Ultrafast probing of coherent structural dynamics in solids

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Abstract

Ultrafast time-resolved studies employing the pump-probe principle have become an increasingly important tool to study microscopic scattering channels in solids that determine their emergent macroscopic properties. Ultrafast techniques now are also becoming technologically relevant, since intense pulses of electromagnetic excitation can drastically modify these emergent properties on a sub-picosecond timescale. A complete understanding of highly nonequilibrium states after intense excitation begins with a full characterization of the structural symmetry of these transient states.

In this work, the coherent dynamics of the structure in solids are studied in two widely different regimes. While resonant excitation is exploited to selectively excite lattice degrees of freedom, intense near-infrared laser pulses can trigger drastic changes in structural symmetry by melting the electronic order in a system.

In the first part of the work, a new kind of coherent phonon spectroscopy relying on the resonant excitation of optical coherent phonons is demonstrated. Specifically, non-fully symmetric modes in single-crystal tellurium were excited by intense sub-picosecond terahertz frequency electromagnetic pulses generated via optical rectification in an organic crystal. The resonantly excited coherent motion was probed in a phase-resolved way by monitoring the anisotropic transient changes in reflectivity with femtosecond near-infrared laser pulses. The structural dynamics after terahertz excitation can be modeled as a collection of Lorentz oscillators driven by the broadband near-single-cycle terahertz pulses. Since terahertz pulses directly couple to the lattice as opposed to methods using above-bandgap excitation to drive coherent phonons, the presented approach allows for a new way of studying coherent phonons with the electronic system being close to equilibrium.

For the second part of the work, changes in structural symmetry during the ultrafast melting of electronic order in charge-density-wave (CDW) systems were studied with time-resolved hard x-ray diffraction, a method that can directly observe the transient structure of a solid.

In the prototypical quasi-one-dimensional Peierls system $K_{0.3}MoO_3$, time resolved x-ray diffraction after intense photoexcitation was used to study the coherent structural dynamics associated with ultrafast melting of electronic order by a femtosecond near-infrared laser pulse. For low excitation fluences, the coherent structural dynamics associated with the amplitude mode of the charge-density-wave ground state could be observed. Fluences large enough to melt the electronic order resulted in a destruction of the periodic lattice distortion of the CDW ground state and, strikingly, a sub-picosecond transient recovery of the periodic lattice distortion. The coherent structural dynamics associated with the melting of the CDW can be explained as a coherent motion along the coordinate of the Peierls distortion in a transient high symmetry potential, triggered by the collapse of electronic order. Owing to the simplicity of the theoretical description of the CDW-to-metal transition in $K_{0.3}MoO_3$, the results provide far-reaching insights into the general nature of ultrafast photoinduced phase transitions. For example, the results
indicate that time scales of changes in structural symmetry after the melting of electronic order in broken symmetry ground states are essentially determined by vibrational modes of the high-symmetry phase.

To accurately describe the coherent motion during the photoinduced symmetry-breaking transition, a transient time-dependent damping has to be introduced. This time-dependent damping was further investigated utilizing time-resolved x-ray diffraction in tandem with double-pump excitation. In these experiments, the first pump pulse melts the electronic order and launches a coherent motion, while the second pump pulse re-excites the electronic system. The experiments confirm the existence of a time-dependent damping and reveal that a second pump pulse can modify the damping of the coherent motion, resulting in a second transient recovery of the periodic lattice distortion.

Finally, results on the ultrafast transition in the quasi-two-dimensional charge density wave compound 4Hb-TaSe2 are presented. Here, in contrast to the one-dimensional system, the coherent motion during the melting of electronic order is highly damped and the change of structural symmetry takes place on a sub-picosecond timescale without a transient recovery.

The thesis is structured as follows:

In the first chapter, a general introduction into ultrafast nonequilibrium physics in solid state systems is given. The pump-probe principle, which is employed for time-resolved experiments throughout this work, is explained in detail. The second chapter more specifically focuses on ultrafast structural dynamics in solids, outlining methods on how to excite and probe the structure of a solid on a sub-picosecond timescale as well as introducing the concept of a coherent phonon.

Chapter 3 starts with an introduction to strongly correlated electron systems and then gives an overview of the physics of the CDW ground state. The two systems studied in this thesis, the quasi-one-dimensional system K0.3MoO3 and the quasi-two-dimensional system 4Hb-TaSe2, are described in detail.

Chapter 4 and Chap. 5 describe the experimental methods utilized in this work to study the coherent structural dynamics of solids, namely time-resolved hard x-ray diffraction as an ultrafast structural probe and intense terahertz frequency pulses as a resonant pump.

In Chap. 6 the coherent phonon spectroscopy experiments using resonant terahertz excitation of single-crystal Tellurium are demonstrated.

The remaining chapters treat the coherent structural dynamics during the ultrafast melting of electronic order in CDW systems. In Chap. 7 time-resolved x-ray diffraction measurements of the coherent structural dynamics during the ultrafast melting of a CDW in K0.3MoO3 are presented. The results are complemented by double-pump excitation studies, which are presented in Chap. 8. Time-resolved x-ray diffraction measurements on the quasi-two-dimensional CDW compound 4Hb-TaSe2 are described in Chap. 9.

Finally, Chap. 10 gives a conclusion and an outlook on how future experiments could answer some open questions raised by this work.
Zusammenfassung

Ultraschnelle kohärente Gitterdynamik in Festkörpern


Die vorliegende Arbeit beschäftigt sich mit der experimentellen Untersuchung der kohärenten Dynamik der Struktur von Festkörpern mithilfe extrem kurzer Impulse elektromagnetischer Strahlung. Dafür werden Impulse aus weiten Teilen des elektromagnetischen Spektrums verwendet, die es zum Beispiel erlauben resonant spezifische Gitterfreiheitsgrade anzuregen oder mit Beugungsmethoden direkt die strukturelle Symmetrie eines Festkörpers im extremen Nichtgleichgewicht zu untersuchen.


Im Gegensatz zu anderen Anregungsformen, mit denen kohärente Gitterzustände in Festkörpern erzeugt werden können, koppelt elektromagnetische Strahlung aus dem Terahertz-Spektralbereich direkt und selektiv an Gitterschwingungen. Da die Energie der Terahertz-Photonen im präsentierten Experiment zu klein ist, um Elektronen über die Bandlücke anzuregen, bleiben die elektronischen Zustände des untersuchten Materials dabei weitestgehend unverändert. Es können daher kohärente Gitterschwingungen mit großer Amplitude untersucht werden, während das elektronische System des Festkörpers sich nahezu im Gleichgewicht befindet — ein Novum in der zeitaufgelösten Gitterspektroskopie. Die Erzeugung der kohärenten Phononen lässt sich im Rahmen eines Modells basierend auf Lorentz-Oszillatoren, die resonant vom elektrischen Feld des Terahertz-Impulses getrieben werden, beschreiben.

Der zweite Teil der Arbeit befasst sich mit der ultraschnellen Änderung der strukturellen Symmetrie in Ladungsdichtewellen-Systemen (charge density wave, CDW) nach Anregung mit
Femtosekunden-Laserimpulsen. Es ist bereits bekannt, dass starke Laserimpulse die elektronische Ordnung im CDW-Grundzustand zerstören können. Bis jetzt konnte die kohärente Bewegung der Atome auf den Koordinaten, die die Struktur des CDW-Grundzustands und der Hochsymmetriephase verbinden jedoch nicht direkt beobachtet werden. Mittels zeitaufgelöster Röntgenbeugung ist es möglich, Änderungen der strukturellen Symmetrie auf Zeitskalen der elementaren Anregungen des CDW-Zustands zu beobachten.

Im quasi-eindimensionalen System K_{0.3}MoO_3, in dem die Ausbildung der CDW im Peierls-Bild beschrieben werden kann, konnten wir so die vollständige relevante kohärente Strukturdynamik während des photoinduzierten Phasenübergangs untersuchen. Für Anregungsdichten über der Zerstörschwelle des CDW-Kondensats zeigt die Gittermodulation unerwarteterweise eine zeitweise Wiederherstellung auf einer Zeitskale unter einer Pikosekunde. Die gemessene Strukturdynamik kann mit einem Modell basierend auf einem interatomaren Potential, dessen Form von der Anregungsdichte abhängt, erklärt werden und erlaubt tiefe Einblicke in die Natur photoinduzierter Phasenübergänge.

Um die gemessenen Daten richtig wiederzugeben, muss zudem eine zeitabhängige Dämpfung der kohärenten Gitterbewegung eingeführt werden. In einem weiterführenden zeitaufgelösten Röntgenbeugungsexperiment konnten wir mittels Anregung mit zwei zeitlich versetzten Laserimpulsen die Existenz der zeitabhängigen Dämpfung bestätigen.

Zum Abschluss der Arbeit werden Messungen zur kohärenten Gitterdynamik während der Zerstörung der kommensurablen CDW im quasi-zweidimensionalen System 4H-TaSe_2 präsentiert. Die Ergebnisse können in einem ähnlichen Modell beschrieben werden, die kohärente Gitterbewegung während des photoinduzierten Phasenübergangs ist jedoch stark gedämpft, sodass keine temporäre Wiederherstellung der Gittermodulation beobachtet werden kann.
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Chapter 1

Introduction to ultrafast solid state science

One of the most important experimental tools to study the solid state has always been spectroscopy with electromagnetic radiation. Electromagnetic radiation spanning the whole spectrum can be used to investigate properties of a solid, ranging from hard x-rays to study the equilibrium structure of a solid with diffraction methods, to low-frequency radiation to study resonances associated with low-lying phonon modes and magnetic excitations.

Conventional solid-state spectroscopy and diffraction methods give access to material properties in thermal equilibrium. These methods can also yield crucial information of the structure and elementary excitations of quantum states of materials, like broken symmetry ground states of strongly correlated systems. The complex interplay of different subsystems, however, can often only be studied when the subsystems are not in equilibrium. Only then can relaxation processes be observed that reveal crucial information about relevant coupling strengths and the interplay of different subsystems.

For a long time there was, however, one major hurdle holding back time-resolved studies of solid state systems: Many intrinsic timescales in solids, for example timescales associated with vibrational motion of lattice atoms or electron-phonon equilibration times, are located somewhere in the femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$) and picosecond regime ($1 \text{ ps} = 10^{-12} \text{ s}$). A rough overview of important timescales in a solid is given in Fig. 1.1. The figure puts an emphasis on processes connected to the ultrafast structural dynamics of a solid, but also gives examples of timescales related to other degrees of freedom in a solid.

With conventional sources of electromagnetic radiation, there was simply no experimental possibility to access these timescales since pulses of electromagnetic radiation with a short enough duration were not available. This problem was overcome with the introduction of mode-locked lasers [1] and the following advances in the generation of ultrashort laser pulses.
Chapter 1: Introduction to ultrafast solid state science

Today, ultrashort pulses spanning nearly the full electromagnetic spectrum from hard x-rays to terahertz (THz) radiation can be produced. In addition to using ultrafast methods as a spectroscopic tool to study nonequilibrium systems, it has become possible to use ultrafast pulses of electromagnetic radiation to manipulate and in some cases even coherently control the solid state. The possibilities to manipulate macroscopic material properties on a femtosecond timescale via ultrafast photoinduced transitions has become an important research field that will offer new possibilities with ever-improving sources of ultrafast radiation, with the newest addition to the ultrafast toolbox being x-ray free electron lasers.

At the heart of almost all ultrafast time-resolved studies lies the pump-probe approach, which is described in detail in the following section. The chapter continues with a discussion of different probe and pump methods and a possible classification of time-resolved experiments. In general, this chapter serves as a phenomenological introduction to the basic ideas behind time-resolved methods to study the solid state and the dynamics of the structure of a solid in particular. The generation of ultrashort pulses in relevant frequency ranges is discussed in detail later when more specific techniques and experimental settings, especially focusing on ultrafast structural dynamics, are discussed for the experiments conducted for this thesis work.

1.1 Accessing nonequilibrium physics using the pump-probe principle

Conventional measurement systems that are based on fast electronics, for example a photodiode signal read out by an oscilloscope, typically have response times exceeding tens of picoseconds. Using a pump-probe approach for time-resolved experiments eliminates this limitation given by detector timescales by utilizing two ultrashort pulses to conduct a measurement: First, the pump pulse excites the sample and triggers a transient change in its properties. The changes after

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1 In the following, an ultrashort pulse refers to a pulse with sub-picosecond duration.
1.1 Accessing nonequilibrium physics using the pump-probe principle

excitation are then measured by a second pulse, the probe pulse. The temporal delay between the two pulses is typically set by a delay stage inserted into either the pump or the probe branch, and varying the delay between the two pulses allows to record a time trace of the evolution of the material properties accessible with the probe pulse. The delay stage will change the length of the beam path and therefore the time of flight for a pulse passing it.

A schematic of a standard pump probe measurement is shown in Fig. 1.2. A schematic of a standard pump probe measurement is shown in Fig. 1.2.

![Schematic of a pump-probe experiment](image)

**Figure 1.2:** (a) Schematic of a pump-probe experiment. The pump pulse hits the sample and triggers a nonequilibrium process. The probe pulse arrives at an adjustable time delay $t$ and interacts with the excited sample. After interaction with the sample, the probe pulse is measured with a detector. (b) Recorded signal of a generic pump-probe experiment, where the pump induces a nonequilibrium state in the sample that relaxes back to the initial state. Different relaxation timescales can correspond to different scattering pathways back to equilibrium. The point when both pulses overlap is referred to as time zero ($t = 0$). When the probe pulse arrives first, negative time delays are assigned; when the pump pulse arrives first, time delays have positive values.

In a typical pump-probe measurement, the changes in properties of the probe pulse after interaction with an excited sample are so small that many pump-probe cycles have to be recorded to acquire a meaningful signal. For a cyclical measurement, the timescale of the transient change triggered by the pump pulse must be shorter than the temporal delay between successive pump-probe pulse pairs, since otherwise the probe pulse of later pump-probe pulse pairs will also record changes induced by earlier pump-probe pairs. Typically, a great number of pump-probe cycles are used for a measurement, relying on the fact that the relaxation process of the measured material property is identical after each excitation pulse.

The time resolution of a pump-probe measurement is determined by both pump and probe pulse duration as well as geometrical factors like the relative incidence angles of pump and probe pulses. If both pulses are derived from the same source, timing jitter between the two pulses can usually be neglected. It can, however, become important when for example stochastic processes are present in one of the branches or pump and probe pulses do not originate from a common source.

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2 A 1 µm flight path corresponds to a time delay of 3.33 fs.
3 In this context, timing jitter corresponds to the fluctuation in relative delay times between pump and probe pulses.
The first ultrafast pump-probe studies were carried out using an all-optical pump-probe scheme, where changes in reflectivity or transmission of the probe pulse after excitation are measured. Optical excitation often presents a very generic excitation method, where the energy of the pulses is dumped into the solid without allowing direct control of a specific degree of freedom.

One of the key strengths of the pump-probe approach lies in the fact that after wavelength conversion processes, widely different parts of the electromagnetic spectrum can be used for pump and probe pulses. This is of course connected to the technological challenge to produce ultrashort pulses in the required wavelength range, but nowadays even electron pulses with durations of close to 100 fs can be generated. An overview of important energy scales in solids is presented in Fig. 1.3.

Recent advancements in generation methods allow the time-resolved study of selective coupling of ultrashort pulses of electromagnetic radiation to certain elementary excitations or subsystems in a solid. In this thesis, which focuses on the ultrafast structural dynamics of solids, THz frequency pulses were employed to resonantly excite vibrational modes and femtosecond x-ray pulses were utilized to directly probe the structure of a solid. The generation of ultrashort pulses in these parts of the electromagnetic spectrum is explained in Chaps. 4 and 5. Using different wavelengths for pump and probe pulses leads to additional experimental challenges like penetration depth matching that often greatly complicates the experimental setting. Especially in the study of correlated systems, however, it provides the possibility to directly probe or pump a specific subsystem of a solid and gather vital information about the interaction of the different coupled degrees of freedom.

