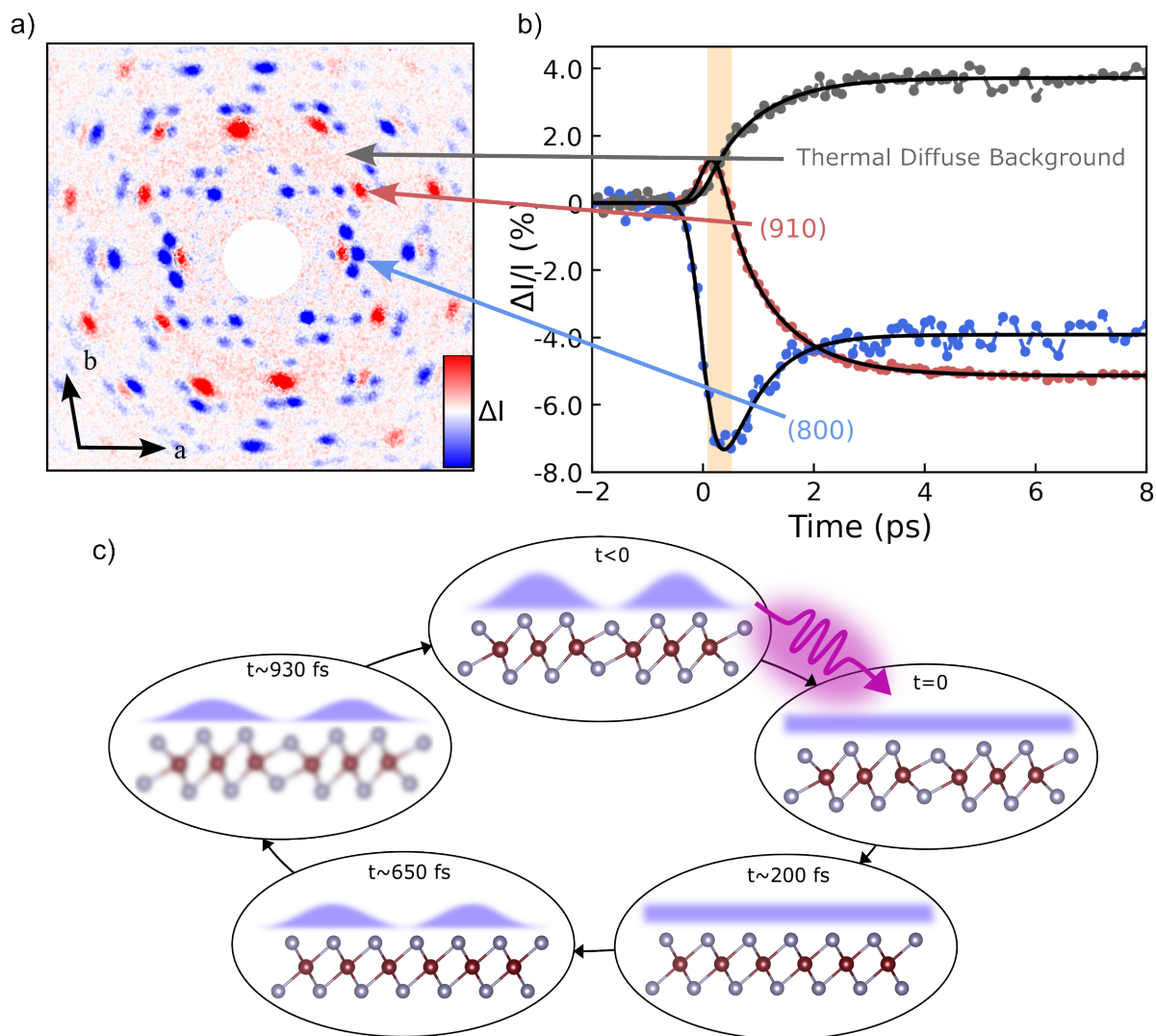


Figure 3.4: (a) Differential diffraction pattern at 300 fs post-excitation. (b) Temporal evolution of select diffraction peaks and background intensity, fitted using exponential decays. The arrows indicate the selected peaks. (c) Proposed stages of the system following photoexcitation.

peak intensity via Debye-Waller effects. The increase in the lattice temperature is illustrated by the gray trace showing the intensity increase in the thermally diffuse background. For quantitative analysis, the Bragg and satellite peak intensity changes are fit to a biexponential function described in Equation 2.25 and reveal a ~ 150 fs initial rise in the Bragg peak followed by a longer suppression ~ 930 fs. The satellite peak decreases sharply in ~ 200 fs and recovers in ~ 650 fs. Similarly, the thermally diffuse background change is fit to a monoexponential and rises in ~ 930 fs. There are two things to notice from these time constants. Firstly, the speed of the increase in the Bragg and decrease in the satellite peak is slightly different. Immediately after photoexcitation, Debye-Waller effects are present as shown in the gray trace. As a result, the increase in the Bragg peak is slightly suppressed while the decrease in the satellite peak is slightly enhanced. Since this Debye-Waller effect is slower (~ 930 fs), it takes slightly longer to reach the satellite peak minimum. Secondly, the recovery of the satellite peak is faster (~ 650 fs) than the Debye-Waller effect which indicates there is an additional process which is causing the modulated charge order to recover faster. This is in contrast to the suppression of the Bragg peak which occurs with the same time constant as the diffuse background (~ 930 fs).

3.3.3 Structure Factor Calculations

To quantify the displacements responsible for these changes in diffraction peak intensities, I calculated the structure factors. The atomic form factors for niobium and tellurium are estimated using a sum of gaussians:

$$f_{Nb/Te}(|K|) = \sum_{i=1}^4 a_i e^{-b_i (\frac{K}{4\pi})^2} + c \quad (3.1)$$

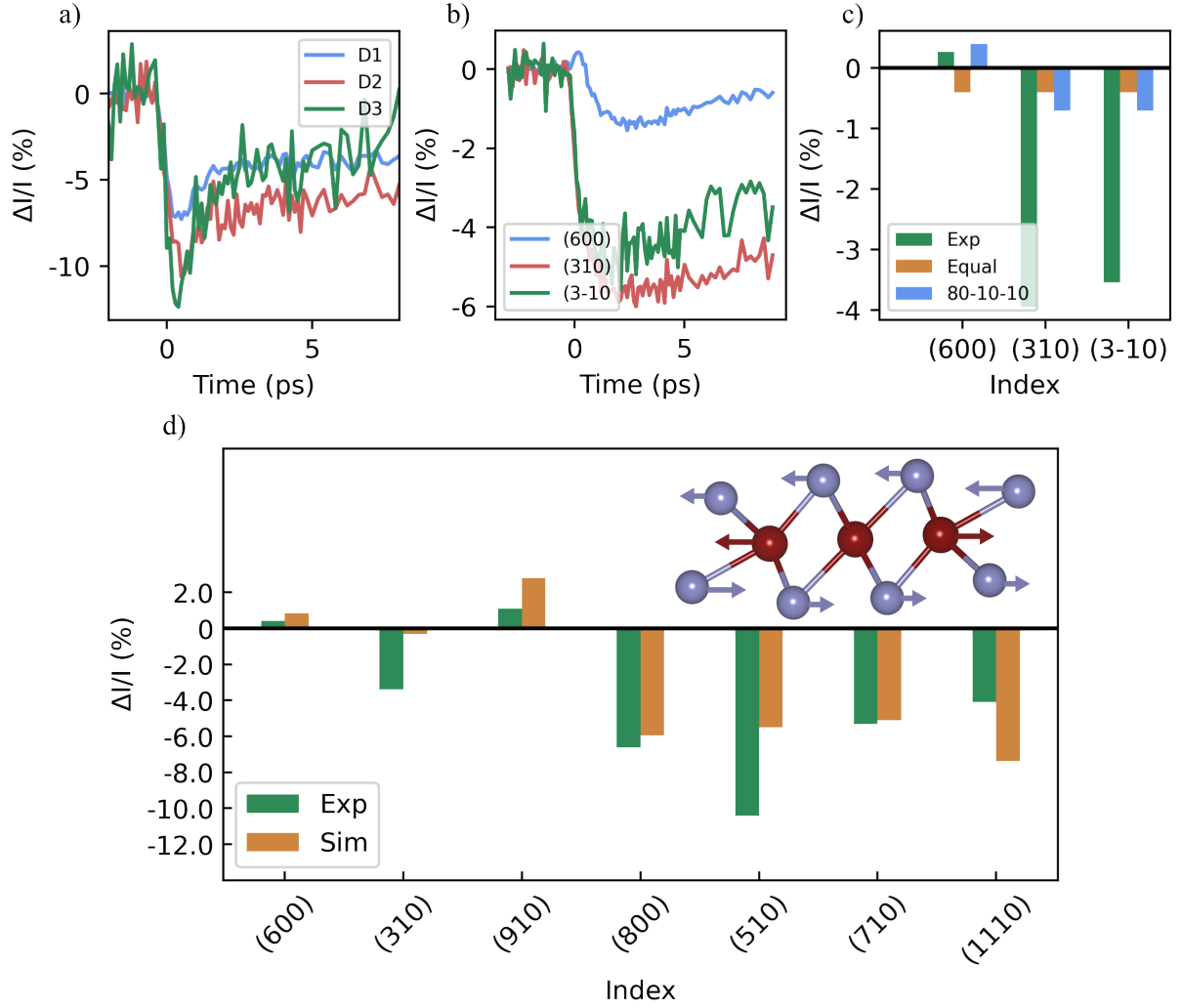


Figure 3.5: Experimentally observed and simulated intensity variations, revealing a 1.3% structural distortion. Inset: atomic displacements used in the undistorted structure model.