### 1.2 Classification of time-resolved methods

Pump-probe experiments can be conceptually classified by means of the magnitude of the applied excitation fluence and the resulting transient changes induced in the material. Possible
applications of ultrafast time-resolved methods range from linear spectroscopic measurements to the study of irreversible phase transitions induced by very intense laser pulses.

**Time-resolved linear spectroscopy** For linear spectroscopic measurements, typically a low excitation fluence that only results in a weak perturbation of the solid under study is chosen. The excitation pulse energy is kept low enough so that basic properties of the system, like frequencies and damping times of elementary excitations, closely resemble values in thermal equilibrium. Values measured in this class of time-resolved experiments are therefore assumed to correspond to results obtained via frequency-domain measurements. When analyzing low perturbation pump-probe measurements, it is usually assumed that coupling strengths can be compared to those present in the system in thermal equilibrium. The measured relaxation dynamics are then often used to gain insight about the equilibrium physics of the system.

A typical example of ultrafast time-resolved linear spectroscopy is THz time-domain spectroscopy, where changes to a THz-frequency pulse after interaction with a sample are detected via electro-optic sampling (see Chap. 5). The experiments on Tellurium presented in Chap. 6 are an example of time-resolved spectroscopy in the linear regime using a novel resonant excitation pathway to trigger structural dynamics.

**Ultrafast reversible photoinduced transitions** Utilizing a high fluence ultrashort pulse as a stimulus of a solid can induce an ultrafast transition to a transient state. It was, for example, shown that an ultrashort laser pulse can destroy broken symmetry ground states like superconductivity [2] or a charge density wave [3]. The created transient state after excitation often resembles the high-temperature phase of the material and can have lifetimes from a few picoseconds to several days [4]. The generation of these transient states has lead to the notion of a photoinduced ultrafast or nonthermal phase transition. It is, however, important to keep in mind that in principle all relevant properties of the transient state have to be measured and compared to the thermodynamic phase — for example, the complete melting the charge-density-wave ground state can only be confirmed by probing the electronic and the lattice subsystem. The use of the expression *nonthermal* often merely indicates that the transient state was not reached through a slow adiabatic transition but rather through the specific destruction of order in a certain subsystem of the solid. In some cases lower energies are required to reach a high-temperature phase than via simple heating of the system [3, 5], indicating that the system in fact does follow a trajectory not accessible in thermodynamic equilibrium.

A defining characteristic of a reversible photoinduced transition is the fact that the system relaxes back to the initial state without a permanent modification or damage to the sample, allowing for a cyclical study of this class of photoinduced transitions. Relaxation timescales observed in nonequilibrium states associated with an ultrafast phase transition can in some case shed light on the equilibrium physics of a system and help understand the origins of a specific macroscopic material property. Ultrafast phase transitions are however scientifically and
technologically interesting in their own right: They facilitate drastic changes of the properties of a solid on unprecedented timescales and for example carry the promise of revolutionizing the way data storage devices work.

The experiments on the charge-density-wave systems $K_{0.3}MoO_3$ and $4H_b-TaSe_2$ presented in this theses fall into this class of time-resolved studies.

**Ultrafast irreversible photoinduced transitions**  The obtainable peak intensities of laser pulses generated with amplified laser systems in tandem with tight focusing can be high enough for solid state samples to be permanently altered. This prevents the application of a cyclical pump-probe approach and pump-probe pairs have to hit the sample at a fresh spot for each time delay, effectively making it a single-shot technique. Using high excitation fluences, melting of the solid state was studied with time-resolved x-ray and electron diffraction [6, 7]. In a broader sense, also industrial material processing methods based on ultrashort laser pulses, like laser ablation or laser welding, fall into this category.
Chapter 2

Ultrafast structural dynamics in solids

The aim of this chapter is to introduce concepts on how the structure of a solid can be investigated and manipulated on ultrafast timescales using short pulses of electromagnetic radiation. The experiments on the structural dynamics of charge density wave systems and on tellurium presented later in this work rely heavily on the methods introduced in this chapter.

Traditional spectroscopic methods that operate in the frequency domain, like static Raman scattering and inelastic neutron scattering, have become indispensable tools to study phonons in solids in thermal equilibrium. Methods based on extremely short pulses of electromagnetic radiation now allow for completely new ways to manipulate the structure of a solid on ultrafast timescales: While frequency domain methods are based on the interaction of light or particles with phonons with arbitrary phase, ultrafast excitation of solids allows to create completely new states of matter. One important example is a so-called coherent phonon, a peculiar state of a structure where all atoms in a macroscopically big volume take part in a concerted, in-phase motion. Another example concerns the structural symmetry of a solid: When changes of structural symmetry accompany an ultrafast phase transition, ultrafast techniques allow to manipulate structural symmetry and investigate changes in symmetry on a femtosecond timescale. Since changes of a structure can only be promoted via normal modes of the lattice, ultrafast changes of structural symmetry are intrinsically linked to coherent phonons.

The chapter is organized as follows. First, a few notes on possible scattering channels between electromagnetic radiation and phonons are given and the most important selection rules for photon-phonon interaction processes are listed. One of the key advantages of ultrafast structural spectroscopy is the possibility to use pulses of electromagnetic radiation containing completely different spectral components for pump and probe pulse, allowing for a separate discussion of the generation and detection methods of a coherent phonon in the following sections. The chapter concludes with a discussion of incoherent modulations of the structure after excitation with an ultrafast laser pulse and how they can be measured using diffraction-based techniques.
2.1 Interaction of electromagnetic radiation and phonons

In this short section, the main selection rules that apply for the interaction between light and photons are shortly reviewed. As an example of a phonon spectrum of a simple structure (that also has some relevance to this work), Fig. 2.1 shows calculated phonon dispersion curves of tellurium. Tellurium has three atoms per unit cell, and as a result three acoustic modes (whose energy $\hbar \omega(q = 0) = 0$), as well as six optical modes. Any scattering process of electromagnetic radiation with photon energy $\hbar \omega$ and phonons naturally has to adhere to energy and momentum conservation. The two fundamental ways through which light can couple to lattice vibrations that are exploited in this work in an ultrafast setting are (1) via a Raman process and (2) via resonant coupling to a polar mode. In the following, only scattering processes that involve one phonon only are considered. Processes that rely on anharmonic phonon coupling are described in section 2.2.3.

(1) Raman scattering A Raman process relies on the change of polarizability associated with an atomic displacement $Q$ along the normal coordinate of a phonon. Written in terms of the electronic susceptibility $\chi$, this implies that $\partial \chi / \partial Q \neq 0$ for a mode to be Raman active. In a conventional Raman spectroscopy experiment, the wavelength of a re-emitted photon after an inelastic scattering event of a monochromatic laser beam with a phonon is measured. In an experiment utilizing broadband radiation like ultrafast laser pulses, phonons with wave vector $q_{\text{phonon}}$ and frequency $\omega_{\text{phonon}}$ can be generated from two photons with slightly different energies contained in the spectrum of the pulses. In both cases, energy and momentum conservation have to be conserved:

$$\hbar q_{\text{photon},1} - \hbar q_{\text{photon},2} = \hbar q_{\text{phonon}} \quad (2.1)$$

$$\hbar \omega_{\text{photon},1} - \hbar \omega_{\text{photon},2} = \hbar \omega_{\text{phonon}} \quad (2.2)$$

where $\hbar q_{\text{photon},1}$ and $\hbar q_{\text{photon},2}$ are the photon momenta before and after the scattering event;
\( \hbar \omega_{\text{photon},1} \) and \( \hbar \omega_{\text{photon},2} \) are the photon energies before and after the scattering event. Frequencies of optical lattice vibrations typically lie in the THz range, in the example of Te they roughly range between \( 2 - 5 \) THz (see Fig. 2.1). A difference of 3 THz for photons corresponds to a change in wave vector \( q_{\text{photon},1} - q_{\text{photon},2} = 10^{-6} \text{ Å}^{-1} \). Relevant values of reciprocal lattice vectors are however of order \( 1 \text{ Å}^{-1} \). As a result, only a very small region of the dispersion curve can be accessed, effectively limiting phonons that can be studied or excited with a Raman process to \( q = 0 \) phonons. Raman scattering of photons from zone-center acoustical modes is also possible and typically referred to as Brillouin scattering.

(2) Resonant coupling Resonant coupling to a phonon mode is only possible if a dipole moment is associated with the atomic displacement along the phonon coordinate — making it a so-called infrared-active mode.

Unlike in a first-order Raman process, where the energy difference of two photons corresponds to the phonon energy, in a resonant process the energy of one photon directly matches the phonon energy, \( \hbar \omega_{\text{photon}} = \hbar \omega_{\text{phonon}} \). Again, only \( q = 0 \) modes can be directly excited: The wavelength of THz-frequency radiation is on the order of 100 µm, much larger than any unit cell in a crystalline solid.

2.2 Generation of coherent phonons

A coherent phonon represents a fundamentally new state of the structure of a solid that cannot be described as a thermodynamic equilibrium state: In thermodynamic equilibrium, the population of phonons is governed by a temperature-dependent Bose distribution, and there are no phase relations between the oscillations of atoms in different unit cells. This is different for a coherent phonon: Atoms move in-phase along a certain normal coordinate of the lattice with a specific wave vector, corresponding to a macroscopic population of a specific phonon mode. While the term coherent phonon might be a bit inappropriate and it could maybe more aptly be called a coherent state of the crystal lattice, coherent phonon has become the accepted term in the literature.

The two ways in which lattice modes can couple to light described in the previous section can both be exploited to generate a coherent phonon, while an indirect excitation via anharmonic coupling of phonon modes or scattering processes involving more than one phonon are also possible.

In a phenomenological picture, a coherent phonon can in many cases be treated classically as a damped harmonic oscillator driven by a force specific to the excitation mechanism. In the following, heavy use of this phenomenological picture is made, but the connection to a quantum mechanical description is also shortly presented.

\footnote{By the same logic, radiation of a LASER could be called a coherent photon.}
2.2.1 Ultrafast stimulated Raman scattering

Terahertz frequency optical coherent phonons in solids were first observed in experiments utilizing femtosecond light illumination of semiconductors and employing a standard pump-probe scheme [9]. Transient changes in electronic susceptibility following absorption of above-bandgap laser pulses were monitored by measuring the time evolution of the intensity of a reflected or transmitted probe beam. In addition to modulations related to carrier relaxation processes, superimposed oscillatory signals could be observed. The frequency of these oscillations were found to match frequencies of Raman active $q = 0$ phonon modes. Reviews describing the first demonstrations of coherent phonon generation can for example be found in [10, 11]. After these first experiments, it was quickly realized that THz coherent phonons can be generated in a variety of solids, provided that the laser pulse duration is shorter than the period of the lattice vibration and Raman selection rules are fulfilled. Terahertz frequency coherent phonons have been observed with standard pump-probe techniques in a wide variety of materials, including semimetals [9, 12, 13], semiconductors [14], metals [15] and transparent materials, as well as strongly correlated materials like superconductors [16] and CDW systems [17].

As a starting point for a phenomenological description of a coherent phonon, we can describe the macroscopically coherent motion along a certain phonon coordinate $Q(t)$ (to that effect, $Q(t)$ can be seen as the amplitude of the coherent phonon) by [18]

$$\frac{\partial^2 Q(t)}{\partial t^2} + 2\gamma \frac{\partial Q(t)}{\partial t} + \omega_q^2 Q(t) = F(t)/\mu \quad (2.3)$$

Here, $\omega_q$ is the angular frequency of the lattice mode and $F(t)$ corresponds to a driving force, $\mu$ corresponds to the reduced mass of the mode and $\gamma$ represents a phenomenological damping constant. A similar expression can be derived starting with the full Hamiltonian of the coupled electron-lattice system [18]. Comparing the results to the phenomenological approach implies that $Q(t)$ is closely related to the coherent amplitude of a phonon with wavevector $q$, defined as $D_q = \langle b_q \rangle + \langle b^\dagger_{-q} \rangle$, where $b_q$ and $b^\dagger_{-q}$ are phonon creation and annihilation operators.

A coherent phonon corresponds to the case where the phonon population of a certain mode becomes macroscopically large. In this case, the motion along that particular phonon coordinate can be treated classically, justifying the application of the equation of motion given in Eq. 2.3. The creation of a coherent phonon is based on the coupling of lattice vibrations to electronic states that are excited by spectral components of the broadband femtosecond laser pulse - a concept widely known as impulsive stimulated Raman scattering [19]. The driving force $F(t)$ and the phase of the resulting coherent motion $Q(t)$ depend on the lifetime of excited electronic states. In the following, limiting cases corresponding to different lifetimes are described in detail. The different limiting cases are also presented in Fig. 2.2.

In transparent media, where the bandgap is larger than the photon energy of the excitation pulse, the coupling to vibrational states occurs via short-lived virtual electronic states (see Fig. 2.2 (a)). In these media, the imaginary part of $\varepsilon$ is negligible and the driving force can be
written as \[^{20}\]
\[ F \propto \sum_{u,v} (\partial \chi_{uv}/\partial Q) E_u E_v \quad (2.4) \]

where \( \chi_{uv} \) is the linear susceptibility, \( (\partial \chi_{uv}/\partial Q) \) corresponds to the nonlinear Raman tensor. \( E_u \) and \( E_v \) are components of the pump pulse field. For small pump pulse durations, \( F(t) \propto |E(t)|^2 \) becomes an impulsive force and leads to \( Q(t) \propto \sin(\omega_p t) \) oscillations.

In absorbing media light can couple to real, long-lived electronic states. The driving force then calculates to (for a full semiclassical treatment, see \[^{19}\]) \( F(t) \propto \int_{-\infty}^{t} E(t')^2 dt' \), which is displacive in nature and results in \( Q(t) \propto 1 - A \cos(\omega_q t) \) oscillations with amplitude \( A \). This limiting case corresponds to the displacive excitation of coherent phonon (DECP) model first introduced by Zeiger \[^{21}\]. The equilibrium positions of lattice atoms depend on the electronic state, after excitation new transient equilibrium positions \( Q_t \) will exist. Lattice atoms will move towards these transient equilibrium positions and start oscillating around the new, displaced, equilibrium positions. In real media, the phase of the oscillation \( Q(t) \) can obtain values between these two limiting cases. The two limiting cases can both be described in the same theoretical framework \[^{19}\].

In a lot of materials, the relaxation time of initially excited high energy electronic states to a transient nonequilibrium state is shorter than the vibrational period of phonon modes. If the transient lattice equilibrium positions in the nonequilibrium state are different from equilibrium positions, this can lead to fully symmetric displacively excited coherent phonons.

An advanced level of coherent control of a structure based on an ultrafast Raman process can be achieved with the use of multiple pump pulses. This method is presented in detail in the description of the double-pump experiments on \( K_0.3 \text{MoO}_3 \) in Chap. 8.

### 2.2.2 Resonant coupling to polar phonon modes

Recent advances in the generation of intense picosecond THz frequency electromagnetic pulses (see Chap. 5) with significant spectral components in the THz range have facilitated the resonant excitation of large-amplitude coherent phonons in solids. The field of THz frequency electromagnetic radiation can directly couple to IR active optical phonon modes at the Brillouin zone center. Since phase-stable THz pulses can be generated, resonantly driven coherent phonons can be detected phase-resolved by standard time-resolved methods. In the case of resonant coupling, the driving force of the coherent phonon in Eq. 2.3 can be identified with the THz field transmitted into the crystal:

\[ F(t) \propto E_{\text{THz}}(t) \quad (2.5) \]

Figure 2.3 shows a schematic of a resonantly excited coherent phonon. One of the goals of this thesis is the demonstration of coherent phonon spectroscopy using resonant THz excitation, which is presented in Chap. 6. The coupling of the polarization induced by a polar lattice mode
Chapter 2: Ultrafast structural dynamics in solids

Figure 2.2: Generation of a coherent phonon via ultrafast Raman scattering triggered by a laser pulse with a pulse duration shorter than the vibration period of the $q = 0$ phonon mode for different excited state lifetimes. (a) Impulsive limit. Spectral components of the excitation pulse couple to a virtual state, resulting in $Q(t) \propto \sin(\omega_p t)$ oscillations. The classical analog is a pendulum pushed out of the equilibrium by a $\delta$-like force. (b) Displacive limit. The excited state is real and long-lived, the transient lattice equilibrium positions can either be induced by the excited state (left) or after subsequent electronic relaxation processes (right).

Figure 2.3: Resonant excitation of an IR active phonon mode by a THz frequency pulse. The red line corresponds to the electric field of a THz-frequency electromagnetic pulse, the black line corresponds to the simulated lattice response. Since in this case no free carriers are created by the below-bandgap THz radiation, the equilibrium position $Q_0$ does not change after excitation. This situation is similar to the impulsive limit of ISRS, although the resonant driving process makes it possible to drive larger amplitude coherent phonons (for an experimental realization, see Chap. 6).
associated with a displacement \( Q(t) \) and the electronic polarization \( P \) can be determined by a set of coupled equation (see for example \[22\]).

There are also methods of coherent phonon generation that rely on the creation of an electromagnetic field with THz spectral components by a femtosecond laser pulse in the solid itself. The created field couples to polar lattice vibrations in the solid. Examples include surface field screening effects in GaAs \[22\] and the ultrafast build-up of a Dember field in Te \[23\]. With these methods IR active LO phonon modes can be coherently excited, but (like for experiments based on ISRS) the excitation process is accompanied by the generation of a highly nonequilibrium electronic system.

### 2.2.3 Anharmonic coupling and two phonon processes

A completely different way to coherently excite a phonon can be realized by exploiting anharmonic coupling of phonons. Conceptually, this can be regarded as a two-step process: A Coherent phonon is excited via an ultrafast Raman process or resonant coupling. The coherently excited phonon in turn couples to another lattice mode via anharmonic phonon-phonon coupling.

One example of such a process is given by ionic Raman scattering: A resonantly excited phonon (amplitude \( Q_{IR} \)) effectively acts as a driving force for Raman active mode via anharmonic coupling. The equation of motion in this case reads \[24\]

\[
\frac{\partial^2 Q(t)}{\partial t^2} + 2\gamma \frac{\partial Q(t)}{\partial t} + \omega_q^2 Q(t) = AQ_{IR}^2
\]

where \( A \) represents an anharmonic coupling constant. This excitation mechanism could be observed in a manganite, where resonant excitation of an infrared active \( E_u \) mode lead to coherent oscillations of a Raman active \( E_g \) mode \[24\].

In processes involving more than one phonon, it is possible to coherently excite modes at wave vectors \( +\vec{q} \) and \( -\vec{q} \), lifting the restrictions of the selection rules applying for one-phonon processes. This for example was exploited to map parts of the transverse acoustic phonon dispersion over large sections of the Brillouin zone in Germanium \[25\] \[26\].

### 2.3 Detection of coherent phonons

There are several ways to study amplitude and phase of coherent phonons using time-resolved techniques. Fundamentally, detection methods can be divided into two different approaches: \textit{Indirect} methods are based on measuring the time-resolved changes of physical properties of a solid that are modulated by a lattice displacement \( Q(t) \) along a certain phonon coordinate. Examples include time-resolved Raman techniques, time-resolved angular resolved photoemission \[27\] \[28\] and emission of THz frequency radiation by phonon-polaritons \[23\]. \textit{Direct}, diffraction-based methods rely on imaging lattice atom coordinates using pulses of radiation or particles with (de Broglie) wavelengths comparable to interatomic distances. Indirect and direct methods offer
distinct advantages and disadvantages and can give complementary information. One of the principal benefits of diffraction based techniques is the ability to gain quantitative information of the coherent lattice displacement.

In the following two methods of coherent phonon detection are discussed: Ultrafast Raman spectroscopy as an indirect and ultrafast x-ray diffraction as a direct time-resolved measure of coherent phonons. To first order, both of these methods are limited to the study of Raman active modes.

2.3.1 Time-resolved Raman spectroscopy

For Raman-active modes, the dielectric susceptibility depends on the lattice displacement \( Q(t) \) along a certain phonon coordinate. To first order in \( Q(t) \), the reflectivity change \( \Delta R(t) \) (or analogously the transmission change) associated with a displacement \( Q(t) \) can be expressed as

\[
\Delta R(t) \propto \vec{E}^r (\partial \chi / \partial Q) \vec{E} Q(t)
\]

Here, \( \vec{E} \) corresponds to the incident and \( \vec{E}^r \) to the reflected probe field. With sufficiently short probe pulses, \( \Delta R(t) \) can be temporally resolved. For fully symmetric phonon modes, the Raman tensor \( \partial \chi / \partial Q \) contains only diagonal elements. In general, the symmetry of the Raman tensor corresponds to the point group representation of a lattice vibration, some examples for coherent phonons observed in solids are given in [29]. For non-fully symmetric modes, the Raman tensor contains off-diagonal elements. \( E \)-modes in Te are for example described by

\[
(\partial \chi / \partial Q) = \begin{pmatrix}
c & 0 & -d \\
0 & -c & 0 \\
-d & 0 & 0
\end{pmatrix}
\]

To separate the (in most cases much stronger) contribution of fully symmetric modes from the signal associated with non-fully symmetric modes, the anisotropic reflectivity changes can be measured. In a geometry very similar to electro-optic sampling, the difference

\[
\Delta R = \Delta R_1 - \Delta R_2 \propto \vec{E}_1^r (\partial \chi / \partial Q) \vec{E} Q(t) - \vec{E}_2^r (\partial \chi / \partial Q) \vec{E} Q(t)
\]

of two orthogonal polarization channels is measured. Changes of the reflectivity associated with diagonal components of the Raman tensor thus cancel out.

Properties of coherent phonons like phase (with respect to the excitation pulse), damping, frequency chirp etc. can be measured with great sensitivity using time-resolved Raman spectroscopy. In various cases, coherent phonon spectroscopy can even surpass traditional Raman scattering in terms of dynamic range and frequency resolution [30, 31]. However, it is extremely difficult to obtain quantitative information of the magnitude of amplitude of a coherent phonon using a probe based on time-resolved Raman spectroscopy.
2.3.2 Time-resolved diffraction methods

During the last decade, it has become possible to create extremely short pulses of x-rays and electrons using a variety of methods that are based on femtosecond laser pulses (see Chap. 4). Interatomic distances in solids can now be probed with a time resolution short enough to resolve coherent optical phonons in solids.

The following discussion is limited to $q = 0$ phonons, which can be excited using one of the generation methods described above. The basic principles of static x-ray diffraction are presented in the appendix A.3.

For zone-center phonons, the movements of atoms in all unit cells in a solid are the same. The coherent motion of atoms $\mathbf{Q}(t)$ along the eigenvector $\mathbf{e}_m$ of a Raman-active mode leads to a time-dependent modulation of the unit cell structure factor $S_{hkl}^0$,

$$S_{hkl} = \sum_j f_j e^{i\mathbf{G} \cdot (\mathbf{r}_{0,j} + \mathbf{Q}(t)e_m)}$$

(2.10)

where the summation includes all $j$ atoms of the unit cell with atomic scattering factors $f_j$ and $\mathbf{r}_{0,j}$ are the equilibrium positions of atoms in the unit cell. In a kinematic approximation (see A.3), the measured x-ray intensity for a certain reciprocal lattice vector $\mathbf{G}$ can be connected to the structure factor via $I_{hkl} \propto |S_{hkl}|^2$. The relative measured change in diffraction intensity (normalized to the equilibrium value)

$$\Delta I_{hkl}(t) = \frac{\left| \sum_j f_j e^{i\mathbf{G} \cdot (\mathbf{r}_{0,j} + \mathbf{Q}(t)e_m)} \right|^2 - 1}{\sum_j f_j e^{i\mathbf{G} \cdot \mathbf{r}_{0,j}}^2}$$

(2.11)

can now be used to compare calculated values of $\Delta I_{hkl}(t)$, assuming a particular displacement amplitude $\mathbf{Q}(t)$, to measured values. If only one mode is excited, this directly leads to the amplitude of the coherent motion along a certain coordinate. If more than one mode are excited, a sufficiently large set of reflections needs to be measured to gain complete knowledge of all atom positions in a unit cell [32] or to at least exclude that specific modes contribute to the coherent motion [33].

The choice which diffraction peaks is measured to characterize a certain mode depends on the magnitude of change in $\Delta I_{hkl}(t)$ for an oscillation along $\mathbf{e}_m$. An example of the influence of atomic displacement along the coordinate of the optical $A_{1g}$ phonon in bismuth on the intensity of different diffraction peaks is given in Fig. 2.4. Owing to the dot product in Eq. 2.10, atomic motions occurring parallel to the diffraction planes will not affect $\Delta I_{hkl}(t)$.

Terahertz frequency coherent optical phonons have been studied in a host of different materials with time-resolved x-ray diffraction, utilizing plasma sources [34], slicing sources [35, 32] and x-ray free electron lasers [36, 37].

The study of THz coherent phonons with ultrafast electron diffraction offers the distinct
advantage of observing a great many diffraction peaks at the same time, owing to the larger
momentum transfer made possible by high-energy electrons. The time resolution of ultrafast
electron diffraction setups is however at this point not sufficient to resolve higher frequency THz
coherent phonons.

Figure 2.4: Example of the changes in structure factor in Bi for different diffraction conditions,
taken from [34]. After excitation, the system oscillates around perturbed equilibrium
positions, resulting in a change with different sign of $|S(h,k,l)|^2$ for the (111) and
the (222) reflection, respectively.

2.4 Comparison of transient structural modulations

In-phase motion of atoms, synchronized over many unit cells, naturally is only a very specific part
of transient structural changes that can be triggered by an ultrafast laser pulse. Typically, a laser
pulse first induces a highly nonequilibrium state in the electron system. Through electron-phonon
coupling, the energy is then transferred to the lattice, resulting in a transient nonequilibrium
population of the phonon system. Different changes to the structure after excitation can be
classified by their respective changes to the unit cell structure factor $S^{hkl}$, the size of unit
cells in excited volumes of the sample and the timescale inherent to the structural changes.
Again, experiments relying on optical or other indirect probes of the structure only give limited
information about these changes of the structure.

Figure 2.5 shows sketches of different transient changes of the lattice of a solid that can be
induced by a pump pulse, as well as their qualitative impact on the rocking curve in a diffraction
experiment.\footnote{A rocking curve corresponds to a scan of the $\omega$-angle in a standard 3- or 4-circle diffractometer (see for example [38] for angle definitions). In a grazing diffraction geometry often utilized in time-resolved diffraction
measurements (see Sec. 4.2), similar cuts through the Ewald sphere can be obtained by rotating the sample around}
2.4 Comparison of transient structural modulations

Coherent phonon As shown in Sec. 2.3.2, a $q = 0$ coherent optical phonon results in a modulation of the unit cell structure factor. For a $q \neq 0$ phonon, additionally an oscillatory signal can be observed for scattering vectors $\vec{Q} = \vec{G} \pm \vec{q}$.

Transient strain The initial temperature increase leads to a sudden expansion of the excited volume, which in combination with the boundary condition given by the sample surface results in a longitudinal strain wave propagating into the material \(^{[39]}\). As a result, the size of unit cells and thus the translational symmetry of a solid will vary along its surface normal, leading to a modulation in reciprocal lattice vectors $\vec{G}$. Consequently, the diffraction peaks shifts to a slightly different positions. Since a strain wave corresponds to a superposition of acoustic phonons, associated timescales are determined by the longitudinal sound velocity in the solid. Typically, the temperature increase in the lattice is promoted through the electron system. However, a direct excitation of the lattice and the following anharmonic decay processes can also lead to the generation of strain waves (see Chap. \(^{[6]}\)).

Incoherent phonon population A sudden increase in temperature after photoexcitation leads to an increase in incoherent phonon population. As the introduced energy has to be transferred to the lattice from the electronic system via electron-phonon scattering, the timescale of this effect is governed by electron-phonon relaxation times. An increased lattice temperature leads to (1) an increase in diffuse scattering away from Bragg reflections and (2) a decrease of diffraction efficiency that is determined by the Debye-Waller factor (see Sec. \(^{[A.3]}\)). To completely

* its surface normal; the exact direction of the cut in reciprocal space is determined by diffraction geometry and sample orientation.
quantify the Debye-Waller-contributions to the reduction in diffraction efficiency for a specific Bragg peak, several Bragg peaks with different $\vec{Q}$ have to be characterized. With pulses from synchrotrons and free electron lasers, it has become possible to also study inelastic scattering from phonons created by the excitation pulse, allowing to study nonequilibrium phonon populations [40] and even phonon dispersion [25] in time-resolved diffuse scattering experiments.

**Domain creation** In materials with a broken symmetry ground state, photoexcitation can lead to the creation of domains with varying phase of the order parameter. Subsequent domain dynamics typically take place on a nanosecond timescale. Changes in the correlation length $\xi$ owing to changes in domain size and distribution result in a decrease of the maximum value of a diffraction peak, as well as a broadening of the measured diffraction peak, provided that the peak width is not determined by the instrument resolution. The width of the peak is determined by $\Delta h \propto 1/\xi$. The exact proportionality constant depends on the domain distribution, but can typically assumed to be less than 2 [41].

### 2.5 Ultrafast phase transitions and structural symmetry

In many correlated systems, a change of structural symmetry is associated with a broken symmetry ground state. By melting the low-temperature phase with an ultrafast pump pulse, the structural symmetry of a solid can thus change on a sub-picosecond timescale. Ultrafast probes of the structural symmetry can again be of indirect or direct nature.

Since a change of structural symmetry results in new Brillouin zone dimensions, additional modes become accessible with $q = 0$ light pulses. The associated change in the spectrum of Raman-active $q = 0$ modes can be measured with all-optical pump-probe spectroscopy [3, 42]. This approach however becomes increasingly difficult when relevant modes are strongly damped and difficult to distinguish from purely electronic contributions to the signal.

A further consequence of a novel structural symmetry lies in the emergence of new diffraction peaks. These new peaks are often labeled *superlattice* (SL) diffraction peaks and can be linked to the underlying lattice by adding the modulation vector $\vec{q}_{\text{SL}}$ to existing reflections. The measured diffraction intensity of a SL peak at scattering vectors $\vec{Q} = \vec{G} + \vec{q}_{\text{SL}}$ is a direct probe of the transient symmetry of a material and phonon modes that connect the low and the high symmetry phase modify the SL peak efficiency. Ultrafast changes in structural symmetry have been studied with time-resolved x-ray or electron diffraction of SL peaks in numerous correlated materials [43, 44, 5, 37]. The time-resolved measurements presented in this work explore the coherent atomic motion during a photoinduced symmetry-breaking transition (see Chaps. 7 and 8).

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[3] If the correlation length increases after photoexcitation, the diffraction peak width can of course also decrease.
Chapter 3

Strongly correlated electron systems and the charge-density-wave ground state

This chapter gives a brief introduction into the general phenomenology of strongly correlated electron systems, before discussing the physics of the charge-density-wave ground state in detail. Fermi-nesting driven charge-density-wave formation as described within the Peierls picture is explained in detail and the theoretical predictions are compared to experimental findings in the quasi-one-dimensional charge-density-wave compound K_{0.3}MoO_3 and the quasi-two-dimensional system 4H_{11}-TaSe_2.