Where a , b and c are parameters previously determined [67]. Then, starting with the ground state structure given by [61], the positions of the atoms inside a unit cell are mapped to their corresponding undistorted positions. This translation vector is defined as

the distortion vector, $\Delta\mathbf{x}$. Here, for simplification, I ignore the distortions in the z-direction which do not change any (hk0) peaks and assume that the coherent motion is primarily along this direction. This is a fair assumption as we will see when we perform transient reflectivity, where the amplitudon mode contributes the largest amplitude oscillations to the signal. The inset of figure 3.5d show the simulated motions of the atoms. Finally, to find the experimental displacements, I minimize the squared difference, SE , between changes in the diffraction peaks (averaged between Friedel pairs to improve signal-to-noise) in figure 3.4a and the calculated squared structure factors by linearly scaling the distortion vector. I also include a variable Debye-Waller factor since the electron-phonon coupling occurs extremely fast, within a picosecond.

$$SE = \sum_{hkl} [\Delta I_{hkl}^{sim}(A\Delta\mathbf{x})e^{-\frac{1}{2}Wq^2} - \Delta I_{hkl}^{exp}]^2 \quad (3.2)$$

Here A and W is the distortion vector amplitude and Debye-Waller factor respectively. ΔI_{hkl}^{exp} is the measured change in intensities in experiment while $\Delta I_{hkl}^{sim}(A\Delta\mathbf{x}) = f_{hkl}^2$ is the squared calculated structure factor. Due to the domain structure of the crystal, care must be taken in choosing which peaks to minimize against. Firstly, only the satellite peaks which align along the a-axis defined in figure 3.4a are chosen. A single domain should be chosen since there is a clear anisotropy as shown in figure 3.5a which shows different levels of CDW suppression for the three different domains. This likely stems from the linear polarization of the pump being preferentially absorbed. This particular domain is chosen since it has the largest contribution to the signal. Next, consider the first order bragg peaks, (600), (310) and (3-10). After rotating by 60 and -60 degrees, the Bragg peak on the a-axis has mixed contributions from these three domains given by:

$$I_{600}^{exp} = aI_{600} + bI_{310} + cI_{3-10} \quad (3.3)$$

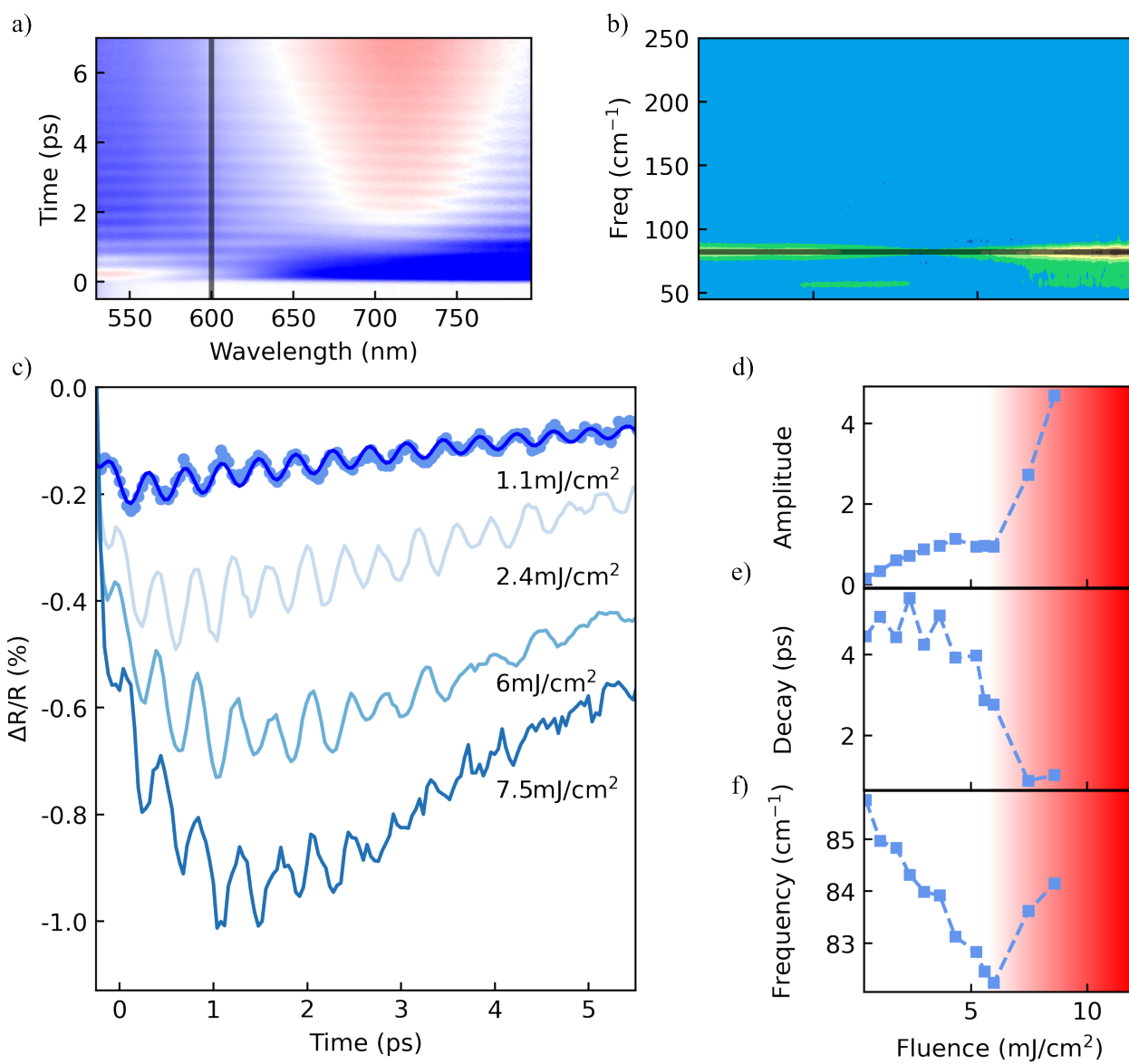
where a , b and c are the contributions from the other domains. The contributions are similar for the other 5 Bragg peaks. Clearly, if all three contributions are equal, i.e. $a = b = c$, then all 6 Bragg peaks should have the same intensity and show the same changes in intensity as shown in figure 3.5c. However, from figure 3.5b, one peak shows different behaviour. To see this increase in a single peak, one domain must be dominant as shown in figure 3.5c.

After minimizing, we obtain a 1.3% undistortion amplitude (100% being completely undistorted) at 300 fs. A comparison of the simulated and experimental changes is shown in figure 3.5d which shows a remarkable similarity. Then, theoretically, if we excite the sample harder, then we would be able to push it even closer to the undistorted phase, however, the thin samples required for UED melt at these fluences.

3.4 Transient Reflectivity

Ultrafast electron diffraction measurements provided insight into the lattice dynamics following photoexcitation. Impulsive excitation causes the atoms to coherently move in the direction of the 1T phase within 200 fs. Here, I perform transient reflectivity measurements which have the advantages of a much faster temporal resolution and is able to resolve the fast phonon modes responsible for this motion. Also advantageous is the use of bulk crystals allowing efficient transfer of heat and therefore, higher melting point excitation thresholds.

Figure 3.6a shows TR data taken with a fluence of 5.6 mJ/cm². The data reveal an initial sharp change in the reflectivity due to carrier excitation followed by a decay due



to carrier relaxation. Superimposed are sinusoidal oscillations corresponding to coherent phonon excitations. The temporal traces at each wavelength is fit to equation 2.25 and the electronic contribution is subtracted to get the FFT shown in 3.6b. Two different modes are present at this fluence centered around 55 and 81 cm^{-1} which we attribute to the A_g^1 and A_g^2 modes respectively. The strongest modulations occur at wavelengths of 600 nm indicating that this wavelength is most sensitive to the modulations of the electronic gap and I shift the focus to these wavelengths.

With a way of monitoring the gap, I systematically varied the excitation fluence and analyze the changes to this amplitudon mode. Figures 3.6c shows the traces at different fluences with the results of the fitting shown for the lowest fluence. Figures d-f show the fitting parameters for the phonon contribution. Here, I identify two different regimes below and above 6 mJ/cm^2 . Within the lower regime, the mode's amplitude scales linearly with the fluence consistent with a single photon absorption mechanism. The mode decays faster and we observe a redshift. As the fluence increases, the higher energy electrons transfer more energy to the lattice, populating the incoherent phonon bath and increasing the lattice temperature. Then, the coherent phonons are more likely to scatter and decay. Also with higher temperatures, the lattice expands causing the restoring forces to weaken, redshifting the frequencies. Approaching 6 mJ/cm^2 , absorption saturates evident by the amplitude saturating [69]. In the second regime, the amplitude grows nonlinearly, indicating a multiphoton absorption scheme and interestingly, we can also see a hardening of the amplitudon occur.

There are multiple competing and cooperative processes which affect the mode's frequency. The increased electronic temperature changes the free energy landscape of the order parameter shown in figure 1.4a [70, 71]. As shown in UED, the wells of the free energy shift closer to 0, but also get less steep. Of course, the restoring forces are proportional

to the gradients of this well and so the frequency of the oscillation decreases. Secondly, with higher excited carrier densities, more energy is transferred to the lattice via electron-phonon scattering and the lattice temperature increases higher. Thermal expansion causes bonds to weaken and frequencies to soften. By contrast, higher carrier densities cause faster diffusion rates which decreases the electronic temperature locally inside the probed region [72]. To distinguish between these processes which have different timescales, time-frequency representations are necessary.

Figure 3.7a shows the SLT of the TR signal at 600 nm using a pump fluence of 3.7 mJ/cm² and reveals the temporal dependence of both the A_g^1 and A_g^2 modes. The SLT uses the Morlet mother wavelet and combines a total of 11 wavelets with 3, 6, 9, ..., 33 cycles in each wavelet. For a more in-depth analysis of the temporal and frequency resolution attained using this particular superlet, I refer the reader to [73]. To track the frequency of the amplitudon, a Lorentzian function is fit to the A_g^2 peak at each time point. The results of one of the fits is shown in figure 3.7b and the time-dependence of the frequency for different pump fluences is shown in figure 3.7c. Starting with the lowest fluence of 0.5 mJ/cm², we can see an initial frequency of 87 cm⁻¹ and then a redshifting due to thermal expansion. Increasing the fluence to 3.7 mJ/cm² results in a lower initial frequency due to potential well softening and again followed by thermal effects. Approaching 6.0 mJ/cm², we can see further softening, but the frequency rehardens over time. In this regime, there are so many carriers that carrier diffusion which rehardens the potential overwhelms the thermal effects. At 7.5 mJ/cm², the initial frequency increases and may indicate a complete melting of the CDW, where the oscillations are strong enough to cross the high symmetry point where $\Delta = 0$ [71, 72]. However, at these large fluences, irreversible transformations occur which may inhibit this conclusion.

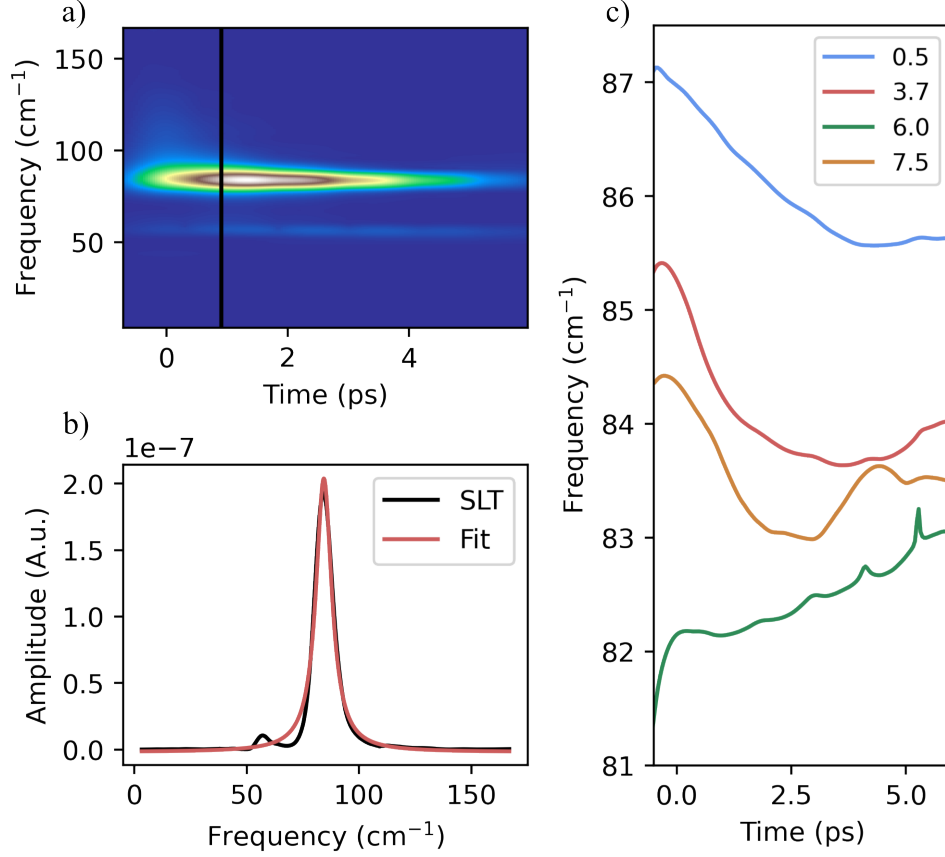


Figure 3.7: a) Superlet transform of the TR signal at 600 nm with a pump fluence of 3.7 mJ/cm². The solid vertical line shows the slice taken for b. b) Time-resolved spectral slice at 1 ps fitted with a Lorentzian to track the peak position. c) Temporal evolution of the phonon mode frequency.

3.5 Recomposition

Figure 3.8 shows Raman spectra before and after exposing the sample to fluences >11 mJ/cm². Before exposure, all the Raman modes agree with the phonon band calculations as well as the literature [62,63]. After irradiation we see the emergence of 6 new modes which are all absent before which is indicative of a structural phase transition. The three

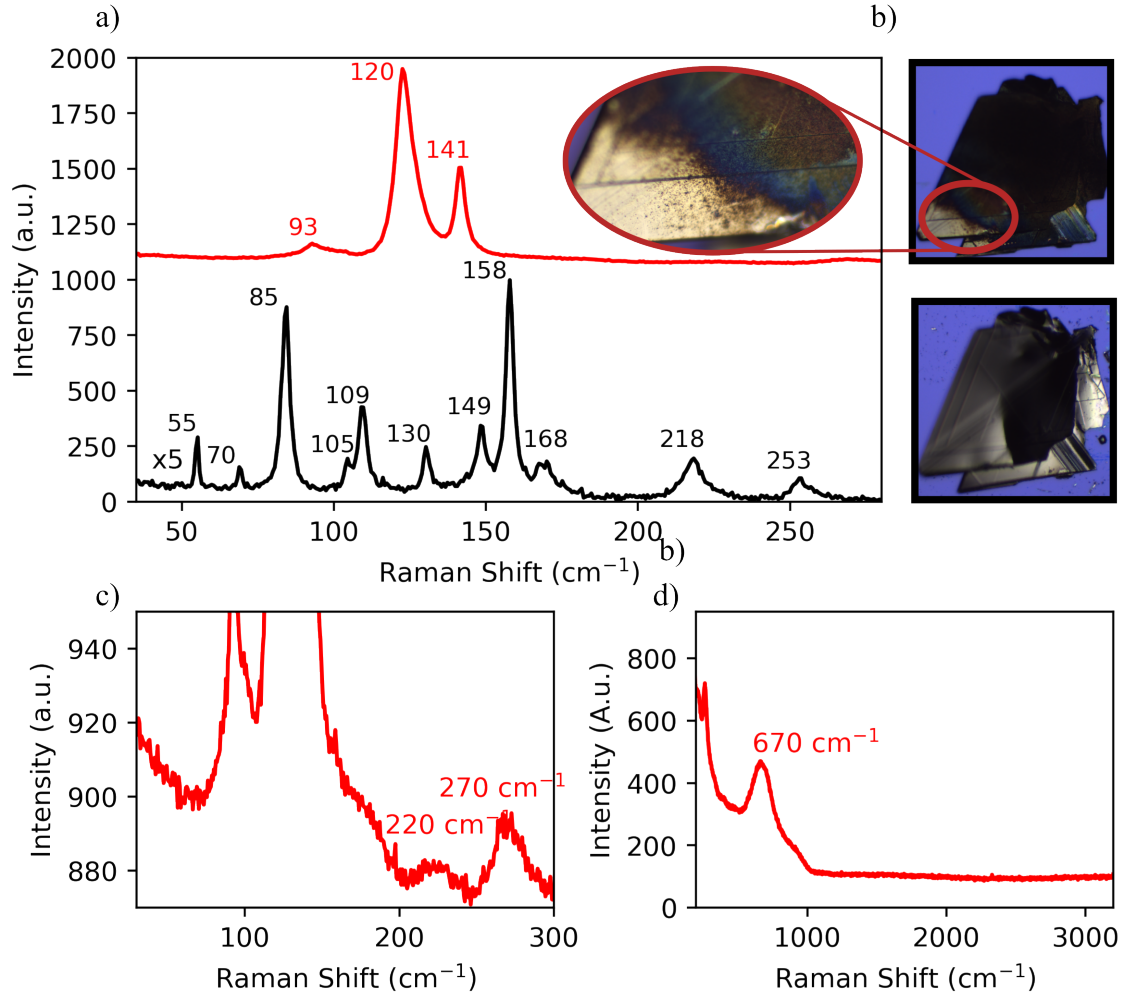


Figure 3.8: a) Raman spectra before and after laser irradiation with the frequencies of each peak labelled. b) Microscope images before (bottom) and after (top) irradiation. c) and d) Zoomed in spectra at higher spectra showing additional, less intense modes.

strongest modes centered around 93, 120 and 141 cm^{-1} suggest tellurium crystallization and exactly corresponds to the frequencies of all 3 Raman-active modes of Te: E^1 , A^1 and E^2 modes respectively [74]. NbTe_2 has been reported decompose around 800 K [52]. The

highest temperature reached can be estimated using:

$$\int_{T_i}^{T_f} C dT = \frac{F(1 - R)M}{\rho\delta} \quad (3.4)$$

Where $T_i=297$ K and T_f are the initial and final temperatures, F is the excitation fluence, R is the reflectance, $M = 348.1$ g/mol is the molar mass, $\rho = 7.09$ g/cm³ is the density and δ is the optical penetration depth. The heat capacity here is estimated using a Dulong-Petit approximation which agrees with similar compounds (TaTe₂ and VTe₂) at high temperatures [75,76]. R is estimated to be 50% according to similar compounds [?,12]. The optical penetration depth was found in literature to be 40 nm with a 400 nm pump [77]. The final temperatures for all the fluences used in this experiment is shown in figure 3.9a. The highest temperature attained is approximately 1200 K which is well above the decomposition temperature.

Further experiments were performed to understand the nature of this tellurium crystallization and are summarized in figure 3.9 and table 3.1. Firstly, figure 3.9c shows the Fourier transform of TR data taken with a fluence of 3.7 mJ/cm² after exposing to different levels of high fluence for more than 10⁷ shots. Before any exposure, we observe the expected A_g^1 and A_g^2 modes. After exposing to an intermediate fluence of 7 mJ/cm², we see the E^1 mode of Te as well as the A_g^2 mode of NbTe₂ indicating a mixture of compositions in the sample. After exposure to the highest fluence of 11 mJ/cm², the sample is completely transformed in Te and we observe its A^1 and E^1 modes. Secondly, figure 3.9b shows the change in reflectivity as a function of shots of 11.2 mJ/cm² after a few ms. After such a long time, the sample is completely relaxed, but a persistent change in the reflectivity indicates a permanent change in the sample. These changes are compounded after each shot until equilibrium is reached after more than 10⁶ shots.

The rate of Te crystallization was investigated by tracking the changes in the two observable phonon modes in [TR](#) after exposing the sample to 14 mJ/cm^2 pulses and the results are summarized in [table 3.1](#). The phonon mode suppression starts quickly, but then slows down which indicates that the crystallization does not facilitate further crystallization which would speed up the transformation process. Instead, the process is likely stochastic with each pulse having a probability of transforming specific regions of the sample. As the sample is further modified, there is less probability of further transforming the sample. Therefore, I propose the following mechanism: Above the threshold fluence of 7.5 mJ/cm^2 , certain regions of the sample absorb sufficient energy, locally evaporating tellurium. The tellurium diffuse within the sample, form clusters and recrystallize. These nucleation regions are influenced by the domain structure, which from [UED](#) measurements, anisotropically absorb the pump allowing a coexistence of NbTe_2 and Te after irradiating with an intermediate fluence.

Total Number of Shots	1 (1 Hz)	5 (1 Hz)	35 (1 Hz)	30035 (6 kHz)	180035 (6 kHz)
A_g^1	91%	60%	47%	Noise	Noise
A_g^2	119%	87%	79%	11%	11%

Table 3.1: Change in phonon amplitudes from the Fourier transform after exposure to a different number of total 14 mJ/cm^2 shots. The phonon amplitudes are taken from data obtained with a pump fluence of 3 mJ/cm^2 . The A_g^1 amplitudes after more than 30000 shots is below the noise.