3.1 Introduction to strongly correlated electron systems

The macroscopic electronic properties of a solid depend on the wavefunctions of electrons of neighboring atoms, and to what extent they overlap. Core electrons are typically not interesting for emerging properties of a solid since they are localized and do not contribute to the macroscopic material properties — interesting phenomena depend on electrons close to the filling level of electronic states, constituting the Fermi surface of a solid. The electronic band structure close to the Fermi surface and the interaction of electrons with the lattice will determine the macroscopic electronic properties of a solid — for example whether a solid is an insulator or a metal.

Conceptually, solids can be very crudely classified into simple materials and strongly correlated materials. In simpler materials, often a single particle description is sufficient to capture, to first order, the main electronic properties. The properties of simple metals and semiconductors can for example be explained in this framework.

There are, however, solids whose macroscopic properties can not at all be explained by using the single particle description. These materials show fascinating and both scientifically and technologically interesting phase transitions to ground states that exhibit phenomena
like superconductivity, charge-density-waves and multiferroicity. For these materials, simple theoretical approaches fall short and theories including correlation effects and more subtle interactions between the lattice, the electronic system at the Fermi level and the spin system have to be included. All these systems have in common that the Fermi surface crucially depends on interactions in the system. These materials are typically termed strongly correlated systems.

In ground states of strongly correlated systems, below a transition temperature $T_c$ new types of order emerge that are not present in the high-temperature phase. For this reason, the ground states of correlated systems are often referred to as broken symmetry ground states. Examples of symmetry breaking order include spin order and the resulting macroscopic magnetization in a ferromagnet or the periodic lattice distortion in a charge-density-wave compound. The breaking of symmetry can also be of a more subtle nature, exemplified by the breaking of gauge symmetry in a superconductor.

To this day, important broken-symmetry ground states like high-temperature superconductivity are not fully understood. Charge-density-wave compounds present an important class of correlated materials that often serve as model systems for solids whose macroscopic properties are determined by strongly coupled degrees of freedom.

### 3.2 Theory of the charge-density-wave ground state

The notion *charge density wave* (CDW) describes a static periodic modulation of the charge density in the conduction band in a solid. The CDW ground state is furthermore characterized by the emergence of a gap in the electronic density of states around the Fermi energy, making the CDW ground state isolating.

Theoretically, the existence of a periodic charge modulation in a one-dimensional gas of free electrons was first predicted by Peierls, although he himself initially did not believe that such a transition could actually be observed in a real solid. The term charge density wave was actually introduced by Fröhlich, who studied the thermodynamic transition to the CDW state in a system where electrons couple to the lattice via Coulomb interactions, additionally leading to a periodic lattice distortion (PLD).

Since these early theoretical considerations, transitions to CDW ground states have been experimentally observed in numerous metals with reduced dimensionality at the Fermi surface. Initially, most of these materials had been classified as systems exhibiting a Peierls transition, but during the last decade it has become increasingly clear that the simple Peierls picture cannot fully explain most of the transitions occurring in real materials. Nevertheless, the Peierls picture is still the essential starting point for an understanding of the main features of the CDW ground state and is presented in Sec. 3.2.1. The time resolved x-ray diffraction studies presented in Chaps. 7 and 8 were carried out on $K_{0.3}MoO_3$, a compound that is widely regarded as a prototypical Peierls insulator. This particular system is discussed in Sec. 3.3.1 and compared to the theoretical predictions of the Peierls picture.
3.2 Theory of the charge-density-wave ground state

3.2.1 Fermi-surface nesting and the Peierls transition

Reducing the effective dimensionality of a system can have dramatic effects on its properties, as fluctuations become more important and small perturbations to the system can lead to drastic changes to the ground state of the system.

It was first noted by Peierls that for a gas of free electrons, reducing the dimensionality leads to a $T = 0$ broken symmetry ground state when a small external perturbation is present. In the following, we discuss the characteristics of this broken symmetry ground state and how they can be connected to the structure of the Fermi surface.

In linear response theory, the induced charge density $\rho_{\text{ind}}$ in the presence of a particular perturbation potential $\phi(\vec{q})$ can be written as:

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

If $\chi(\vec{q})$ diverges at a specific wave vector $\vec{q}$, even a weak perturbation potential $\phi(\vec{q})$ will lead to a periodic modulation of the charge density $\rho_{\text{ind}}$, resulting in a CDW.

The response function $\chi(\vec{q})$ for a free electron gas in $d$ dimensions is called the Lindhard susceptibility. It can be calculated applying first-order perturbation theory and reads [45]

$$\chi(\vec{q}) = \int \frac{d^d k}{(2\pi)^d} \frac{f(E_k) - f(E_{k+q})}{E_k - E_{k+q}}$$ (3.2)

Here, $f(E_k)$ is the Fermi function and $E_k$ the energy of an electron with wave vector $k$. This expression already makes it evident how the Fermi surface must be structured for $\chi(\vec{q})$ to become very large: There have to exist many states for which $E_k \approx E_{k+q}$, and for these states, $f(E_k) \neq f(E_{k+q})$, implying that $\vec{q}$ must span from an occupied to an unoccupied state. These conditions can be fulfilled if large parts of the Fermi surface are parallel to each other. The vector connecting these parallel parts of the Fermi surface is accordingly called the Fermi nesting vector.

The Fermi surfaces of a strictly one-dimensional system and a two-dimensional system are shown in Fig. 3.1, showcasing perfect nesting for $q_{\text{CDW}} = 2k_f$ for the one-dimensional case. Perfect nesting results in a divergence in $\chi(q)$ at $q = 2k_f$, and as mentioned above, the system becomes inherently unstable to the formation of a periodic charge modulation when a perturbation with Fourier components at $2k_f$ is introduced.

The topology of the Fermi surface for the two-dimensional free electron gas does not allow for a common nesting vector, and as a result the two-dimensional Lindhard response only shows an anomaly at $2k_f$. In a quasi-one-dimensional system, where the dispersion is small in only one direction, large pockets of the Fermi surface that show good nesting are still possible. An actual example in a real system is shown in Fig. 3.7 as part of the discussion of the quasi-one-dimensional system $K_{0.3}$MoO$_3$. A classical example that introduces the lattice is given by a linear chain of equally spaced atoms (spacing $a$), coupled to non-interacting electrons in the conduction
band of a metal. Above $T_c$, electronic states are filled up to the Fermi energy $E = (\hbar^2 k_f^2)/(2m)$. Assuming a half-filled conduction band, below $T_c$ the instability of the electronic system at $2k_f$ introduces a periodic lattice distortion with period $2a$. Consequently, the Brillouin zone size reduces from $k_f/a$ to $k_f/(2a)$ and an energy gap $2\Delta$ forms in the electronic states. The gap reduces the energy of the electronic system, since occupied states just below the Fermi surface are lowered in energy. The discussion using this simplified example gives some basic characteristics of a lattice coupled to an electronic band with reduced dimensionality. The natural question that arises now is whether the anomaly in $\chi(q)$ in an actual metal with reduced dimensionality is large enough to cause a transition to a broken symmetry ground state with a CDW below a certain transition temperature $T_c$, or put another way, if there are temperatures for which the energy associated with the formation of a gap in the electronic system is larger than the energy associated with the formation of a periodic lattice distortion. To answer this question,
3.2 Theory of the charge-density-wave ground state

Figure 3.2: Comparison of the conduction band and the lattice positions in the metallic state ($T > T_c$) and the CDW state ($T < T_c$) for a half-filled band coupled to a lattice with lattice constant $a$. 

(a) Above $T_c$, the dispersion corresponds to a free electron gas. Below $T_c$, a gap opens at $k_f$, lowering the energy of occupied states close to the Fermi energy. 

(b) Electron density (lines) and lattice ion (spheres) positions. Below $T_c$, a periodic modulation develops in both coupled subsystems, the unit cell size increases to $2a$. 

(c) Schematics of the free energy in the metallic and the CDW state.

The coupling of the electronic system to the lattice has to be considered in a more precise way, so that predictions of theory can be compared to experiments.

3.2.2 Mean-field theory and the charge-density-wave ground state

A one-dimensional free electron gas interacting with lattice displacements was first discussed by Fröhlich [46], with the goal in mind to describe the formation of a superconducting condensate in a one-dimensional system. He started from the Hamiltonian considering a coupled electron-lattice system:

$$H = \sum_k E_k a_k^\dagger a_k + \sum_q \hbar \omega_q b_q^\dagger b_q + \sum_{k,q} g a_k^\dagger a_{k+q} \left( b_q^\dagger + b_q \right)$$  \hspace{1cm} (3.3)
Chapter 3: Strongly correlated electron systems and the CDW ground state

It includes the following terms:

(1): Energy of the electronic subsystem with creation and annihilation operators of electrons with energy $E_k$, $a_k^\dagger$ and $a_k$

(2): Energy of the lattice subsystem with creation and annihilation operators of phonons with energy $h\omega_q$, $b_q^\dagger$ and $b_q$

(3): Coupling of the two subsystems with a dispersionless electron-phonon coupling constant $g$.

Assuming a divergence of $\chi$ at $2k_f$ and using a mean field approximation, several properties of the transition to a CDW ground state can be derived from the Fröhlich-Hamiltonian:

**Periodic lattice distortion and Kohn anomaly**  The coupling of the unstable electronic system to the lattice leads to a renormalization of phonon frequencies. The renormalization is most prominent for phonon wave vectors at $2k_f$. The renormalized dispersion relation of an acoustic phonon branch is shown in Fig. 3.3, the softening around $2k_f$ is called Kohn anomaly. A mean field (MF) transition temperature $T_{c}^{\text{MF}}$ to a state with a static periodic lattice can be defined for when the phonon frequency at $2k_f$ goes to zero. Below $T_{c}^{\text{MF}}$, the mode becomes macroscopically populated and a complex order parameter of the CDW state can be defined by

$$
|\Delta| \exp(i\phi) \propto \left( \langle b_{2k_f} \rangle + \langle b_{-2k_f}^\dagger \rangle \right)
$$

(3.4)

![Figure 3.3: Renormalized Dispersion of an acoustic phonon branch at the mean field transition temperature for a strictly one-dimensional free electron gas coupled to the lattice.](image)

**Single particle gap and condensation energy**  The dispersion of electrons in the conduction band is renormalized as well, resulting in a gap in the density of states near $\pm k_f$. The value of the full single-particle gap thus has a total gap energy $2\Delta$ around $E_f$ (see Fig. 3.2 (a) ).
The energy difference of the system between the metallic (ungapped) state and the CDW state is given by the condensation energy \[45\]

\[ E_{\text{con}} = E_{\text{metallic}} - E_{\text{CDW}} = \frac{n(E_f)}{2} \Delta^2 \]  

(3.5)

Here, \( n(E_f) \) corresponds to the normal state density of states at the Fermi energy \( E_f \).

**Charge density wave amplitude and phase**  The modulation of the charge density along the chain direction \( x \) is, in the weak coupling limit (\( \Delta \ll E_f \)), given by \[45\]

\[ \rho(x) = \rho_0 \left( 1 + \frac{\Delta}{\hbar v_f k_f \lambda} \cos(2k_f x + \phi) \right) \]  

(3.6)

Here, \( v_f \) is the electron velocity at the Fermi surface and \( \lambda \) is the dimensionless electron-phonon coupling constant.

Finally, the size of the gap is related to the mean field transition temperature by \[45\]

\[ 2\Delta = 3.52k_B T_{c}^{\text{MF}} \]  

(3.7)

where \( k_B \) is the Boltzmann constant. Remarkably, all defining characteristics of the CDW ground state are theoretically determined by the gap size \( \Delta \) and material constants, mainly related to the Fermi surface.

An intuitive picture of the transition to the CDW can be given with Landau theory. Close to \( T_c \), the free energy \( G \) of the system can be written as an expansion in \( |\Delta| \), supposing that a change in the phase of the CDW \( \phi \) does not change the energy of the system \[47\]

\[ G = \int dx \left( a(T - T_c)\Delta^2 + u\Delta^4 + ... \right) \]  

(3.8)

Here, \( a \) and \( u \) are constants that determine the equilibrium state of the system and can in principle be connected to a microscopic theory, and close to \( T_c \) higher order terms can be omitted.

Figure 3.2 (c) shows the different shapes of the free energy around \( T_c \). Below \( T_c \), the system resides in one of the minimums of the broken symmetry free energy. Above \( T_c \), it resides in the minimum of a high symmetry free energy, corresponding to an unmodulated system. In thermal equilibrium, Landau theory can be used to derive critical exponents for the evolution of material parameters around \( T_c \). While Landau theory in principle only applies for systems in thermodynamic equilibrium, expressions similar to the Landau free energy are often used to describe the evolution of a nonequilibrium system through a symmetry breaking transition.

Derived from a microscopic theory, the function describing the temperature dependence of

\[ ^1\text{Here, it is also assumed that the system is homogeneous and a gradient term } \nabla \Delta \text{ can be neglected.} \]
\( \Delta \) in fact is the same as the one given by BCS theory for the superconducting gap \[48\]. In the framework of the presented mean field approach for a strictly one-dimensional system, the temperature dependence of quantities like gap size or amplitude of the periodic lattice distortion is therefore completely determined. In systems with a higher dimensionality the equations given in this section are not strictly valid any longer, although the main phenomenology remains the same.

The resemblance of the CDW ground state to the superconducting ground state also manifests in a more fundamental way. While the superconducting ground state corresponds to a condensate of correlated electron-electron pairs with a total momentum of \( q = 0 \), the CDW ground state consists of correlated pairs of electrons and holes, but this time with a total momentum corresponding to the magnitude of the nesting vector \( q = 2k_f \). Typical mean field transition temperatures to the CDW ground state are however much higher than in superconductors. In a CDW system, the relevant energy is given by the Fermi energy. In a BCS superconductor, the relevant energy scale is given by the Debye Frequency, corresponding to a much lower energy and consequently a much lower transition temperature.

Up to this point, fluctuation effects were completely neglected by following a mean field approach. In a strictly one-dimensional chain, fluctuations in fact will prohibit any long range order. Only due to interchain coupling in a three-dimensional solid can long range order actually develop. The difference between equations given by mean field theory and actual transition temperatures is briefly addressed in Chap. 3.3.1.

### 3.2.3 Excitations of the charge-density-wave ground state

There are two types of elementary excitations in the CDW ground state, namely excitations of quasiparticles over the single particle CDW gap and collective excitations of the complex order parameter of CDW the ground state. The creation of quasiparticles can be observed in the optical conductivity for photon energies \( \hbar \omega > 2\Delta \).

Excitations of the complex order parameter \( \Delta = |\Delta| \exp(i\varphi) \) correspond to changes of the amplitude and the phase of the CDW. Figure 3.4 shows the concerted displacement of the periodic lattice distortion and the CDW for both possible collective excitations, usually referred to as amplitude mode (AM) and phase mode (PM).

The AM corresponds to a modulation of the amplitude of the CDW, accompanied by a rearrangement of lattice ions along the coordinate of the Peierls distortion. Looking at Eq. 3.5 an excitation of the AM also results in oscillations of the CDW gap. The structural motion associated with the amplitude mode corresponds to the phonon mode that shows softening towards the transition temperature \( T_c \). In principle, all phonon modes at \( 2k_f \) can couple to the condensate and show softening towards \( T_c \), sometimes making a clear definition of an AM difficult \[30\]. The AM is Raman active and can therefore be investigated with Raman spectroscopy and x-ray diffraction.
3.3 Charge density waves in solid state systems

Figure 3.4: (a) Collective excitations of the CDW ground state described by a Landau free energy. The amplitude mode corresponds to an excitation of the amplitude $|\Delta|$ of the order parameter, resulting in a modulation of the amplitude of the CDW and the associated periodic lattice distortion. The phase mode corresponds to an excitation of the phase $\varphi$ of the order parameter, resulting in an overall shift of the CDW with respect to the lattice ions.