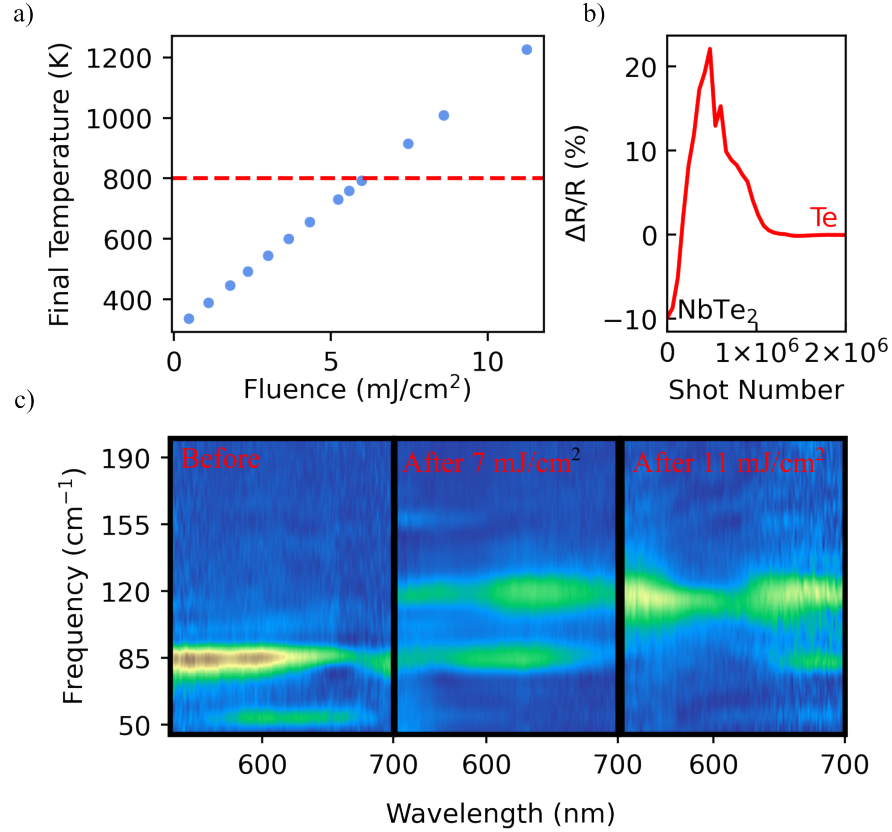


Figure 3.9: a) Peak temperatures as a function of excitation fluence. The decomposition temperature threshold is shown with a red dotted line. b) Changes in reflectivity before and after complete Te crystallization as a function of number of shots at a fluence of 11.2 mJ/cm². c) Fourier transforms of [TR](#) data using a fluence of 3.7 mJ/cm² after exposing the sample to different levels of high fluence.

Chapter 4

Conclusion and Outlook

4.1 Conclusion

The work done in this thesis investigates the lattice dynamics of the charge density wave 2D material, NbTe₂ after ultrafast photoexcitation using ultrafast electron diffraction and transient reflectivity. The complicated domain structure observed in the UED images was disentangled allowing quantitative analysis of the structure. Following the highest possible photoexcitation prior to melting, I reveal that coherent motions of the atoms towards the high symmetry phase occur in less than 200 fs. With phonon band calculations, this motion is identified to be a collective excitation of the CDW order parameter, the amplitudon, with a characteristic frequency of $\sim 85\text{cm}^{-1}$, much faster than the temporal resolution of the UED instrument. TR measurements were performed which feature the resolution necessary to resolve these fast phonon dynamics and reveal a threshold fluence. With increasing excitation, the CDW is further suppressed up to the threshold of 7.5 mJ/cm^2 where it is non thermally melted, characterized by the sudden increase in the amplitudon's

frequency as well as its extreme damping. Such melting has never before been seen by simply increasing the temperature of the sample up to 800 K where it starts to decompose. Finally, we reveal a recomposition occur above the threshold, where tellurium crystallizes. With sufficient irradiation, the modes of NbTe₂ vanish and 6 new modes appear. Three of which are identified as the modes of Te. Additional work investigated the nature of this transformation and revealed a probabilistic, nucleation process, in which the growth of Te is influenced by the domain structure and with each shot, these regions are stochastically transformed. The ability to control the structure using light opens new avenues for tailoring material properties on demand.

4.2 Outlook

Although a thorough investigation of the ultrafast dynamics of NbTe₂ has been done, there still exists a plethora of unanswered questions. Additional analysis should be done to investigate the effects of Te crystallization on the TR data. Specifically, Te formation may lead to phonon confinement effects [78, 79] resulting in shifted frequencies and altered observed phonon amplitudes. Alternatively, more experiments may be performed to directly observe CDW melting. In the UED experiments performed in this thesis, the optical penetration depth of our pump is much larger than the films used and likely reaching the mesh which they are sitting on. As a result, the mesh is heated and the pump reflects back into the sample which is likely limiting the fluence. By simply aligning the samples behind the mesh, both of these effects may be negated. Alternative excitations should also be considered. Using THz pulses which are resonant with the amplitudon, the mode can be directly excited, leaving the electronic system unperturbed and the lattice essentially cold, bypassing the melting problem altogether. With TR, one could employ a double pump-probe

scheme, where the first pump is above the identified threshold of 7.5 mJ/cm^2 . If the first pump truly melts the [CDW](#), then the following pump should not be able to excite any of its corresponding phonon modes. Still, there is an abundance of information left in the [UED](#) data collected in this thesis such as the inelastic background which provides information about the out-of-equilibrium momentum-resolved phonon dynamics and [CDW](#) peak profiles which provide information about the correlation lengths. A two-temperature model can also be implemented to track the dynamical energy exchange between the hot electrons and the cold lattice. Then, by obtaining the transient temperatures, the order parameter can be calculated and compared with experiment, using time dependent Ginzburg-Landau simulations, to obtain Ginzburg-Landau parameters, phase transition temperatures and an electron-phonon coupling constant. Finally, once the magnitude of the order parameter suppression is known, [DFT](#) calculations can be done to explore whether this facilitates Te crystallization.

References

- [1] Edbert J. Sie, Clara M. Nyby, C. D. Pemmaraju, Su Ji Park, Xiaozhe Shen, Jie Yang, Matthias C. Hoffmann, B. K. Ofori-Okai, Renkai Li, Alexander H. Reid, Stephen Weathersby, Ehren Mannebach, Nathan Finney, Daniel Rhodes, Daniel Chenet, Abhinandan Antony, Luis Balicas, James Hone, Thomas P. Devereaux, Tony F. Heinz, Xijie Wang, and Aaron M. Lindenberg. An ultrafast symmetry switch in a Weyl semimetal. *Nature*, 565(7737):61–66, 2019.
- [2] Germán Sciaini, Maher Harb, Sergei G. Kruglik, Thomas Payer, Christoph T. Hebeisen, Frank J. Meyer Zu Heringdorf, Mariko Yamaguchi, Michael Horn Von Hoegen, Ralph Ernstorfer, and R. J. Dwayne Miller. Electronic acceleration of atomic motions and disordering in bismuth. *Nature*, 458(7234):56–59, 2009.
- [3] Thomas Danz, Till Domröse, and Claus Ropers. Ultrafast nanoimaging of the order parameter in a structural phase transition. *Science*, 371(6527):371–374, 2021.
- [4] Aditya Sood, Xiaozhe Shen, Yin Shi, Suhas Kumar, Su Ji Park, Marc Zajac, Yifei Sun, Long-Qing Chen, Shriram Ramanathan, Xijie Wang, William C. Chueh, and Aaron M. Lindenberg. Universal phase dynamics in VO₂ switches revealed by ultrafast operando diffraction. *Science*, 373(6552):352–355, 2021.

- [5] Neil Ashcroft and David Mermin. *Solid State Physics*. Cengage Learning, 1976.
- [6] Charles Kittel. *Introduction to Solid State Physics*. Wiley, 8 edition, 2005.
- [7] D. N. Basov, R. D. Averitt, and D. Hsieh. Towards properties on demand in quantum materials. *Nature Materials*, 16(11):1077–1088, 2017.
- [8] Chenhang Xu, Cheng Jin, Zijing Chen, Qi Lu, Yun Cheng, Bo Zhang, Fengfeng Qi, Jiajun Chen, Xunqing Yin, Guohua Wang, Dao Xiang, and Dong Qian. Transient dynamics of the phase transition in VO₂ revealed by mega-electron-volt ultrafast electron diffraction. *Nature Communications*, 14(1):1265, 2023.
- [9] Allan S. Johnson, Daniel Perez-Salinas, Khalid M. Siddiqui, Sungwon Kim, Sungwook Choi, Klara Volckaert, Paulina E. Majchrzak, Søren Ulstrup, Naman Agarwal, Kent Hallman, Richard F. Haglund, Christian M. Günther, Bastian Pfau, Stefan Eisebitt, Dirk Backes, Francesco Maccherozzi, Ann Fitzpatrick, Sarnjeet S. Dhesi, Pierluigi Gargiani, Manuel Valvidares, Nongnuch Artrith, Frank de Groot, Hyeongi Choi, Doo-geun Jang, Abhishek Katoch, Soonnam Kwon, Sang Han Park, Hyunjung Kim, and Simon E. Wall. Ultrafast X-ray imaging of the light-induced phase transition in VO₂. *Nature Physics*, 19(2):215–220, 2023.
- [10] Maximilian Eichberger, Hanjo Schäfer, Marina Krumova, Markus Beyer, Jure Demsar, Helmuth Berger, Gustavo Moriena, Germán Sciaini, and R. J. Dwayne Miller. Snapshots of cooperative atomic motions in the optical suppression of charge density waves. *Nature*, 468(7325):799–802, 2010.
- [11] Tzong-Ru T. Han, Faran Zhou, Christos D. Malliakas, Phillip M. Duxbury, Subhendra D. Mahanti, Mercouri G. Kanatzidis, and Chong-Yu Ruan. Exploration of

- metastability and hidden phases in correlated electron crystals visualized by femtosecond optical doping and electron crystallography. *Science Advances*, (5):e1400173, 2015.
- [12] Hiroshi Tanimura, Norihiko L. Okamoto, Takao Homma, Yusuke Sato, Akihiro Ishii, Hitoshi Takamura, and Tetsu Ichitsubo. Nonthermal melting of charge density wave order via nucleation in VTe_2 . *Physical Review B*, 105(24):245402, 2022.
- [13] Alfred Zong, Anshul Kogar, Ya-Qing Bie, Timm Rohwer, Changmin Lee, Edoardo Baldini, Emre Ergeçen, Mehmet B. Yilmaz, Byron Freelon, Edbert J. Sie, Hengyun Zhou, Joshua Straquadine, Philip Walmsley, Pavel E. Dolgirev, Alexander V. Rozhkov, Ian R. Fisher, Pablo Jarillo-Herrero, Boris V. Fine, and Nuh Gedik. Evidence for topological defects in a photoinduced phase transition. *Nature Physics*, 15(1):27–31, 2019.
- [14] Martin R. Otto, Jan-Hendrik Pöhls, Laurent P. René de Cotret, Mark J. Stern, Mark Sutton, and Bradley J. Siwick. Mechanisms of electron-phonon coupling unraveled in momentum and time: The case of soft phonons in TiSe_2 . *Science Advances*, 7(20):eabf2810, 2021.
- [15] Anshul Kogar, Alfred Zong, Pavel E. Dolgirev, Xiaozhe Shen, Joshua Straquadine, Ya-Qing Bie, Xirui Wang, Timm Rohwer, I-Cheng Tung, Yafang Yang, Renkai Li, Jie Yang, Stephen Weathersby, Suji Park, Michael E. Kozina, Edbert J. Sie, Haidan Wen, Pablo Jarillo-Herrero, Ian R. Fisher, Xijie Wang, and Nuh Gedik. Light-induced charge density wave in LaTe_3 . *Nature Physics*, 16(2):159–163, 2020.
- [16] S. K. Sundaram and E. Mazur. Inducing and probing non-thermal transitions in semiconductors using femtosecond laser pulses. *Nature Materials*, 1(4):217–224, 2002.