(b) Schematics of amplitude mode and phase mode in the $q = 0$ limit. The lines in the schematics show the charge density in the conduction band, while the spheres correspond to the positions of lattice ions.

(c) Schematics of the dispersion of amplitude mode and phase mode frequency $\omega_a$ and $\omega_\varphi$ as calculated by mean field theory. Pinning leads to a finite phase mode frequency $\omega_\varphi$ at $q = 0$.

The PM involves a displacement of the CDW with respect to the lattice atoms, making it infrared active. Figure 3.4 shows a schematic of both collective excitations in the $q = 0$ limit. The dispersion relation of AM and PM can be calculated using Landau theory \[45\] and is also shown in Fig. 3.4. While Landau theory predicts a gapless PM, impurity pinning leads to a non-zero energy at $q = 0$. A gapless PM in fact would render the CDW ground state superconducting, since sliding of the CDW would be possible without bringing energy into the system.

3.3 Charge density waves in solid state systems

The formation of a CDW and the associated metal-to-insulator transition has been experimentally observed in numerous materials, Fig. 3.5 shows the basic phase diagrams of some of the most widely studied CDW compounds. The classification into different dimensionality classes can
be a bit arbitrary, since it depends on the level of electronic anisotropy in the materials. The presentation in the figure uses the classification most prevalent in the literature. Often, multiple transitions between different CDW states occur in one compound. An important distinction of CDWs in a solid is the fact whether the modulation period along a specific direction is commensurate or incommensurate with the periodicity of the underlying lattice. Following the Peierls picture, the wave vector of the CDW is expected to correspond to the band filling of the conduction band in the metallic state, which need not be a rational number. To this point, only

\[
\begin{array}{c|c|c}
\text{quasi 1D} & \\
\hline 
K_{0.3}\text{MoO}_3 & IC & 183 K \\
(TaSe_4)_2\text{I} & IC & 263 K \\
\hline 
\text{quasi 2D} & \\
\hline 
\text{NbSe}_3 & IC & 59 K, 145 K \\
\text{TbTe}_3 & IC & 336 K \\
1T-\text{TiSe}_2 & C & 200 K \\
4H_{1b}-\text{TaSe}_2 & C & 410 K, IC & 600 K \\
1T-\text{TaS}_2 & C & 183 K, NC & 353 K, IC & 543 K \\
\end{array}
\]

**Figure 3.5:** Phase diagram for several widely studied quasi one- and two-dimensional CDW compounds. For first-order phase transitions with hysteresis loops, the phase transition upon cooling is given. C: commensurate. NC: nearly commensurate. IC: incommensurate. The high-temperature phase always corresponds to the unmodulated structure. Values for transition temperatures taken from: $K_{0.3}\text{MoO}_3$: \[49\]. $(TaSe_4)_2\text{I}$: \[50\]. NbSe$_3$: \[51\]. TbTe$_3$: \[27\]. 1T-TiSe$_2$: \[52\]. 4H$_{1b}$-TaSe$_2$: \[53\]. 1T-TaS$_2$: \[53\].

the Peierls picture assuming an instability in the electronic system based on Fermi surface nesting as a driving force of CDW formation was discussed. In a lot of compounds the predominant mechanism leading to CDW formation is however still not completely clear. A metal-to-CDW transition in a real solid can only be classified as a Peierls transition if the CDW ground state closely resembles the discussed idealized one-dimensional case. Most importantly, the Fermi surface must show parallel parts and the nesting vector has to correspond to the modulation vector of the CDW and the periodic lattice distortion, $q_{\text{nest}} = q_{\text{CDW}}$. Moreover, the susceptibility should be strongly peaked at $q_{\text{CDW}}$ and a Kohn anomaly should be present in all phonons if
allowed by symmetry, with at least one phonon showing softening towards $T_c$.

In a work by Johannes and Mazin [54], it was shown that in most cases, nesting vectors do not correspond to $q_{\text{CDW}}$. For the quasi-two-dimensional CDW systems NbSe$_2$, TaSe$_2$ and CeTe$_3$, they claim that it is indeed $q$-dependent electron-phonon coupling that is more important to the transition than nesting. This claim was further supported by studies looking at the $q$-dependent electron-phonon coupling in detail. As a reminder, the electron-phonon coupling constant in the Peierls picture can be assumed completely dispersionless, $g_q = g$.

In other materials like TiSe$_2$, even more possible mechanisms have been proposed, for example a band Jahn-Teller effect or the formation of an excitonic condensate. The debate is still ongoing and most recently, time-resolved methods have been utilized to shed light on the interplay and importance of the electronic and the lattice dynamics during the CDW transition [5, 55, 56].

Charge density wave systems are great model systems to study ultrafast photoinduced dynamics and the interplay of lattice and electrons in a transient state after photoexcitation. The results can however only be generalized and classified within a well-defined theoretical framework when the formation of the CDW is at least fully understood in thermal equilibrium. The quasi-one-dimensional conductor K$_{0.3}$MoO$_3$ is widely considered to be a textbook example exhibiting a Fermi nesting driven metal-to-CDW transition. In the following, the system is presented in detail and characteristics of the CDW transition are compared against predictions by the Peierls picture.

### 3.3.1 A prototypical example: K$_{0.3}$MoO$_3$

K$_{0.3}$MoO$_3$ belongs to a class of transition metal oxides termed molybdenum bronzes. Members of the particular stoichiometry class $A_{0.3}$MoO$_3$, where $A$ = K, Rb or Tl is an alkali metal are often called blue bronzes, owing to their deep blue color. The blue bronze K$_{0.3}$MoO$_3$ has a highly anisotropic electronic conductivity that was first recognized by Travaglini et al. [57]. The crystal structure of K$_{0.3}$MoO$_3$ is depicted in Fig. 3.6. At room temperature, K$_{0.3}$MoO$_3$ has space group $C2/m$ and unit cell constants $a = 18.162$ Å, $b = 7.554$ Å and $c = 9.816$ Å, with a monoclinic angle $\beta = 117.39^\circ$ [58]. Layers of K-atoms separate chain-like clusters comprising MoO$_6$ octahedra. The octahedra are linked along the $\vec{b}$-axis via corner-sharing, resulting in a high conductivity along the MoO$_6$ chains. In fact, the conductivity along the $\vec{b}$-direction ($\sigma_b = 3 \times 10^2$ $(\Omega \text{cm})^{-1}$) is significantly higher than in the two perpendicular directions ($\sigma_{2a-c} = 10$ $(\Omega \text{cm})^{-1}$ and $\sigma_{2a+c} = 0.5$ $(\Omega \text{cm})^{-1}$), illustrating the one-dimensional character of the compound [45]. Upon cooling below $T_c = 183$ K, K$_{0.3}$MoO$_3$ undergoes a second order phase transition to an incommensurate CDW ground state with a modulation wave vector $\vec{q} = (1 \ q_b \ 0.5)$ [59, 49]. The modulation along $\vec{b}^*$ varies with temperature and takes a value of $q_b = 0.748$ at $T = 100$ K. The doubling of the unit cell along the $c^*$-axis results from Coulomb repulsion of neighbouring chains. [60, 58].

In the following, experimental observations on the CDW ground state are compared to predictions of the Peierls picture. The starting point for such a comparison should always be an
investigation of the Fermi surface for possible nesting vectors that can then be compared to the observed modulation wave vector along the axis of high conductivity, $q_b$. Figure 3.7 shows a Fermi energy intensity map recorded with angle-resolved photoemission spectroscopy, symmetrized around $\Gamma Y$ [61]. Two bands cross $E_f$ along the $\vec{b}^*$ direction, resulting in a Fermi surface that essentially consists of four lines. The slight curvature of the lines shows that the system cannot be treated as strictly one-dimensional, but the depicted modulation vector $q_{CDW}$ is in excellent agreement with the measured CDW modulation vector [62]. The intimate connection between the nesting vector and the CDW vector is furthermore supported by a comparison of the temperature dependence of both vectors [63]. These findings make it indeed very convincing to describe CDW formation in $K_{0.3}MoO_3$ as driven by Fermi surface nesting.

Figure 3.6: Schematics of the structure of $K_{0.3}MoO_3$, based on x-ray diffraction measurements [58]. Linear chains of high conductivity are aligned with the monoclinic $b$-axis. Crystals of $K_{0.3}MoO_3$ can cleaved along the plotted $(2\ 0\ 1)$ plane.

Figure 3.7: Fermi energy intensity map taken at 300 K showing that in $K_{0.3}MoO_3$, the Fermi surface consists of four almost linear lines. The modulation vector $q_{CDW}$ is in excellent agreement with the observed nesting. The variable $q_{CDW}$ used in the reference corresponds to $q_b$ used in the rest of this work. Figure taken from [61].
The metal-to-CDW transition in $K_{0.3}MoO_3$ has profound effects on the electronic state spectrum. The opening of the gap in the electron density of states around the Fermi energy below $T_c$ can be observed with angle-resolved photoemission spectroscopy \cite{28} and in conductivity data \cite{64}. Figure 3.8 shows a decrease in DC conductivity of several orders of magnitude below $T_c$.

![Conductivity of $K_{0.3}MoO_3$](image)

**Figure 3.8:** Conductivity of $K_{0.3}MoO_3$ in the DC limit (solid line) and for various frequencies in the GHz range. For higher frequencies, the conductivity does not drop due to collective phase mode excitation. Taken from \cite{64}.

The periodic lattice distortion in the CDW ground state of $K_{0.3}MoO_3$ has been extensively studied using x-ray and neutron diffraction. Figure 3.9 shows the temperature dependence of the intensity of the $(1 \,(4 - q_b) \,0.5)$ superlattice peak measured by x-ray diffraction \cite{60}.

Mean field theory predicts a BCS-like temperature evolution of the order parameter $\Delta$ in the broken symmetry state. As given by Eq. 3.6, the amplitude of the CDW and consequently the periodic lattice distortion is determined by $\Delta$. A BCS-like temperature behavior is therefore also expected for the structure factor of Bragg reflections associated with the broken symmetry ground state. This is indeed the case, as evidenced by the good agreement of the temperature evolution of the superlattice peak to BCS theory. As shown in Fig. 3.3, the coupling of the lattice to a divergent $\chi(q)$ results in a renormalization of phonon frequencies at $q_{CDW}$. The phonon branch corresponding to the amplitude mode excitation as well as phonon branches displaying a Kohn anomaly above $T_c$ can be observed in $K_{0.3}MoO_3$ with inelastic neutron scattering. The amplitude mode can furthermore be measured via Raman scattering, since the backfolding of $2k_f$ turns it into a $q = 0$ mode. Figure 3.10 shows a combination of Raman and Neutron data.
Figure 3.9: Temperature dependence of the intensity of the $(1 (4 - q_0 \overline{1} 5))$ superlattice peak, measured by x-ray-diffraction. The observed intensity is related to the structure factor of the reflection via $I \propto |F^{SL}|^2$. The solid line corresponds to $\Delta^2$ predicted by BCS theory. Figure taken from [60].

In an acoustic phonon branch, the onset of a Kohn anomaly at $T = 230$ K can clearly be seen. The Kohn mode splits into amplitude and phase mode when cooling the system below the transition temperature $T_c$, which is also reflected by the data.

Figure 3.10: (a) Combination of Raman and neutron data of amplitude and phase mode (below $T_c$) and Kohn mode (above $T_c$). (b) Low-lying phonon modes in $K_{0.3}$MoO$_3$ recorded with inelastic neutron scattering at $T = 230$ K. The onset of a Kohn anomaly indicated with an arrow in an acoustic phonon branch at $q_{CDW}$ can be clearly observed. Figures taken from [65].

Following mean field theory, the amplitude mode is, however, expected to show complete softening towards $T_c$, which evidently is not observed in the presented Raman data. The fact
that simple mean field theory does not quantitatively describe the transition to the CDW state also becomes evident when comparing the expected transition temperature according to Eq. 3.7
$$T_{MF}^{c} \approx 320 \text{ K}$$
to the observed transition temperature
$$T_{c} = 183 \text{ K}$$.
A possible explanation for the departure from mean field theory considers fluctuation effects in the quasi-one-dimensional system. These effects lower the actual transition temperature to the three-dimensional correlated ground state, explaining the discrepancy between measured and predicted values [45, 65, 67]. Following these arguments, the amplitude mode would show complete softening at $$T_{MF}^{c}$$, but at the actual transition $$T_{c}$$ only incomplete softening can be observed.

An alternate explanation is given in [30], assuming a linear coupling of electronic order to $$2k_f$$ phonons and utilizing time-dependent Ginzburg-Landau theory. This approach can not only explain the observed incomplete softening, but also the temperature dependence of damping and frequency of other zone-folded phonons in the CDW ground state.

3.3.2 Ultrafast dynamics in $K_0.3MoO_3$

As a model Peierls system, $K_0.3MoO_3$ has been extensively studied employing different time-resolved techniques. It is often used to gain insights into the interaction between the electronic system and the lattice in a correlated material, and the simplicity of the underlying theory makes it possible to generalize results to other systems where electronic order and the lattice are coupled.

Similar to ultrafast experiments in other correlated systems, pump-probe studies that so far have been carried out in the CDW state of $K_0.3MoO_3$ can be roughly divided into (i) spectroscopic measurements with low fluences that try to shed light on the nature of the CDW state under weakly nonequilibrium conditions [17, 30, 68] (ii) measurements with higher pump fluences that lead to highly nonequilibrium states after excitation, allowing to study the ultrafast CDW-to-metal transition [3], domain creation [28] or anharmonic coupling between modes [28].

The first time-resolved measurements performed by Demsar et al. in 1999 [17] already showed the great potential of ultrafast pump-probe spectroscopy to investigate the CDW ground state. Below $$T_c$$, the Raman active $$\nu = 1.7 \text{ THz}$$ amplitude mode can be observed as a coherent oscillation in the transient reflectivity. Furthermore, quasiparticle excitation across the CDW gap and the subsequent relaxation can be observed as a transient reflectivity change on a sub-picosecond timescale. In later experiments, numerous $$q = 0$$ modes could be observed, and higher laser fluences were found to transiently melt the CDW [3]. Figure 3.11 shows a mode spectrum based on a time trace of the transient reflectivity after excitation with femtosecond pump pulses with a range of fluences. It is evident that above a certain threshold fluence (given as $$F \approx 200 \text{ µJ/cm}^2$$), the amplitude mode disappears. It requires fluences around an order of magnitude higher than this threshold fluence until other zone-folded modes disappear. The disappearance of the zone-folded modes was interpreted as a destruction of the periodic lattice distortion by the laser

\[^2\text{Calculated with } \Delta = 50 \text{ meV as reported in [66].}\]
pulses, corresponding to a transition to a transient high symmetry state. Since the amplitude mode already vanishes at much lower fluences, it was proposed that the electronic order is melted earlier on sub-picosecond timescales while the lattice remains unperturbed. A more refined look at the interplay between lattice and electronic order revealed that indeed the electronic order does not adiabatically follow the lattice modulation [30].

**Figure 3.11:** Fluence dependence of the $q = 0$ mode spectrum in the CDW of $K_{0.3}MoO_3$ recorded with all optical pump probe spectroscopy. Taken from [3].

More recently, time- and angle-resolved photoemission spectroscopy was carried out in the CDW state of $K_{0.3}MoO_3$ and the dynamics of the CDW gap could be observed [28]. After excitation, a reduction of the CDW gap as well as a signature of coherent gap oscillations corresponding to the amplitude mode were revealed in the photoemission spectra. A slower oscillation in the gap of the anti-bonding band was in fact interpreted as oscillations associated with coherently excited large wave-vector phase modes, claiming a coupling of real and imaginary parts of $\Delta$ after photoexcitation.