- [17] S. Bar-Ad and D.S. Chemla. Quantum kinetics regime during and immediately after laser excitation of semiconductors. *Materials Science and Engineering: B*, 48(1-2):83–87, 1997.
- [18] H. J. Zeiger, J. Vidal, T. K. Cheng, E. P. Ippen, G. Dresselhaus, and M. S. Dresselhaus. Theory for displacive excitation of coherent phonons. *Physical Review B*, 45(2):768–778, 1992.
- [19] Lisa Dhar, John A. Rogers, and Keith A. Nelson. Time-resolved vibrational spectroscopy in the impulsive limit. *Chemical Reviews*, 94(1):157–193, 1994.
- [20] R. Merlin. Generating Coherent THz Phonons With Light Pulses. *Solid State Communications*, 102(2):207–220, 1997.
- [21] A. V. Kuznetsov and C. J. Stanton. Theory of Coherent Phonon Oscillations in Semiconductors. *Physical Review Letters*, 73(24):3243–3246, 1994.
- [22] Watheq Al-Basheer, Christian Viernes, Meixin Cheng, Ruofei Zheng, Sam Netzke, Kostyantyn Pichugin, and German Sciaini. Determining the Out-of-Plane Longitudinal Sound Speed in GeS by Broadband Time-Domain Brillouin Scattering. *ACS Omega*, 9(13):15463–15467, 2024.
- [23] Watheq Al-Basheer, Christian Viernes, Ruofei Zheng, Sam Netzke, Kostyantyn Pichugin, and German Sciaini. Out-of-Plane Longitudinal Sound Speed Determination in GaS by Broadband Time-Domain Brillouin Scattering. *ACS Omega*, 9(48):47475–47479, 2024.
- [24] Patrick Gicala, Meixin Cheng, Tyler S. Lott, Kai Du, Sang-Wook Cheong, Ariel A. Petruk, Kostyantyn Pichugin, and German Sciaini. Time-resolved broadband impul-

- sive stimulated Brillouin scattering in single crystal hematite. *Applied Physics Letters*, 118(26):264101, 2021.
- [25] Nicolas Rivas, Shazhou Zhong, Tina Dekker, Meixin Cheng, Patrick Gicala, Fangchu Chen, Xuan Luo, Yuping Sun, Ariel A. Petruk, Kostyantyn Pichugin, Adam W. Tsen, and Germán Sciaini. Generation and detection of coherent longitudinal acoustic waves in ultrathin 1T'-MoTe₂. *Applied Physics Letters*, (22):223103, 2019.
 - [26] C. Thomsen, H. T. Grahn, H. J. Maris, and J. Tauc. Surface generation and detection of phonons by picosecond light pulses. *Physical Review B*, 34(6):4129–4138, 1986.
 - [27] George Grüner. *Density Waves in Solids*. Routledge Book, 1994.
 - [28] P.C. Hohenberg and A.P. Krekhov. An introduction to the Ginzburg–Landau theory of phase transitions and nonequilibrium patterns. *Physics Reports*, 572:1–42, 2015.
 - [29] Y.R. Shen. *Principles of Nonlinear Optics*. Wiley, 2002.
 - [30] Frederick Wooten. *Optical Properties of Solids*. Academic Press, 1972.
 - [31] George Turrell. *Infrared and Raman Spectra of Crystals*. Academic Press, 1972.
 - [32] Claude Cohen-Tannoudji, Bernard Diu, and Franck Laloe. *Quantum Mechanics*, volume 2. Wiley, 2020.
 - [33] A. M. Michalik, E. Ya. Sherman, and J. E. Sipe. Theory of ultrafast electron diffraction: The role of the electron bunch properties. *Journal of Applied Physics*, 104(5):054905, 2008.
 - [34] Germán Sciaini. Recent Advances in Ultrafast Structural Techniques. *Applied Sciences*, 9(7):1427, 2019.

- [35] Klaus Floettmann. ASTRA, 1997.
- [36] M.T. Menzel and H.K. Stokes. POISSON SUPERFISH, 1987.
- [37] Martin Reiser. *Theory and Design of Charged Particle Beams*. Wiley, 1994.
- [38] Edwin Cartlidge. European XFEL to shine as brightest, fastest x-ray source. *Science*, 354(6308):22–23, 2016.
- [39] P. Emma, R. Akre, J. Arthur, R. Bionta, C. Bostedt, J. Bozek, A. Brachmann, P. Bucksbaum, R. Coffee, F. J. Decker, Y. Ding, D. Dowell, S. Edstrom, A. Fisher, J. Frisch, S. Gilevich, J. Hastings, G. Hays, Ph Hering, Z. Huang, R. Iverson, H. Loos, M. Messerschmidt, A. Miahnahri, S. Moeller, H. D. Nuhn, G. Pile, D. Ratner, J. Rzepiela, D. Schultz, T. Smith, P. Stefan, H. Tompkins, J. Turner, J. Welch, W. White, J. Wu, G. Yocky, and J. Galayda. First lasing and operation of an ångstrom-wavelength free-electron laser. *Nature Photonics*, 4(9):641–647, 2010.
- [40] Makina Yabashi, Hitoshi Tanaka, and Tetsuya Ishikawa. Overview of the SACLA facility. *Journal of Synchrotron Radiation*, 22(3):477–484, 2015.
- [41] Pengfei Zhu, Y Zhu, Y Hidaka, L Wu, J Cao, H Berger, J Geck, R Kraus, S Pjerov, Y Shen, R I Tobey, J P Hill, and X J Wang. Femtosecond time-resolved MeV electron diffraction. *New Journal of Physics*, 17(6):063004, 2015.
- [42] S. P. Weathersby, G. Brown, M. Centurion, T. F. Chase, R. Coffee, J. Corbett, J. P. Eichner, J. C. Frisch, A. R. Fry, M. Gühr, N. Hartmann, C. Hast, R. Hettel, R. K. Jobe, E. N. Jongewaard, J. R. Lewandowski, R. K. Li, A. M. Lindenberg, I. Makasyuk, J. E. May, D. McCormick, M. N. Nguyen, A. H. Reid, X. Shen, K. Sokolowski-Tinten,

- T. Vecchione, S. L. Vetter, J. Wu, J. Yang, H. A. Dürr, and X. J. Wang. Mega-electron-volt ultrafast electron diffraction at SLAC National Accelerator Laboratory. *Review of Scientific Instruments*, 86(7), 2015.
- [43] Fengfeng Qi, Zhuoran Ma, Lingrong Zhao, Yun Cheng, Wenxiang Jiang, Chao Lu, Tao Jiang, Dong Qian, Zhe Wang, Wentao Zhang, Pengfei Zhu, Xiao Zou, Weishi Wan, Dao Xiang, and Jie Zhang. Breaking 50 Femtosecond Resolution Barrier in MeV Ultrafast Electron Diffraction with a Double Bend Achromat Compressor. *Physical Review Letters*, 124(13):134803, 2020.
- [44] A. W. Overhauser. Observability of Charge-Density Waves by Neutron Diffraction. *Physical Review B*, 3(10):3173–3182, 1971.
- [45] Dinh Loc Duong, Gihun Ryu, Alexander Hoyer, Chengtian Lin, Marko Burghard, and Klaus Kern. Raman Characterization of the Charge Density Wave Phase of 1T-TiSe₂ : From Bulk to Atomically Thin Layers. *ACS Nano*, 11(1):1034–1040, 2017.
- [46] R. Samnakay, D. Wickramaratne, T. R. Pope, R. K. Lake, T. T. Salguero, and A. A. Balandin. Zone-Folded Phonons and the Commensurate-Incommensurate Charge-Density-Wave Transition in 1T- TaSe₂ Thin Films. *Nano Letters*, 15(5):2965–2973, 2015.
- [47] Yong Zhang, Heng Zhang, Tianyu Qiu, Yiyang Zhang, Chong Zhang, Tongshuai Zhu, Zhicheng Zhong, Fucong Fei, Xiaoxiang Xi, Fengqi Song, and Xuefeng Wang. Trimerization-induced zone-folded phonons in 1T-TaTe₂. *Applied Physics Letters*, 125(19):191903, 2024.
- [48] Boualem Boashash. *Time-Frequency Signal Analysis and Processing: A Comprehensive Reference*. Academic Press, 2 edition, 2015.

- [49] Vasile V. Moca, Harald Bârzan, Adriana Nagy-Dăbâcan, and Raul C. Mureşan. Time-frequency super-resolution with superlets. *Nature Communications*, 12(1):337, 2021.
- [50] Won-Jun Jang, Junyoung Sim, Jin Eun Heo, Heeyoon Noh, Ryung Kim, Seo Hyoungh Chang, Sangjun Jeon, and Hyo Won Kim. Direct observation of multiband charge density waves in NbTe₂. *Physical Review B*, 106(12):125110, 2022.
- [51] Shoichi Nagata, Tsuyoshi Abe, Shuji Ebisu, Yutaka Ishihara, and Kitomi Tsutsumi. Superconductivity in the metallic layered compound NbTe₂. *Journal of Physics and Chemistry of Solids*, 54(8):895–899, 1993.
- [52] Natsuki Mitsuishi and Kyoko Ishizaka. Electronic Landscape of Group-5 Transition Metal Ditellurides MTe₂ (M = V, Nb, Ta): Multiple Crystal Phases with Local Bonds and Flat Bands. *Journal of the Physical Society of Japan*, 93(11):1–13, 2024.
- [53] J. Van Landuyt, G. Remaut, and S. Amelinckx. Electron microscope study of the substructure of niobium ditelluride single crystal. *Materials Research Bulletin*, 5(8):731–741, 1970.
- [54] J. van Landuyt, G. van Tendeloo, and S. Amelinckx. The direct imaging of two-dimensional charge density waves and of commensurate superlattices in NbTe₂ and TaTe₂. *Physica Status Solidi (a)*, 29(1):11–13, 1975.
- [55] John A. Wilson. Questions concerning the form taken by the charge-density wave and the accompanying periodic-structural distortions in 2H TaSe₂, and closely related materials. *Physical Review B*, 17(10):3880–3898, 1978.
- [56] Corsin Battaglia, Hervé Cercellier, Florian Clerc, Laurent Despont, Michael Gunnar Garnier, Christian Koitzsch, Philipp Aebi, Helmuth Berger, László Forró, and Claudia

- Ambrosch-Draxl. Fermi-surface-induced lattice distortion in NbTe₂. *Physical Review B*, 72(19):195114, 2005.
- [57] Haifeng Feng, Zhongfei Xu, Jincheng Zhuang, Li Wang, Yani Liu, Xun Xu, Li Song, Weichang Hao, and Yi Du. Role of Charge Density Wave in Monatomic Assembly in Transition Metal Dichalcogenides. *Advanced Functional Materials*, 29(15):1900367, 2019.
- [58] D. Cukjati, A. Prodan, N. Jug, H.J.P. Van Midden, S.W. Hla, H. Bhm, F.W. Boswell, and J.C. Bennett. The Instability of the NbTe₂ Surface Structure. *physica status solidi (a)*, 193(2):246–250, 2002.
- [59] Yusong Bai, Tao Jian, Zemin Pan, Jinghao Deng, Xiaoyu Lin, Chao Zhu, Da Huo, Zhengbo Cheng, Yong Liu, Ping Cui, Zhenyu Zhang, Qiang Zou, and Chendong Zhang. Realization of Multiple Charge-Density Waves in NbTe₂ at the Monolayer Limit. *Nano Letters*, 23(6):2107–2113, 2023.
- [60] Heng Jin, Tan Wei, and Bing Huang. Incognizant 1T/1H Charge-Density-Wave Phases in Monolayer NbTe₂. *Nano Letters*, 24(35):10892–10898, 2024.
- [61] B. E. Brown. The crystal structures of NbTe₂ and TaTe₂. *Acta Crystallographica*, 20(2):264–267, 1966.
- [62] Aarón Hernán Barajas-Aguilar, J. C. Irwin, Andrés Manuel Garay-Tapia, Torsten Schwarz, Francisco Paraguay Delgado, P. M. Brodersen, Rajiv Prinja, Nazir Kherani, and Sergio J. Jiménez Sandoval. Crystalline structure, electronic and lattice-dynamics properties of NbTe₂. *Scientific Reports*, 8(1):16984, 2018.
- [63] Hasan Erdogan and Roger D. Kirby. Raman spectrum and lattice dynamics of NbTe₂. *Solid State Communications*, 70(7):713–715, 1989.

- [64] Shujia Li, Qing Dong, Jiajia Feng, Yanju Wang, Mingqiang Hou, Wen Deng, Resta A. Susilo, Nana Li, Hongliang Dong, Shun Wan, Chunxiao Gao, and Bin Chen. Evolution of Structural and Electronic Properties in NbTe₂ under High Pressure. *Inorganic Chemistry*, 60(11):7857–7864, 2021.
- [65] T. Malis, S. C. Cheng, and R. F. Egerton. EELS log-ratio technique for specimen-thickness measurement in the TEM. *Journal of Electron Microscopy Technique*, 8(2):193–200, 1988.
- [66] Petr Brázda, Mariana Klementová, Yaşar Krysiak, and Lukáš Palatinus. Accurate lattice parameters from 3D electron diffraction data. I. Optical distortions. *IUCrJ*, 9(6):735–755, 2022.
- [67] P. J. Brown, A. G. Fox, E. N. Maslen, M. A. O’Keefe, and B. T. M. Willis. Intensity of diffracted intensities. In *International Tables for Crystallography*, pages 554–595. International Union of Crystallography, Chester, England, 2006.
- [68] T. Huber, S. O. Mariager, A. Ferrer, H. Schäfer, J. A. Johnson, S. Grübel, A. Lübcke, L. Huber, T. Kubacka, C. Dornes, C. Laulhe, S. Ravy, G. Ingold, P. Beaud, J. Demsar, and S. L. Johnson. Coherent structural dynamics of a prototypical charge-density-wave-to-metal transition. *Physical Review Letters*, 113(2):026401, 2014.
- [69] Kang Zhang, Ming Feng, Jiabin Yang, Yan Li, Jinyue Xie, Yuanhao Li, Dongdong Han, Feng Song, and Wei Huang. Niobium tellurium as a novel broadband saturable absorber for pulsed fiber lasers. *Journal of Materials Chemistry C*, 10(36):13201–13209, 2022.

- [70] Pavel E. Dolgirev, A. V. Rozhkov, Alfred Zong, Anshul Kogar, Nuh Gedik, and Boris V. Fine. Amplitude dynamics of the charge density wave in LaTe_3 : Theoretical description of pump-probe experiments. *Physical Review B*, 101(5):054203, 2020.
- [71] É. D. Murray, D. M. Fritz, J. K. Wahlstrand, S. Fahy, and D. A. Reis. Effect of lattice anharmonicity on high-amplitude phonon dynamics in photoexcited bismuth. *Physical Review B*, 72(6):060301, 2005.
- [72] Samuel W. Teitelbaum, Taeho Shin, Johanna W. Wolfson, Yu-Hsiang Cheng, Ilana J. P. Molesky, Maria Kandyla, and Keith A. Nelson. Real-Time Observation of a Coherent Lattice Transformation into a High-Symmetry Phase. *Physical Review X*, 8(3):031081, 2018.
- [73] Christian Gentry, Chen-Ting Liao, Wenjing You, Sinéad A. Ryan, Baldwin Akin Varner, Xun Shi, Meng-Xue Guan, Thomas Gray, Doyle Temple, Sheng Meng, Markus Raschke, Kai Rossnagel, Henry C. Kapteyn, Margaret M. Murnane, and Emma Cating-Subramanian. Super-resolved time–frequency measurements of coupled phonon dynamics in a 2D quantum material. *Scientific Reports*, 12(1):19734, 2022.
- [74] A. S. Pine and G. Dresselhaus. Raman Spectra and Lattice Dynamics of Tellurium. *Physical Review B*, 4(2):356–371, 1971.
- [75] A. A. Vinokurov, A. V. Tyurin, A. L. Emelina, K. S. Gavrichev, and V. P. Zlomanov. Thermodynamic properties of VTe_2 . *Inorganic Materials*, 45(5):480–485, 2009.
- [76] T. Sörgel, J. Nuss, U. Wedig, R. K. Kremer, and M. Jansen. A new low temperature modification of TaTe_2 -Comparison to the room temperature and the hypothetical 1T- TaTe_2 modification. *Materials Research Bulletin*, 41(5):987–1000, 2006.

- [77] Linnan Jia, Chang-Fu Huo, Xiao-Qing Yan, Jiayang Wu, Yu-Zhe Zhang, Yunyi Yang, Wenxiong Xu, Qiannan Cui, Daohong Song, Baohua Jia, Zhi-Bo Liu, Zhigang Chen, and David J. Moss. Ultrafast Carrier Dynamics in 2D NbTe₂ Films: Implications for Photonic and Optoelectronic Devices. *ACS Applied Nano Materials*, 5(12):17348–17355, 2022.
- [78] D. Bersani, P. P. Lottici, and Xing-Zhao Ding. Phonon confinement effects in the Raman scattering by TiO₂ nanocrystals. *Applied Physics Letters*, 72(1):73–75, 1998.
- [79] S. Osswald, V. N. Mochalin, M. Havel, G. Yushin, and Y. Gogotsi. Phonon confinement effects in the Raman spectrum of nanodiamond. *Physical Review B*, 80(7):075419, 2009.
- [80] Khalid M. Siddiqui, Daniel B. Durham, Frederick Cropp, Colin Ophus, Sangeeta Rajpurohit, Yanglin Zhu, Johan D. Carlström, Camille Stavrakas, Zhiqiang Mao, Archana Raja, Pietro Musumeci, Liang Z. Tan, Andrew M. Minor, Daniele Filippetto, and Robert A. Kaindl. Ultrafast optical melting of trimer superstructure in layered 1T-TaTe₂. *Communications Physics*, 4(1):152, 2021.

APPENDICES

Appendix A

Python Code

A.1 Functions used to fit traces

```
1 #!/usr/bin/env python3
2 # -*- coding: utf-8 -*-
3 """
4 Created on Fri Apr 11 14:17:45 2025
5
6 @author: Christian Viernes
7 """
8
9 from scipy.optimize import least_squares
10 import numpy as np
11 from scipy.special import erf
12 pi = np.pi
13 def set_size(w,h, ax=None):
14     """Changes axis size to have width w and height h
15     """
```

```

16     if not ax: ax=plt.gca()
17     l = ax.figure.subplotpars.left
18     r = ax.figure.subplotpars.right
19     t = ax.figure.subplotpars.top
20     b = ax.figure.subplotpars.bottom
21     figw = float(w)/(r-l)
22     figh = float(h)/(t-b)
23     ax.figure.set_size_inches(figw, figh)
24
25 def constant(t, t0, tau_irf, b):
26     """Constant convoluted with gaussian IRF
27     """
28     return b * (0.5 - erf((t-t0)/(np.sqrt(2)*tau_irf)))
29
30 def exp_decay(t,t0,tau_irf,a,k):
31     """Exponential decay convoluted with Gaussian IRF
32     """
33     return a*0.5*np.exp(0.5*k**2*tau_irf**2-k*(t-t0)) * (1+erf((t-t0-k*
tau_irf**2)/np.sqrt(2)/tau_irf))
34
35 def osc(t, t0, a, k, f, p):
36     """Exponentially decaying sine function
37     """
38     return a*np.exp(-k*(t-t0))*np.sin(2*pi*f*(t-t0)+p)*np.heaviside(t-t0
,1)
39
40 def model_exp(t, *params):
41     """Model with variable number of decays. At least 3 parameters
required + 2 for each required decay
42     """

```

```

43     num_decays = (len(params)-3)//2
44     out = 0
45     t0, tau_irf, b = params[-3:]
46     for i in range(num_decays):
47         out += exp_decay(t,t0,tau_irf,params[2*i],params[2*i+1])
48     out += constant(t, t0, tau_irf, b)
49     return out
50
51 def model_osc(t, *params):
52     """Model with variable number of decays. At least 3 parameters
53     required + 2 for each required decay. Includes a single exponentially
54     decaying oscillation
55     """
56     num_decays = (len(params)-7)//2
57     a, k, f, p, t0, tau_irf, b = params[-7:]
58     out = 0
59     for i in range(num_decays):
60         out += exp_decay(t,t0,tau_irf,params[2*i],params[2*i+1])
61         out += osc(t, t0, a, k, f, p)
62     out += constant(t, t0, tau_irf, b)
63     return out

```

A.2 Functions used to analyze UED data

```

1 # -*- coding: utf-8 -*-
2 """
3 Created on Mon Sep 30 11:53:17 2024
4
5 @author: Christian
6 """