All reported measurements have one common shortcoming: They are mostly sensitive to the electronic order of the system, and the structural symmetry of the system in the transient state after photoexcitation can only be indirectly inferred. To fully understand the nonequilibrium state, complete information of the multicomponent order parameter is needed — demanding a direct view of the lattice with a time resolution short enough to resolve coherent dynamics associated with collective excitations of the CDW ground state. These structurally sensitive measurements have been performed as a part of this work and complete the picture of the photoinduced CDW-to-metal transition in $K_{0.3}MoO_3$, and reveal completely new phenomena occurring during ultrafast phase transitions (see Chap. 7 and 8).
3.3.3 A quasi-two-dimensional charge-density-wave compound: 4H$_b$-TaSe$_2$

Transition metal dichalcogenides like 4H$_b$-TaSe$_2$ are layered compounds with a highly two-dimensional character [53]. They exhibit various phase transitions to broken symmetry phases with several different types of electronic and structural order; the phase diagram of selected examples is shown in 3.5.

In all transition metal dichalcogenides, two chalcogen layers sandwich a layer made of transition metal, forming the basic building blocks of the structure. These three-atom-thick layers are only weakly coupled through van-der-Waals forces to neighboring layers along the crystallographic $c$-axis. The intralayer coordination of covalently bound atoms as well as the stacking of different layers determine the polytype of a transition metal dichalcogenide, which is typically indicated in front of the stoichiometric formula. The number indicates the number of stacked layers that constitute one unit cell and the letter is related to the symmetry within the layers. Different polytypes of a specific transition metal dichalcogenide exhibit varying transition temperatures and also differ in the type of CDW order in the respective ground states. Examples of the structure of different TaSe$_2$ polytypes are presented in Fig. 3.12 (a). There are two possible intralayer coordinations (H and T), and the stacking order determines the polytype. In the case of 4H$_b$-TaSe$_2$, H- and T-layers alternate.

![Figure 3.12: (a) Structure of different TaSe$_2$ polytypes. In 4H$_b$-TaSe$_2$, the unit cell is made of four three-atom-thick layers, namely two H- and two T-layers. (b) View along the crystallographic $c$-axis on the high-symmetry structure of 4H$_b$-TaSe$_2$. The arrows indicate the displacement of Ta atoms in the commensurate CDW ground state.](image)
In its high-symmetry phase (above $T = 600$ K), $4H_b$-TaSe$_2$ has space group $P6_3/mmc$ with unit cell constants $a = b = 3.45$ Å and $c = 25.15$ Å [69]. In the room-temperature commensurate phase, a $(\sqrt{13}a \times \sqrt{13}a \times c)$ superstructure develops and symmetry reduces to $P6_3/m$ [69]. The displacement of atoms associated with the CDW state predominantly occurs in the $T$ layers. In Fig. 3.12 (b), the displacements of the Ta atoms, occurring mainly perpendicular to the $c$-axis, is shown. The displacement of the Se atoms is smaller and occurs mainly along the $c$-axis.

In the previous section, predictions of the Peierls picture were compared to experimental results on the quasi-one-dimensional system $K_0.3MoO_3$. Most measured quantities fit very well into the picture of Fermi-nesting driven CDW formation. This is not at all the case for quasi-two-dimensional transition metal dichalcogenides. For example, there does not seem to be a close relationship between Fermi nesting vectors and modulation vectors of the periodic lattice distortion in the different CDW ground states of transition metal dichalcogenides [70]. Furthermore, the phase transition between different ground states, for instance the transition between the commensurate and the incommensurate state in $4H_b$-TaSe$_2$ is of first order [71]. Recently, it has become more and more clear that momentum-dependent electron-phonon coupling is a significant driving force behind CDW formation [72, 73].

Besides being promising materials for future electronics devices [74], transition metal dichalcogenides have been widely used as quasi-two-dimensional model systems to study ultrafast photoinduced phase transitions. These studies include optical pump-probe spectroscopy [75], time-resolved x-ray diffraction [5, 76] and ultrafast electron diffraction [44, 77]. The direct observation of the coherent motion of atoms during the ultrafast melting of the CDW in $4H_b$-TaSe$_2$ is presented in Chap. 9.
Chapter 4

Time-resolved x-ray diffraction

In recent years, it has become possible to generate x-ray pulses with sub-picosecond time durations, enabling a new class of time-resolved experiments directly sensitive to the structure of a solid. Sub-picosecond x-ray pulses can probe the structure in nonequilibrium states of matter, where transient states cannot be described by a thermodynamic distribution and transport phenomena are not yet important. They can, for example, access timescales associated with THz frequency optical phonons and relaxation through electron-phonon coupling.

The generation of sub-picosecond pulses of x-ray radiation can be realized with different methods, which are discussed and compared in this chapter. The focus lies on the source that was utilized for time-resolved x-ray measurements in this work, the FEMTO slicing source at the Swiss Light Source. By the time of this writing, the FEMTO slicing source was the only operational synchrotron-based source of femtosecond hard x-ray pulses. At the moment, a transition to hard x-ray free electron lasers (FELs) is taking place. In most aspects important for ultrafast diffraction measurements, FELs are vastly superior to any other source.

Time resolved x-ray diffraction measurements are typically designed using the pump-probe approach. The need to introduce a pump pulse into the setup and additional constraints related to penetration depth matching and time smearing complicate the geometry in a time-resolved diffraction experiment compared to a static x-ray experiment. Considerations concerning the experimental geometry in a time-resolved x-ray diffraction experiment are discussed in detail in Sec. 4.2. Specific setups for the experiments conducted for this work are shown in the particular chapter for each experiment.

4.1 Sources of ultrashort x-ray pulses

Sources of sub-picosecond hard x-ray pulses can in general be divided into two categories: First, accelerator based sources at synchrotrons and FELs, and second, laser-driven plasma sources that can be operated in a smaller-scale laser laboratory. All these sources in principle allow the study of sub-picosecond structural dynamics, but different limitations apply to different sources.
and can render a specific experiment impossible at a certain source. For all time-resolved x-ray experiments in this work the FEMTO slicing source at the Swiss Light Source was used. The discussion about this source is therefore more detailed, including a discussion on data acquisition and background signal aspects that are important for the analysis of the data. It is, however, also important to introduce other sources as well to be able to compare them in detail and have a better understanding of limitations. Especially FEL-based sources are becoming more and more important since available pulse energies are orders of magnitude larger than for any other source.

The discussion is focused on utilizing ultrashort x-ray pulses as a probe for sub-picosecond structural dynamics and therefore on the hard x-ray regime, but emerging experimental possibilities in other areas are also mentioned.

In Sec. 4.1.3, the most important parameters of different sources for time-resolved solid state diffraction measurements are compared and a short comparison to ultrafast electron diffraction is presented.

4.1.1 Synchrotron slicing and the FEMTO slicing source

In third generation synchrotron light sources \[78\] like the Swiss Light Source (SLS), the electron bunch length in the storage ring typically lies between 30 to 100 ps. The resulting x-ray pulses originating from bending magnets or undulators have around the same length. At the SLS, a highly stable 500 MHz pulse train of 85 ps x-ray pulses is available for experimental use at the different experimental endstations. The electron bunch length can be further reduced when the synchrotron is operating in a so-called low-alpha mode. Here, alpha refers to the momentum-compaction-factor, and pulse lengths of around 10 ps can be achieved in this particular operation mode\[1\] with reduced bunch current. Synchronizing these pulses to a pump source allows for picosecond time-resolved x-ray diffraction, but to be able to utilize even shorter x-ray pulses, a different modulation of the electron bunches is required.

The idea to use the only means of producing femtosecond duration pulses of light — the mode-locked laser — to generate sub-picosecond x-ray pulses from synchrotron radiation was introduced in 1996 \[80\] and experimentally demonstrated at the Advanced Light Source in 2000 \[81\].

The general idea \[80\] goes as follows: The field of a femtosecond laser pulse is used to modulate the energy of a slice of an isolated electron bunch in a synchrotron\[2\]. When the energy modulation introduced by the laser pulse is significantly larger than the energy spread of electrons in the bunch, the modulated part can be separated from the unmodulated core beam by a dispersive electron optic. The modulated (or sliced) part of the electron bunch is then used to produce femtosecond x-ray pulses, which can be separated from the core x-ray beam by apertures. The

\[1\]For more on low-alpha operation, see for example details on the low-alpha mode operation at the synchrotron SOLEIL \[79\].

\[2\]For stability reasons, at synchrotrons there typically exists a gap in the filling pattern. One single bucket within this gap can be filled with electrons for time-resolved x-ray experiments. This isolated electron bunch is often called the camshaft bunch.
different steps are summarized in Fig. 4.1. Quantities in the following detailed description are
innate to the FEMTO slicing source [82, 35].

![Diagram of the generation of femtosecond x-ray pulses via synchrotron slicing.](image)

**Figure 4.1:** Example of the generation of femtosecond x-ray pulses via synchrotron slicing. The figure corresponds to a top view of the different elements. Laser pulse and isolated electron bunch are overlapped in a wiggler, leading to a energy modulation of the electron bunch. Modulated parts are separated from the main bunch in the dispersive section (in this picture, this is just a simple bending magnet). Radiation is produced in the undulator, and the sliced photons can be separated from the main beam as they differ in position and propagation direction.

**Energy modulation and bunch separation** A 100 fs laser pulse with wavelength $\lambda_L = 800$ nm originating from an amplified Ti:Sapphire laser is temporally and spatially overlapped with the electrons of an isolated bunch in a wiggler, which basically is a series of dipole magnets with alternating field direction. In the wiggler, electrons are on a trajectory with a significant transversal modulation and can be accelerated or decelerated by the field of the laser pulse via the Lorentz force. To ensure that a net energy gain or loss of the electrons overlapped with the co-propagating laser pulse occurs after passing through the wiggler, the wiggler period $\lambda_U$ and the laser wavelength $\lambda_L$ have to fulfill the resonance condition [81]

$$\lambda_U = \frac{2 \gamma^2 \lambda_L}{1 + K^2/2}$$

(4.1)

Here, $\gamma$ is the Lorentz factor and $K$ is the deflection parameter, which is related to the maximum deflection angle of the electron path.

The laser pulse energy has to be high enough to provide sufficient energy separation of the modulated electrons from the unmodulated electrons in the bunch. At the FEMTO slicing source, this is achieved with 2 mJ laser pulses.

After passing through the wiggler, electrons that have experienced an energy modulation are separated from the core electron beam in a dispersive section: In the magnetic field of a three-dipole chicane, the electron trajectory depends on the energy of the electrons, resulting in a spatial separation of the different parts of the electron beam. These parts are the unmodulated core beam and the two modulated, or sliced, electron bunches (one of which experienced a net
energy gain, the other a net energy loss). The current of the two sliced parts is around a factor of $10^{-4}$ weaker than the current of the unmodulated bunch [82], which already makes it evident that the pulses of the sliced beam will constitute much less flux compared to normal synchrotron operation. Additionally to the low slicing efficiency, the usable repetition rate for time-resolved experiments is reduced to 2 kHz, which is the repetition rate of the laser amplifier used for slicing operation at FEMTO. The small effect on the electron bunches in the synchrotron storage ring however allows for slicing operation without any noticeable consequences for other experimental endstations of the synchrotron.

**X-ray generation and optics** After passing the dispersive section, core and modulated electron bunches are sent into an undulator. An undulator is, much like a wiggler, a series of dipole magnets with alternating field directions. However, the field strength is typically chosen lower, resulting in a lower deflection parameter $K$. The radiation from an undulator corresponds to odd harmonics of the fundamental oscillation period [78]. Tuning the undulator gap at FEMTO allows tuning of the x-ray energy between 4.2 keV and 14 keV. For the study of structural dynamics of solids when no restrictions due to the presence of nearby absorption edges in the sample have to be considered, usually an x-ray energy of 7 keV is chosen at FEMTO, corresponding to a wavelength of 1.77 Å. This corresponds to the x-ray wavelength with the highest x-ray flux utilizing the 5th harmonic of the undulator.

Core and sliced beam are separated by slits, the maxima of the spatial profile of core and sliced beam at the separation point are roughly 2 mm apart and have an angular separation of $0.5^\circ$ [35]. The beam is first loosely focused by a toroidal mirror and can then be focused by a Kirkpatrick-Baez (KB) mirror system [83]. For most experiments in a grazing incidence geometry it is focused to a beam size of 10 µm vertically and left unfocused horizontally, resulting in a horizontal spot size of around 250 µm. The bandwidth of the x-ray pulses can either be set by a Si or Ge monochromator, or with a multilayer mirror. The multilayer mirror has a 1.3% bandwidth acceptance and is usually used in diffraction experiments because of the higher photon throughput. With the KB mirrors used for vertical focusing and the multilayer mirror in the beam, usually a flux of around 300 photons/shot at the sample position can be achieved.

Figure 4.2 summarizes the actual realization of slicing operation at the FEMTO slicing source. In the laser hutch, $\lambda = 800$ nm seed pulses from a mode-locked Ti:Sapphire oscillator are branched into two chirped amplification schemes, labeled *phase I* and *phase II*. The oscillator is phase-locked to the radiofrequency-master of the synchrotron, also ensuring phase-stability between the isolated bunches used for slicing and the seed pulses of the laser system. The amplified *phase I* pulses (repetition rate 1 kHz) are used as pump pulses and travel through an evacuated transfer line into the x-ray hutch. There, they pass a delay stage used to vary the time.

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3 The layout of the laser system in the laboratory at ETH is similar to the branches of the FEMTO laser system. It is explained in detail in the appendix, Sec. A.1.
4.1 Sources of ultrashort x-ray pulses

Figure 4.2: Schematics of the FEMTO experimental station, consisting of the laser system in the laser hutch and the slicing interaction region in the wiggler, after which the sliced x-ray pulses are sent to the x-ray hutch. CPA: chirped pulse amplification. ML: multilayer mirror. KB: Kirkpatrick-Baez mirror system.

delay to the sliced x-ray pulses. In the x-ray hutch, the wavelength of Ti:sapphire fundamental pulses can be converted with an OPA, also allowing for efficient THz generation using organic crystals.

The phase II pulses (repetition rate 2 kHz) are used for the slicing process. After the interaction region of electron bunches and pulses of the phase II amplifier, sliced x-ray pulses enter the x-ray hutch. The overlap of electron bunches and phase II pulses in the wiggler is adjusted with a piezo-driven mirror. The modulation of the electron bunches acts as a source of low-frequency THz radiation [35] that can be measured with a Helium-cooled bolometer and used to optimize overlap between electron and laser pulses. After the interaction region, the x-ray pulses enter the hutch and pass several beamline optics that can be moved in and out of the beam, catering to the needs of the experimental setting.

The beamline also allows for time-resolved experiments with an 85 ps unsliced beam, but since sliced beam and core beam have different positions and deflection angles, beamline optics and apertures have to be adjusted when switching between the two modes of operation.

Data acquisition and signal background After interacting with the sample, the diffracted x-ray pulses can be detected with an avalanche photodiode (APD) that measures the integrated intensity over its $10 \times 10 \text{mm}^2$ aperture, or with a single-photon-counting pixel detector (PILATUS 100 K [84]). Usually the pixel detector is only used for alignment, and an APD is used for data acquisition during the actual experiment.

When using the APD, the signal is amplified and then fed into a gated integrator. The gate has to be set so that only the sliced part of the beam is measured, temporally corresponding to
the isolated electron bunch in the camshaft. There are two types of background contributions that affect the signal. First, remaining core beam that has not been fully blocked by the slits. Second, the so-called halo, corresponding to signal from previously sliced electron bunches from earlier round-trips through the storage ring that are on damped trajectories but still influence the signal.

To minimize background from core beam, the acquisition gate around the signal has to be as short as possible without clipping the diode signal too much. To minimize core beam contributions, the slits selecting only the sliced x-ray photons can be adjusted to be more restrictive. This in turn also reduces the throughput of sliced photons, and depending on the type of experiment, a good balance between reducing core contributions and not clipping the sliced beam too much has to be found. For measurements with low photon count, scattered x-ray photons from optics and windows can furthermore become a significant part of the signal. In this case, apertures in front of the APD can be placed to minimize these contributions.

The halo contribution can be quantified by the readout of a second gated integrator, with the gate set to the previous round-trip of the synchrotron. When the time-resolved diffraction signal is analyzed, the halo contribution has to be considered. As an example, Figure 4.3 shows a sample rotation scan of a Bi diffraction peak measured with the gated APD, where one gate is set to the signal and one is set to the halo. The APD gated for the halo contribution shows a typical signal level of around 20% of the actual sliced signal. As a result, it can be assumed that for this experiment, around 20% of the sliced signal corresponds to halo signal. In a time-resolved experiment, the halo contribution will not show the same dynamics as the sliced pulses and needs to be subtracted from the signal to gain precise information about background levels. Since the halo pulses take a different trajectory through the storage ring, they slightly differ in energy from the sliced pulses, resulting in a small shift of the peak position.

At the sample, the x-ray pulse length is around 100 fs and the laser pulse length, if the Ti:Sapphire fundamental is utilized, is around 120 fs. Since the x-ray pulses are generated from pulses originating from the same oscillator as the pump pulses, arrival time jitter can usually be neglected and the experimental time resolution is set by x-ray and laser pulse length and the geometry of the specific measurement.

Due to the low photon flux at the sample position, measured diffraction signals are relatively low. As an example, superlattice reflections associated with the periodic lattice distortion in CDW compounds typically have diffraction efficiencies on the order of less than $10^{-4}$, resulting in measured diffraction signals on the order of 10 photons/second. In these situations, single-photon counting with an APD becomes applicable and every event above a certain voltage threshold is counted as one photon.

The errorbars throughout this work when results from slicing measurements are discussed correspond to one standard deviation according to the Poisson distribution: For a mean number of $N$ counted photon, the standard deviation is given by $\sqrt{N}$. 
4.1 Sources of ultrashort x-ray pulses

Figure 4.3: Sample rotation scan of the bismuth (111) diffraction peak measured with an APD with a gate set to two different times: Gated to the current isolated electron bunch of the current round-trip (sliced signal, black) and to the previous round-trip (halo, red). The halo contribution corresponds to around 20% of the sliced signal and is slightly offset in energy, resulting in a small shift of the rocking curve.

4.1.2 Free electron lasers

The working principle of a free electron laser (FEL) can be understood in a very similar way to synchrotron slicing. The important difference lies in the fact that no external light pulse is used to manipulate electron bunches, but rather radiation emitted by the electrons themselves leads to a modification of the temporal structure of electron bunches.

In an FEL, electron bunches are first accelerated to relativistic velocities in a linear accelerator. The electron bunches then enter an undulator, where they interact with the radiation they themselves produce. If a very similar resonance condition to the one given by Eq. 4.1 is met, now connecting the undulator period $\lambda_U$ and the resonance wavelength $\lambda$, a process called microbunching begins, leading to modulations in the electron density along the path of the undulator \[86, 87\]. Since the period of these microbunches corresponds to the resonance wavelength, the electrons begin to emit in phase, in turn leading to a further enhancement in microbunching and a gain in radiation intensity over the length of the undulator.

Since the process is started spontaneously by shot noise in the electron beam, free electron lasers based on this principle are usually called self-amplified spontaneous emission (SASE) FELs.

The first FEL built in the 1970s emitted light in the infrared, at a wavelength of 3.4 $\mu$m.
Since then, the wavelength has been continuously pushed to shorter values. First lasing at angstrom-wavelengths was reported at the Linac Coherent Light Source (LCLS) at the Stanford Linear Accelerator Center (SLAC) in the USA \cite{89}, making the observation of ultrafast structural dynamics in solids possible with an FEL. Free electron lasers offer a lot of advantages compared to synchrotron sources. Due to the microbunching process, radiation is completely coherent and peak intensities are orders of magnitude larger than for synchrotron sources (see comparison in Tab. 4.1). Owing to the SASE operation mode, the beam is however much less stable than a typical synchrotron beam. A more stable operation mode based on self-seeding has recently been demonstrated at LCLS \cite{90} and should become a viable operation mode for ultrafast solid state experiments in the future.

A drawback of the working principle and the dimensions of an FEL (LCLS, including linear accelerator and undulator, has a length of around 3.2 km), is jitter between the pump pulses and x-ray pulses in a pump-probe experiment. With arrival time monitors that measure the cross correlation between x-ray pulses and split parts of the pump pulses, jitter is now however not a limiting factor anymore, and even in the hard x-ray regime, an experimental time resolution well below 100 fs can be achieved \cite{36}.

One of the main limitations for the time-resolved study of structural dynamics in solids with FEL pulses is their limited availability. By the time of this work, only two FELs working in the hard x-ray regime that can offer atomic resolution were operational: LCLS and SACLA at Spring-8 in Japan \cite{91, 92}. A comparison between FELs and other sources of ultrashort x-ray pulses is presented in Tab. 4.1 showcasing that with increased availability of FELs (by the time of this writing, the European XFEL in Germany \cite{93} and SwissFEL in Switzerland \cite{94} are under construction) in the future, they will take the premier role for time-resolved x-ray diffraction measurements in the solid state.

The combination of transverse coherence, tunability, extreme brightness and short pulses also opens up new possibilities for a lot of different experiments in solid state systems, for example time-resolved resonant x-ray diffraction \cite{95, 96}. One of the main driving forces behind FELs however is a biological application: Free electron laser pulses offer the promise of single-shot imaging of the structure of proteins and viruses. The three-dimensional reconstruction of randomly oriented larger viruses has already been demonstrated \cite{97}, but various challenges, for example concerning reconstruction algorithms, timescales associated with sample damage and parasitic scatter by beamline optics, still remain \cite{98}.

### 4.1.3 Other sources for sub-picosecond diffraction experiments

As an example of a table-top source for ultrashort x-ray pulses with angstrom-wavelengths, plasma sources were already mentioned. Plasma sources rely on the interaction of intense femtosecond laser pulses with thin metallic targets \cite{99, 100}. The x-ray pulse duration is mostly determined by the laser pulse length and electron deceleration kinetics. With 50 fs pulses from an amplified Ti:Sapphire laser, x-ray pulses with durations of around 100 fs can be generated. Radiation is
emitted to the full solid angle and has to be focused onto the sample. Plasma sources are not tunable and mostly emit radiation at inner shell edges of atoms of the target material, and a weaker background of Bremsstrahlung. While the total flux on the sample can be bigger than with slicing sources (see Tab. 4.1), strong focusing of the x-ray pulses leads to a high divergence at the focus on the sample and consequently a much smaller brilliance. Nevertheless, coherent oscillations associated with the $A_{1g}$ mode in bismuth have been measured with x-ray pulses from a plasma source. The acquisition of the coherent $A_{1g}$ oscillation in Bi can to some extent be used as benchmark to compare different femtosecond hard x-ray sources for experiments looking at sub-picosecond structural dynamics. It took several days to acquire a time trace showing the $A_{1g}$ oscillation with a plasma source. Using the FEMTO slicing source, a similar quality trace can be recorded in less than an hour. At LCLS, it is only a matter of minutes.

Another accelerator-based source of sub-picosecond x-rays, that was mainly used as a testing ground for LCLS is not operational anymore and only mentioned here for completeness: The sub-picosecond-pulse source (SPPS) at SLAC relied on compression of electron bunches in a storage ring and went out of operation when LCLS was constructed.

A comparison of different sources of sub-picosecond operating in the hard x-ray regime is presented in Tab. 4.1. The table can serve as a quick (and, given the complexity and number of important parameters of these sources, rather rough) reference for estimates of expected photon flux, experimental time resolution and possible energy tuning range. All these parameters are crucial when planning an experiment focusing on the ultrafast structural dynamics in a solid state system. The table also recapitulates references on technical details of the different sources and exemplary experiments of ultrafast x-ray diffraction measurements.

A completely different approach to study structural dynamics in the solid state has produced promising results in recent years, namely ultrafast electron diffraction (UED) using sub-picosecond electron pulses. In a typical UED setup, electron pulses are emitted by a photocathode driven by a femtosecond laser pulse and are then accelerated to energies in the tens keV, some sources even operate in the MeV regime. Using electron optics, they are focused on the sample under study. Typical electron pulse lengths at the sample are around $\geq 300$ fs. Shorter pulse lengths are difficult to obtain due to space-charge effects temporally broadening the electron pulses.

Working with electrons in time-resolved diffraction experiments has distinct differences to x-ray diffraction. X-rays have a small scattering cross section in solids, making schemes like a grazing angle incidence experiment or thin film samples necessary to match optical penetration depths (see Sec. 4.2). High energy electrons, on the other hand, have a much smaller mean free path in a solid, requiring sample thicknesses of $\leq 100$ nm for a Laue diffraction experiment. This requirement poses a severe constraint on the choice of possible samples, and often it is not

\footnote{The brilliance of a source can be defined as photons/ (second $\cdot$ mrad$^2$ $\cdot$ mm$^2$ $\cdot$ 0.1% bandwidth) and can be used to compare different sources for diffraction experiments independently of x-ray optics. For example, the large angular divergence of a plasma source results in a small brilliance.}
possible to grow or cleave thin-film single-crystalline samples of particular classes of materials.

The high kinetic energy of electrons in a UED experiment in Laue geometry makes it possible to capture a big section of reciprocal space simultaneously for any time delay point when working with an area detector (in most cases a phosphor screen). This can be advantageous when trying to, for example, quantify the Debye-Waller contributions of an observed transient signal (see Sec. \ref{sec:2.4}). With this comes however a low momentum resolution, making it in turn difficult to evaluate correlation lengths by studying the width of diffraction peaks, that are usually limited by the experimental resolution of a UED setup.

Multiple CDW systems that can be cleaved to thin films \cite{105} have been studied with UED \cite{44, 77, 106}, and the results of these experiments are later compared to the results of time-resolved x-ray diffraction measurements conducted for this work. One of the main challenges to observe sub-picosecond coherent dynamics associated with elementary excitations of broken symmetry ground states still is the electron pulse length at the sample. This should, however, change in the near future with better bunch compression methods or techniques like single-electron diffraction \cite{107}. 
Comparison of ultrafast x-ray sources that can operate in the hard x-ray regime

<table>
<thead>
<tr>
<th>Source</th>
<th>ph/pulse</th>
<th>energy (keV)</th>
<th>bwd</th>
<th>rate (kHz)</th>
<th>t_{x-ray} (fs)</th>
<th>jitter (fs)</th>
<th>energy range (keV)</th>
<th>tech. publ.</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLS FEMTO</td>
<td>4·10^2</td>
<td>7</td>
<td>0.1 %</td>
<td>2</td>
<td>~100</td>
<td>&lt; 50</td>
<td>4.2 - 14</td>
<td>35, 82</td>
<td>[35, 82]</td>
</tr>
<tr>
<td>LCLS (FEL)</td>
<td>2.3·10^{12}</td>
<td>8.3</td>
<td>0.5 %</td>
<td>0.12</td>
<td>~50</td>
<td>~300*</td>
<td>0.25-2.5-9.5</td>
<td>[89, 110, 36]</td>
<td>[35, 82]</td>
</tr>
<tr>
<td>SACLA (FEL)</td>
<td>2·10^{11}</td>
<td>10</td>
<td>0.5 %</td>
<td>0.03</td>
<td>&lt; 30</td>
<td>~500*</td>
<td>4.5-15</td>
<td>[92, 111]</td>
<td>[35, 82]</td>
</tr>
<tr>
<td>Laser plasma</td>
<td>5·10^{3}***</td>
<td>8</td>
<td>0.25 %</td>
<td>1</td>
<td>~100</td>
<td>&lt; 50</td>
<td>8; 17.5</td>
<td>[99, 100]</td>
<td>[35, 82]</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison of reported values for different experimental parameters at x-ray sources that can operate with wavelengths short enough to provide atomic resolution and (in the case of large-scale facilities) are operational by the time of this writing. The different values should be used as estimates, losses by beamline optics are not reflected in the photons/pulse values.

Explanation of the columns:

- **ph/pulse**: Photons per pulse for the given energy and x-ray bandwidth (bwd). Can be multiplied with the rate to get the flux per second.
- **Rate**: Maximum possible repetition rate of x-ray pulses.
- **t_{x-ray}**: Estimate of FWHM x-ray pulse duration in the hard x-ray regime.
- **energy range**: Possible tuning range of x-ray energies, limitations by x-ray optics are not included and can limit the usable range.
- **Jitter**: Estimate of the jitter between laser pump and x-ray probe. The time resolution of an experiment using a certain source is determined by pump pulse length, x-ray pulse length, timing jitter (if there is no arrival time monitoring) and experimental geometry.
- **Tech. publ.**: Technical publications focusing on parameters of the source. Parameters from these publications have been used for the table. If a certain parameter was not found in a publication or was different from measured parameters during experiments at these sources, the experienced value is given.
- **Exp.**: Selected experiments on sub-picosecond coherent structural dynamics observed using the source.

* At LCLS, a timing tool that cross-correlates x-ray pulses and laser pump pulses is operational [36]. Timing jitter therefore does not affect the experimental time resolution.

** At SACLA, a timing tool is in development, but was not operational by the time of this writing.

*** Plasma sources emit x-rays into the full solid angle, the reported value is an estimate at the sample position. See section 4.1.3 for comments on the brilliance of a plasma source.
4.2 Experimental geometry: Grazing incidence diffraction

Time-resolved x-ray diffraction poses several constraints on possible experimental geometries, as excitation pulses have to hit the sample while it is set up for a diffraction measurement. Often, this prevents the use of a standard x-ray diffractometer setup. A further complication stems from the fact that the x-ray absorption length in a solid can easily exceed 1 µm, since the imaginary part of the refractive index for small wavelengths far away from any material resonances is close to zero. By contrast, typical optical penetration depths in a solid lie around 100 nm. In a collinear geometry this leads to a big penetration depth mismatch and only a small fraction of the probed volume is excited by the pump. To avoid this problem, a time-resolved experiment can be performed in a grazing incidence geometry. Close to the critical angle, the x-ray absorption length can become comparable to the optical absorption length. An example of the x-ray absorption length for bismuth is shown in Fig. 4.4.

![Absorption length for 7 keV x-ray radiation in bismuth as a function of the grazing angle.](image)

To obtain an absorption length comparable to the optical penetration depth of around 20 nm, a grazing angle below $\alpha = 1^\circ$ has to be set.

In a typical time-resolved grazing incidence diffraction measurement, the incidence angle has to be set around $\alpha < 1^\circ$. The sample surface thus becomes a crucial parameter: Already small surface irregularities can distort the measured diffraction intensity and lead to non-excited volumes probed by the x-rays. CDW systems are low-dimensional systems that in most cases can be cleaved along certain lattice planes, but it is often not possible to produce a flat surface area larger than the x-ray footprint on the sample in a grazing geometry. Some time-resolved experiments that rely on an unambiguous diffraction signal, like time-resolved diffuse scattering, are often strongly impaired by the surface quality of CDW compounds.

If the excitation process does not rely on certain specific transitions, changing the pump wavelength also offers some leeway for better penetration depth matching. In experiments where
lower frequency pump pulses (e.g. in the THz regime) are used to directly excite structural degrees of freedom, the importance of the grazing angle becomes less severe. Even at strong resonances, THz penetration depths typically still exceed 1 µm.

In order to preserve time resolution, also the pump pulses have to hit the sample at an angle. Figure 4.5 shows a schematic of a typical time-resolved grazing incidence experiment.

Figure 4.5: Experimental geometry in a time-resolved grazing incidence experiment. The x-ray probe pulses hit the sample at the grazing angle $\alpha$, the laser pump at an angle $\beta$. The sample can be rotated around an angle $\varphi$ so that the Bragg conditions is met.