```

```

7
8 import numpy as np
9 import matplotlib.pyplot as plt
10 from matplotlib.animation import FuncAnimation
11 from scipy.constants import speed_of_light as c
12 from scipy.optimize import curve_fit
13 import os
14 from Fitting import *
15 from scipy.interpolate import interp1d
16 import sip_parser as sip
17 from scipy.ndimage import median_filter
18 def set_size(w,h, ax=None):
19     """ w, h: width, height in inches """
20     if not ax: ax=plt.gca()
21     l = ax.figure.subplotpars.left
22     r = ax.figure.subplotpars.right
23     t = ax.figure.subplotpars.top
24     b = ax.figure.subplotpars.bottom
25     figw = float(w)/(r-l)
26     figh = float(h)/(t-b)
27     ax.figure.set_size_inches(figw, figh)
28 def import_sif(path,shape1,shape2):
29
30     """
31     delay length is number of numbers in delay stage length
32     shape1 and shape2 are the pixel sizes of the images
33     """
34     files = []
35     numbers = []
36     for file in os.listdir(path):

```

```

37         if file.endswith('.sif') and 'pump' not in file:
38             files.append(file)
39
40     data = np.zeros((len(files),shape1,shape2))
41     numbers = np.zeros(len(files))
42     for i in range(len(files)):
43         data[i] = sif.np_open(path+files[i])[0]
44         index = files[i].index('OmW_') + 4
45         index2 = files[i].index('mm_')
46         numbers[i] = files[i][index:index2]
47         #numbers[i] = int(path[11:-3])
48
49     indices = numbers.argsort()[::-1]
50     numbers = numbers[indices]
51     data = data[indices]
52
53     return numbers, data
54
55 def compress_data(path,delay1,delay2,shape1,shape2):
56
57     """
58     delay1 and delay2 are indices where delay position is stated
59     shape1 and shape2 are the pixel sizes of the images
60     """
61     files = []
62     numbers = []
63     for file in os.listdir():
64         if file.endswith('asc'):
65             files.append(file)
66             numbers.append(file[delay1:delay2].replace('m','0'))

```

```

67     data = np.zeros((len(files),shape1,shape2))
68     numbers = np.array(numbers,dtype=float)
69     indices = numbers.argsort()[::-1]
70     numbers = numbers[indices]
71     for i in range(len(files)):
72         data[i] = load_data(files[i])
73     data = data[indices]
74
75     return numbers, data
76
77 def time_points(delays, delay_zero):
78     """Convert delay stage positions to time in ps.
79     """
80     times = (delays - delays[delay_zero]) / c *1e9*2
81     return times * -1
82
83 def animate(data,numbers):
84     """Animate data using numbers as titles
85     """
86     plt.figure(figsize=(10,10))
87     plot = plt.imshow(data[-1],animated=True)
88     title = plt.title(numbers[-1])
89     i = 0
90     def updatefig(*args):
91         global i
92         if (abs(i)<len(signal_data)):
93             i -= 1
94         else:
95             i=0
96     plot.set_array(data[i])

```

```

97     title.set_text(str(numbers[i]))
98     return plot, title
99
100     ani = FuncAnimation(fig, updatefig, blit=False)
101     return ani
102 %%NORMALIZE DATA FUNCTIONS
103 def normalize_mask(data, centers, radius):
104     """Normalize data using total intensities while excluding the main
105     beam located at centers with radius.
106     """
107     totals = np.zeros(data.shape[0])
108     for i in range(data.shape[0]):
109         mask = create_circular_mask(data[i].shape[0], data[i].shape[1],
110         centers[i], radius) ###exclude center
111         data[i] -= np.mean(data[i,:20,:20]) ###subtract baseline
112         totals[i] = np.sum(data[i]*mask)
113     fluctuation = totals[1]/totals
114     normalized = np.copy(data)
115     for i in range(data.shape[0]):
116         normalized[i] = data[i] * fluctuation[i]
117     return normalized
118 %%SUBTRACT BACKGROUND FUNCTIONS
119 def radial_profile(data, center):
120     """Return average radial profiles of data around center
121     """
122     y, x = np.indices((data.shape))
123     r = np.sqrt((x - center[0])**2 + (y - center[1])**2)
124     r = r.astype(np.int)
125     r_array = np.arange(r.min(),r.max())
126     tbin = np.bincount(r.ravel(), data.ravel())

```

```

125     nr = np.bincount(r.ravel())
126     radialprofile = tbin / nr
127     return r_array, radialprofile
128 def minimum_profile(data, center):
129     """Return minimum radial profiles of data around center
130     """
131     y, x = np.indices((data.shape))
132     r = np.sqrt((x - center[0])**2 + (y - center[1])**2)
133     r = r.astype(np.int_)
134     r_array = np.arange(r.min(), r.max())
135     minimum = np.zeros(len(r_array))
136     np.minimum.at(minimum, r.ravel(), data.ravel())
137     return minimum
138
139 def subtract_bkg(data, center, quantile, binning):
140     """Finds the quantile at each radius and subtracts from individual
141     data image. Binning will find quantiles at multiple radii together to
142     make it faster. SLOW
143     """
144     y, x = np.indices(data.shape)
145     r = np.sqrt((x - center[0])**2 + (y - center[1])**2)
146     r = r.astype(np.int_)
147     r_array = np.arange(r.min(), r.max(), binning)
148     minimum = np.zeros(r_array.shape)
149     corrected = np.copy(data)
150     for i in range(len(r_array)):
151         condition = np.where(np.abs(r - r_array[i]) < binning)
152         minimum[i] = np.quantile(data[condition], quantile)
153         corrected[condition] = data[condition] - minimum[i]
154     return corrected, r_array, minimum

```

```

153
154 def radialAvg_correction(data,centers):
155     """Subtracts average radial profile from data set. FAST
156     """
157     corrected = np.copy(data)
158
159     for j in range(data.shape[0]):
160         y, x = np.indices(data[j].shape)
161         r = np.sqrt((x - centers[j][0])**2 + (y - centers[j][1])**2)
162         r = r.astype(np.int)
163         r_array, rprofile = radial_profile(data[j],centers[j])
164         function = interp1d(np.append(r_array,np.max(r_array)+1),rprofile
165         )
166         background = function(r)
167         corrected[j] -= background
168     return corrected
169
170 def radialMin_correction(data, centers):
171     """Subtracts minimum radial profile from data set. FAST
172     """
173     corrected = np.copy(data)
174     for i in range(data.shape[0]):
175         print('Correcting ' + str(i))
176         y, x = np.indices(data[i].shape)
177         r = np.sqrt((x - centers[i][0])**2 + (y - centers[i][1])**2)
178         r = r.astype(np.int_)
179         r_array = np.arange(r.min(),r.max())
180         minimum = np.zeros(len(r_array)+1) + np.max(data[i])
181         np.minimum.at(minimum, r.ravel(), np.abs(data[i].ravel()))
182         smooth = median_filter(minimum, size = 10)

```

```

182         function = interp1d(np.append(r_array,np.max(r_array)+1), smooth)
183         background = function(r)
184         corrected[i] -= background
185         if i==0:
186             plt.plot(np.append(r_array,np.max(r_array)+1) , minimum)
187     return corrected
188
189 def radialQuant_correction(data, centers,binning,quantile):
190     """Subtracts quantile radial profile from data set. slow
191     """
192     corrected = np.copy(data)
193     for i in range(data.shape[0]):
194         print('Correcting ' + str(i))
195         corrected[i], r_array, minimum = subtract_bkg(data[i],centers[i],
196 quantile,binning)
197     return corrected
198
199 #%%FIND PEAK FUNCTIONS
200
201 def twoD_Gaussian(xy, amplitude, xo, yo, sigma_x, sigma_y, theta):
202     """2D anisotropic Gaussian centered around (x0,y0). Theta rotates the
203     gaussian.
204     """
205     x, y = xy
206     xo = float(xo)
207     yo = float(yo)
208     a = (np.cos(theta)**2)/(2*sigma_x**2) + (np.sin(theta)**2)/(2*sigma_y
209 **2)
210     b = -(np.sin(2*theta))/(4*sigma_x**2) + (np.sin(2*theta))/(4*sigma_y
211 **2)
212     c = (np.sin(theta)**2)/(2*sigma_x**2) + (np.cos(theta)**2)/(2*sigma_y
213 **2)

```

```

207     g = amplitude*np.exp( - (a*((x-xo)**2) + 2*b*(x-xo)*(y-yo)
208                             + c*((y-yo)**2)))
209     return g.ravel()
210
211 def fit_2Dgaussian(data, x0=None, cut_off=False, show_fit=False):
212     x = np.arange(0,data.shape[0],1)
213     y = np.arange(0,data.shape[1],1)
214     x, y = np.meshgrid(x,y)
215
216
217     if x0 == None:
218         x0 = np.random.random(8)
219     if cut_off:
220         x0[-1] = np.max(data)
221     x0[0] = np.max(data)
222     x0[1] = x.max()/2
223     x0[2] = y.max()/2
224     x0[3] = x.max()/5
225     x0[4] = y.max()/5
226     x0[6] = data[0,0]
227     if x.max()<30:
228         x0[-1] = np.inf
229     popt, pcov = curve_fit(twoD_Gaussian2, (x,y), data.ravel(), p0 = x0,
maxfev=10000)
230     if show_fit:
231         popt2 = popt
232         popt2[-1] = np.inf
233         data_fitted = twoD_Gaussian((x, y), *popt2)
234         data_reshaped = data_fitted.reshape(data.shape[0],data.shape[1])
235         fig, axs = plt.subplots(1,2)

```

```

236     axs[0].imshow(data, cmap=plt.cm.jet, origin='lower',
237                   extent=(x.min(), x.max(), y.min(), y.max()))
238     axs[0].contour(x, y, data_reshaped, 8, colors='w')
239
240     axs[1].plot(data[data.shape[0]//2,:], label = 'data')
241     axs[1].plot(data_reshaped[data_reshaped.shape[0]//2,:], label='fit
242     ')
243     axs[1].legend()
244     data_fitted = twoD_Gaussian2((x, y), *popt).reshape(data.shape[0],
245     data.shape[1])
246     residual = np.mean(data - data_fitted.reshape(data.shape[0], data.
247     shape[1]))
248     return popt, pcov, data_fitted
249
250 def twoD_Gaussian2(xy, amplitude, xo, yo, sigma_x, sigma_y, theta, offset,
251 cutoff=np.inf):
252     """2D anisotropic Gaussian centered around (x0,y0). Theta rotates the
253     gaussian. Cutoff included to fit saturated peaks
254     """
255     x, y = xy
256     xo = float(xo)
257     yo = float(yo)
258     a = (np.cos(theta)**2)/(2*sigma_x**2) + (np.sin(theta)**2)/(2*sigma_y
259     **2)
260     b = -(np.sin(2*theta))/(4*sigma_x**2) + (np.sin(2*theta))/(4*sigma_y
261     **2)
262     c = (np.sin(theta)**2)/(2*sigma_x**2) + (np.cos(theta)**2)/(2*sigma_y
263     **2)
264     g = offset+amplitude*np.exp( - (a*((x-xo)**2) + 2*b*(x-xo)*(y-yo)
265     + c*((y-yo)**2)))

```

```

258     g[g>cutoff] = cutoff
259     return g.ravel()
260 def gaussians(xy, *params):
261     """Multiple gaussians using variable number of params. 6 parameters
262     for each gaussian + an extra parameter for baseline intensity
263     """
264     out = 0
265     for i in range(0, len(params) - 1, 6):
266
267         out += twoD_Gaussian(xy, *params[i:i+6])
268
269     return out + params[-1]
270
271 def fitGaussians(data, peaks = None, p0 = None, bounds=(-np.inf, np.inf)):
272     """Fit Data to multiple gaussians. peaks are the initial guesses for
273     peak centers, p0 is initial guess for all parameters. parameters can
274     be bounded using bounds.
275     """
276
277     x = np.arange(0, data.shape[1], 1)
278     y = np.arange(0, data.shape[0], 1)
279     x, y = np.meshgrid(x, y)
280
281     if not isinstance(p0, np.ndarray):
282         num_peaks = len(peaks)
283         p0 = np.zeros(num_peaks*6 + 1)
284         for i in range(num_peaks):
285             p0[6*i] = data[int(peaks[i][0]), int(peaks[i][1])]
286             p0[6*i+1] = peaks[i][0]
287             p0[6*i+2] = peaks[i][1]
288             p0[6*i+3] = 5

```

```

285         p0[6*i+4] = 5
286         p0[-1] = data[0,0]
287         lb = (0.95*p0 - 10)
288         ub = (1.05*p0 + 10)
289         popt, pcov = curve_fit(gaussians, (x,y), data.ravel(), p0=p0,bounds =
                bounds)#, maxfev=10000)
290         return popt, pcov
291
292 def find_centers(data,center,radius):
293     """Find center of diffraction image by fitting main peak
294     """
295     centers = np.zeros(data.shape[0],dtype=object)
296     params = np.zeros((data.shape[0],8))
297     residuals = np.zeros(data.shape[0])
298     for i in range(data.shape[0]):
299         popt, pcov, residual = fit_2Dgaussian(data[i][center[1]-radius:
                    center[1]+radius,center[0]-radius:center[0]+radius])
300         centers[i] = (popt[1]-radius+center[0],popt[2]-radius+center[1])
301         params[i] = popt
302         #residuals[i] = residual
303     return centers, params, #residuals
304 ###FIND INTENSITY FUNCTIONS
305
306 def create_circular_mask(h, w, center=None, radius=None):
307     """Creates a circular mask array with dimensions (h x w) centered
308     around center with radius radius.
309     """
310     if center is None: # use the middle of the image
311         center = (int(w/2), int(h/2))
312     if radius is None: # use the smallest distance between the center and

```

```

312     image walls
313         radius = min(center[0], center[1], w-center[0], h-center[1])
314
315     Y, X = np.ogrid[:h, :w]
316     dist_from_center = np.sqrt((X - center[0])**2 + (Y-center[1])**2)
317
318     mask = dist_from_center >= radius
319     return mask
320
321 def ROI(data, ROIs, radius, show_mask = False):
322     """Integrates a circular region around ROI with radius radius.
323     """
324     ROI_data = np.zeros((np.shape(data)[0], np.shape(data)[1]))
325
326     mask = create_circular_mask(data.shape[0], data.shape[1], ROIs,
327 radius)
328     ROI_data = data*~mask
329
330     indices = np.where(mask == 0)
331     mean_intensities = np.mean(ROI_data[indices])
332
333     if show_mask:
334         fig, ax = plt.subplots()
335
336         circle = plt.Circle(ROIs, radius, facecolor='none', edgecolor='black
337 ')
338         ax.add_patch(circle)

```

```

339         ax.imshow(data)
340
341         #plt.imshow(np.sum(ROI_data,axis=0))
342
343     return mean_intensities
344 def peak_intensities(data, peaks, radius, save=True):
345     """Obtain intensities around peaks with radius r.
346     """
347     intensities = np.zeros(peaks.shape)
348
349     for i in range(data.shape[0]):
350         intensities[i] = ROI(data[i],peaks[i],radius)
351     if save:
352         np.save('intensities.npy',intensities)
353     return intensities

```

A.3 Example script used to extract intensities from a set of diffraction data

```

1  # -*- coding: utf-8 -*-
2  """
3  Created on Fri Nov 29 17:12:55 2024
4
5  @author: Christian
6  """
7
8  import sys
9  import matplotlib
10 from UED import *

```

```

11 from scipy.signal import find_peaks
12 from matplotlib import cm, ticker
13 data = np.load('averaged_data.npy') ###Diffraction data series
14 numbers = np.load('numbers.npy') ###Delay Stage positions
15 times = time_points(numbers,10)
16
17 ###Select Main Peak and fit first image
18 region =30
19 plt.imshow(data[0], vmax = 0.015*np.max(data[0]), vmin=0)
20 figManager = plt.get_current_fig_manager()
21 figManager.window.showMaximized()
22 main = plt.ginput(1, timeout = 0, mouse_add=None)
23 plt.close()
24 roi = data[:,int(main[0][1])-region:int(main[0][1])+region,int(main
    [0][0])-region:int(main[0][0]+region)]
25 plt.imshow(roi[0] , vmax = 0.015*np.max(data[0]), vmin=0)
26 figManager = plt.get_current_fig_manager()
27 figManager.window.showMaximized()
28 peaks = plt.ginput(0, timeout = 0, mouse_add=None)
29 plt.close()
30
31 x = np.arange(0,roi.shape[2],1)
32 y = np.arange(0,roi.shape[1],1)
33 x, y = np.meshgrid(x, y)
34
35 params = np.zeros((roi.shape[0], len(peaks)*6+1))
36 lb = np.ones(params[0].shape) * -np.inf
37 ub = np.ones(params[0].shape) * np.inf
38
39 params[0], _ = fitGaussians(roi[0], peaks=peaks, bounds=(lb,ub))

```

```

40 z = gaussians((x,y), *params[0]).reshape(roi[0].shape)
41
42 ###Check fits of first image
43 plt.figure(figsize=(2,2))
44 plt.contour(z,np.logspace(np.log10(z.min()),np.log10(z.max()), 15),zorder
    =2, locator=ticker.LogLocator(),cmap='Blues')
45 plt.imshow(roi[0],vmax=4000,zorder=1,cmap='inferno')
46 for j in range(len(peaks)):
47     plt.scatter(params[0][6*j+1],params[0][6*j+2], color='red',zorder=3,s
    =1)
48 plt.axis('off')
49 ###Fit all the images
50 fits = np.zeros(roi.shape)
51 fits_peaks = np.zeros((len(peaks),roi.shape[0],roi.shape[1],roi.shape[2])
    )
52 for i in range(roi.shape[0]):
53     print(i)
54
55     if i != 0:
56         lb = params[i-1] - 0.1 * np.abs(params[i-1])
57         ub = params[i-1] + 0.1 * np.abs(params[i-1])
58         params[i], _ = fitGaussians(roi[i], p0 = params[i-1],bounds = (lb
    ,ub))
59     for j in range(len(peaks)):
60         fits_peaks[j,i] = twoD_Gaussian((x,y), *params[i,6*j:6*(j+1)]).
    reshape(roi[i].shape)
61     fits[i] = gaussians((x,y), *params[i]).reshape(roi[i].shape)
62 ###Check all the fits
63 plt.ion(); plt.figure()
64 i=0

```

```

65 while i < roi.shape[0]:
66     print(i)
67     plt.clf()
68     plt.contour(fits[i], np.logspace(np.log10(fits[i].min()), np.log10(fits
69 [i].max()), 10), zorder=2)
70     plt.imshow(roi[i], vmax=15000, zorder=1)
71     for j in range(len(peaks)):
72         plt.scatter(params[i, 6*j+1], params[i, 6*j+2], color='red', zorder
73 =3)
74     plt.pause(0.1)
75     plt.draw()
76     i+=5
77
78 ###Find intensities by integrating around each fitted peak
79 r = [20, 15, 8, 8, 8] ##radii to integrate around each peak
80 img = np.copy(roi)
81 for i in range(len(peaks)):
82     img -= fits_peaks[i, :]
83 img -= params[:, -1, None, None]
84 relative = np.zeros((len(peaks), roi.shape[0]))
85 fig, axs = plt.subplots(1, 2, figsize= (4, 2))
86 axs[0].imshow(roi[0], vmin = 0, vmax=np.max(0.2*roi[0]))
87 axs[0].axis('off')
88
89 #colors = ['cornflowerblue', '#77DD77', '#FF8439', 'indianred']
90 for i in range(len(peaks)):
91     mask = np.zeros(roi.shape)
92     img2 = img + fits_peaks[i, :]
93     for j in range(roi.shape[0]):
94         radius = r[i]
95         center = (params[j, 6*i+1], params[j, 6*i+2])
96         mask = create_circular_mask(img.shape[1], img.shape[2], center,

```

```

radius)
93     img2[j][mask] = 0
94     intensities = np.mean(np.mean(img2,axis=1),axis=1)
95     neg_intensities = np.mean(intensities[:10])
96     relative[i] = (intensities - neg_intensities)/neg_intensities
97     circle = plt.Circle(center, radius=radius, facecolor='none',
edgecolor='red')
98     axs[0].add_patch(circle)
99     axs[0].text(center[0],center[1],str(i))
100    axs[1].plot(relative[i],label=str(i))
101    axs[1].legend()
102
103    ### Save the data
104    save = False
105    save_indices = [0,1,2,3] ###Peak indices to save
106    centers = np.zeros((len(peaks),2))
107    for i in range(len(peaks)):
108        centers[i,0] = main[0][0] + params[0,6*i+1] - region
109        centers[i,1] = main[0][1] + params[0,6*i+2] - region
110    plt.figure(figsize=(10,10))
111    plt.imshow(data[0],vmax=40000,vmin=0)
112
113    if save:
114        if 'intensities.npy' in os.listdir():
115            loaded = np.load('intensities.npy')
116            loadedc = np.load('peaks.npy')
117            if centers[-1] not in loadedc:
118                new = np.vstack((loaded, relative[save_indices]))
119                newc = np.vstack((loadedc, centers[save_indices]))
120                np.save('intensities.npy', new)

```

```
121         np.save('peaks.npy', newc)
122     for i in range(newc.shape[0]):
123         plt.text(newc[i,0], newc[i,1], str(i))
124     plt.savefig('Spots.png')
125 else:
126     np.save('intensities.npy', relative)
127     np.save('peaks.npy', centers)
```