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$^{5}$Preserving the time resolution for a normal incidence pump beam is in principle also possible, but requires a setup allowing for pulse-front tilt of the pump pulses [114].
Chapter 5

Generation and detection of terahertz frequency pulses

The terahertz (1 THz = 10^{-12} Hz = 1 ps^{-1}) frequency range is loosely defined as the part of the electromagnetic spectrum spanning from around 0.1 THz to 30 THz. It bridges the gap between conventional electronics and optics, posing new conceptual and technological challenges and possibilities. Terahertz frequency radiation is extremely useful in the study of the solid state, since a lot of elementary excitations are located in the THz range. Examples include phonons, multiferroic and antiferromagnetic excitations as well as collective excitations associated with broken symmetry ground states. When these excitations are dipole-active, THz radiation can resonantly couple to them. Terahertz radiation has been used as a spectroscopic tool for quite some time, but for a long time there existed a lack of strong sources that can generate sufficient field strengths to drive resonances in a solid with appreciable amplitude. This fact has led researchers to coin the term THz gap to describe the absence of THz frequency radiation for technological and scientific applications.

In recent years, impressive advances in the generation of THz radiation have been made, especially in the area of pulsed sources with very high peak fields driven by ultrafast laser pulses. With these phase-stable pulses of intense THz radiation, completely new ways to study and manipulate materials on an ultrafast timescale are possible.

Working with THz radiation poses several experimental challenges, mostly because optical elements and imaging devices that can be taken for granted when working with optical or infrared light often do not exist or only exist in an early stage for THz radiation. The chapter begins with a discussion on the properties of THz radiation and how the design of ultrafast pump-probe experiments is affected by these properties.

The most important generation methods of sub-picosecond THz pulses are presented in Sec. 5.2. The main focus lies on optical rectification in nonlinear crystals, since THz pulses generated utilizing this method were used as a resonant pump for experiments on single-crystal tellurium (see Chap. 6).
Owing to the small energy of THz photons, detectors relying on electron-hole creation in general are not a viable option in the THz range and new detection schemes have to be employed. Probably the most important time-resolved detection method relies on sampling the THz electric field with an ultrashort laser pulse exploiting the linear electro-optic effect, allowing for amplitude-and phase-resolved detection of the THz electric field. This approach and other detection methods are described in Sec. 5.3.

5.1 Properties of terahertz radiation

Experiments using THz radiation, especially when performed in tandem with ultrafast laser or x-ray pulses, typically demand a great deal of control of temporal and spatial properties of the THz radiation. Typically, THz radiation is propagated through free space from the source to the sample under study and transmission optics are avoided wherever possible. As already mentioned, THz photons have energies close to a lot of low-lying excitations in solids and transmission optics will lead to a a distortion of the THz spectrum. Additionally, a lot of rotational transitions of water vapor are located at lower THz frequencies [115, 116], leading to water absorption lines in the THz spectrum. Figure 5.1 shows the spectral amplitude of a broadband THz pulse after a propagation path through air, demonstrating the need for humidity control of the volume containing the beam path of the THz radiation.

![Terahertz spectrum](image)

**Figure 5.1:** Terahertz spectrum of a pulse generated in the organic crystal DSTMS via optical rectification (see Sec. 5.2.1) after a propagation path \( l \approx 50 \text{ cm} \) through air with relative humidity \( \approx 50\% \) at room temperature. Numerous absorption lines associated with rotational transitions of water vapor can be observed in the spectrum.

Focusing of THz beams is usually achieved with reflective optics. The long wavelength of THz radiation compared to optical wavelengths (for example, 1 THz corresponds to a wavelength \( \lambda = 300 \text{ \mu m} \)) and broadband contributions in the case of near single-cycle pulses can make focusing difficult. To understand this in detail, we can write down the evolution of the electric
field during propagation along $z$ as a Gaussian beam in a paraxial approximation [117]:

$$E(r, z) = E_0 \frac{w_0}{w(z)} \exp\left(\frac{-r^2}{w^2(z)}\right) \exp\left(-i\left[kz - \arctan\left(\frac{z}{z_R} + \frac{kr^2}{2R(z)}\right)\right]\right)$$  \hspace{1cm} (5.1)$$

Here, $r$ is the distance to the propagation axis, $E_0$ is the peak field amplitude, $w_0$ is the beam radius at the beam waist and $R(z)$ is the beam curvature radius. The Rayleigh length $z_R = \pi w_0^2/\lambda$ determines the evolution of the spot size with propagation, since the beam parameter $w(z)$ is given by $w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2}$. For values $z >> z_R$, the beam divergence angle is given by

$$\Theta = \frac{\lambda}{\pi w_0}$$  \hspace{1cm} (5.2)$$

For THz radiation, this leads to some interesting consequences: The THz spot size at the generation position usually is around 1 mm. This is actually comparable to the wavelength of THz photons, leading to a highly divergent beam. Moreover, since broadband THz pulses can contain significant spectral components corresponding to wavelengths ranging from for example 300 µm to 30 µm (1 THz to 10 THz), there is a big difference in $z_R$ and divergence angles for different wavelengths, resulting in an inhomogeneous distribution of frequencies at the focal spot. As an example, Fig. 5.2 presents the spot size of different spectral components when propagating through a typical optical system consisting of two lenses, calculated assuming Gaussian beam propagation. Not only are spot sizes at the focus position different, but there is also a big variation in the focus position along the propagation axis. A further complication when focusing

![Figure 5.2: Spotsizes of different THz spectral components when propagating through an optical system, calculated using Gaussian beam propagation. The Source diameter is 1 mm, both lenses (L1 and L2) each have a focal length $f = 0.1$ m. Arrows indicate the $z$ position of different focus positions, which vary a lot along $z$.](image-url)
Chapter 5: Generation and detection of terahertz frequency pulses

THz beams is connected to the poor available imaging options. In a lot of setups, off-axis parabolic mirrors are used for focusing, which can introduce severe aberrations [118]. Without a good image of the THz spot size, it is, however, difficult to improve the spot quality at the focus position.

5.2 Generation of terahertz pulses

Nowadays, numerous different methods for the generation of THz radiation have been demonstrated and, at least for spectroscopic applications, the THz gap appears to be fully closed. The generation of high peak electric fields needed for the use of THz radiation for resonant excitation in solid state systems can still be a challenge for parts of the THz spectrum, but huge advances have been made over the last few years. Table 5.1 gives a summary of selected high-field THz sources reported in the literature. All of the listed sources produce THz pulses, in most cases with sub-picosecond duration. While there are continuous-wave sources that emit in the THz range with considerable average power, the associated peak fields are much weaker than for pulsed sources. An example of a continuous-wave source is the quantum cascade laser based on semiconductor heterostructures [119].

Fundamental properties needed for the study of coherent structural dynamics and other coherences in a solid that can be probed in a phase-resolved way with ultrafast laser pulses is carrier-to-envelope phase (CEP) of the generated THz pulses, as well as stable synchronization to the probe pulse source. This is for example not easily provided for THz pulses generated via transition radiation of electron bunches.

The most promising generation methods for solid state applications that produce CEP stable pulses and can produce high peak field strengths are based on optical rectification (OR) and difference frequency generation (DFG) in nonlinear materials, two closely related processes. Pulses generated via OR were used for the experiments in Chap. 6 and the generation method is discussed in detail, accompanied by data taken in the laboratory at ETH. Terahertz generation using photoconductive switches is important for THz time domain spectroscopy and is briefly discussed.
## Table 5.1: Comparison of different generation methods for pulsed THz radiation. Different examples from the literature are chosen to showcase estimates of the highest field strengths that can currently be achieved with a certain method. Peak field strength, peak frequency and bandwidth crucially depend on the specific experimental setup and for the same generation method in the same material reported values can therefore vary a lot. In the table, the measured peak field is given. Note that the obtainable field strength at a focus position is in general much higher for higher frequencies for the simple reason that the diffraction limited spot size gets smaller. Furthermore, the reported field strength depends a lot on the quality of the optical systems used to focus the THz pulses and is therefore not inherent to the generation source. In principal the pulse energy is a better figure of merit to compare different sources, however detectors measuring pulse energies in the THz range are notoriously hard to calibrate.
5.2.1 Optical rectification in a nonlinear crystal

Femtosecond laser pulses generated by standard mode-locked lasers can have a spectral bandwidth close to $\Delta \nu = 10$ THz and can be amplified to very large pulse energies using a chirped amplification scheme. The different spectral components of a laser pulse can create a nonlinear polarization at THz frequencies in a crystal - a process usually referred to as optical rectification (OR).

In the following, the nonlinear generation process is first idealized as a simple example that introduces the main concepts of THz generation via OR. The full spectrum of a broadband laser pulse is simplified to the contribution of two monochromatic waves, which allows to discuss the fundamentals of the generation process. Following the simple example, an expression that can be used to calculate the generated THz spectrum by a real material is presented and important parameters of the conversion process are discussed.

In the simple example, we assume a scalar electric susceptibility $\chi(E)$ of the generation crystal, connecting the polarization $P$ and the applied electric field $E$ via $P = \chi(E)E$. For small applied fields $E$, to first order the value of the susceptibility does not depend on the field strength, $\chi(E) = \chi$, and we can use a linear relationship between $P$ and $E$:

$$P = \frac{\chi E}{P_{L}}$$  \hspace{1cm} (5.3)

For high applied fields, however, we have to expand $\chi(E)$ since higher order terms can no longer be neglected:

$$P = \chi^{(1)}E + \left(\chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots\right)$$  \hspace{1cm} (5.4)

Optical rectification corresponds to a second-order nonlinear process that is governed by $\chi^{(2)}$. It can therefore only occur in nonlinear media without inversion symmetry.

The nonlinear polarization can act as a source for radiation at frequencies different from the frequency of the initial driving field. If we assume an applied electric field given by the sum of two monochromatic fields oscillating at frequencies $\omega_1$ and $\omega_2$

$$E(t) = E_0 \cos(\omega_1 t) + E_0 \cos(\omega_2 t),$$  \hspace{1cm} (5.5)

the second-order nonlinear polarization $P_{NL} = \chi^{(2)}E^2(t)$ calculates to

$$P_{NL} = \chi^{(2)} \left(\frac{2E_0^2}{\text{DC}} + \frac{E_0^2}{\text{SHG}} \cos(2\omega_1 t) + \frac{E_0^2}{\text{DFG}} \cos(2\omega_2 t) + \frac{E_0^2}{\text{SFG}} \cos((\omega_1 - \omega_2)t) + \frac{E_0^2}{\text{SFG}} \cos((\omega_1 + \omega_2)t)\right)$$  \hspace{1cm} (5.6)

Neglecting higher orders, the nonlinear polarization $P_{NL}$ is given by the following terms: A constant polarization (DC) resulting from rectification of the applied fields, as well as second
harmonic generation (SHG) of the two frequency components of the applied field. Moreover, a component of \( P_{NL} \) oscillates at the difference frequency \( \omega_1 - \omega_2 \) (difference frequency generation, DFG) and another component oscillates at the sum frequency \( \omega_1 + \omega_2 \) (sum frequency generation, SFG).

The important term for THz generation by optical rectification is the DFG term\(^1\). If we consider a femtosecond laser pulse, the full nonlinear polarization contains DFG contributions of all frequencies contained in the bandwidth of the pulse. Neglecting all other material parameters, the possible obtainable THz bandwidth is therefore connected to the bandwidth of the driving laser pulse. For a transform-limited laser pulse with a Gaussian envelope function in time and FWHM-duration \( t_{\text{FWHM}} \), the FWHM-width of the spectrum \( \nu_{\text{FWHM}} \) is determined by \(^{131}\)

\[
t_{\text{FWHM}} \cdot \nu_{\text{FWHM}} = 0.441 \tag{5.7}
\]

Assuming for example pump pulses with a duration \( t_{\text{FWHM}} = 100 \, \text{fs} \), we can therefore roughly estimate that THz frequency pulses with a bandwidth \( \nu_{\text{FWHM}} = 4.4 \, \text{THz} \) can be generated.

In order to now give a realistic estimate of the THz spectrum emitted by a crystal via OR, the nonlinear polarization \( P_{NL} \) has to be evaluated for the complete broadband spectrum of a laser pulse and the propagation of the generated THz field through the nonlinear crystal must be taken into account. From \( P_{NL} \), the emitted THz spectrum can then be calculated. This calculation was performed by Schneider et al., leading to a rather lengthy description for the spectrum of the THz pulse after propagation through a length \( z \) of the generation crystal \(^{129}\): 

\[
E(\omega,z) = \frac{\mu_0 \omega \chi^{(2)} I_0(\omega)}{n(\omega_0) \left( \frac{c}{\omega} \left( \frac{\alpha_T(\omega)}{2} + \alpha_0 \right) + i(n(\omega) + n_g) \right)} \\
\exp \left( -i \frac{\omega n(\omega)}{c} z \right) \exp \left( -i \frac{\omega n_g}{c} z \right) \exp(-\alpha_0 z) \exp \left( -\alpha_T(\omega) \frac{c}{2} z \right)
\tag{5.8}
\]

Here, \( I_0(\omega) \) is the spectrum of the laser pulse with center frequency \( \omega_0 \), \( n(\omega) \) is the refractive index, \( n_g \) is the optical group index (assumed to be dispersionless), \( \alpha_T(\omega) \) and \( \alpha_0 \) are the absorption coefficient for THz frequencies and frequencies within the laser pulse, respectively.

This equation gives a lot of insight into the emitted THz spectrum and also on how to select a nonlinear crystal for efficient THz generation. Looking at the equation, it becomes apparent how parameters like crystal thickness, pump wavelength etc. have to be chosen:

(i) **Large second order nonlinearity** Clearly, \( \chi^{(2)} \) has to be as large as possible for efficient THz generation. For simplicity, to this point we assumed that Eq. 5.4 can be written as a scalar

\(^1\)Typically, THz generation via DFG of two laser pulses with different center wavelengths is referred to as *difference frequency generation* in the literature. The fundamental mechanism behind optical rectification and difference frequency generation is however exactly the same.
equation. In the general case, a tensor description using a third rank tensor \( \chi^{(2)}_{ijk} \) is needed. For the experimental realization, this means that the polarization of the laser pulses with respect to the axis with a high second-order nonlinearity are crucial and determine the efficiency of the conversion as well as the polarization of the generated THz pulses.

(ii) **Velocity matching** The length along \( z \) where THz radiation is efficiently generated depends critically on the term \( n(\omega) - n_g \) in the second fraction in equation 5.8. Achieving the condition \( n(\omega) \approx n_g \) is called velocity matching or phase matching. What this actually means is that if the phase velocity of the generated THz radiation and the group velocity of the laser pulse are different, generated THz radiation from different points along \( z \) will not constructively interfere and, for a too large velocity mismatch, can even reduce the generated THz field before reaching the end of the crystal. The length for which efficient THz generation is possible is usually called the coherence length. A full expression for the effective generation length for OR in a nonlinear crystal can be found in [129].

If the pump wavelength cannot be tuned in a way that the phase matching condition is met, a widely used scheme is to apply pulse-front tilting of the optical laser pulses. This scheme is most prominently used for optical rectification of high-energy 800 nm pulses in LiNbO\(_3\) [132, 123]. In Tab. 5.2, pump wavelengths that allow for velocity matching in the THz region are listed for several widely-used generation crystals.

(iii) **Scaling with input power** The spectral amplitude of the THz field \( \mathbf{E}(\omega, z) \) scales linearly with the intensity of the pump pulse. Scaling the THz field strength is therefore possible using high laser pulse energies, putting several demands on an experimental realization: First, large pulse energies must be obtainable at pump wavelengths suitable to achieve velocity matching in the generation crystal. Second, the generation crystal must withstand high fluences without degradation. If large-aperture crystals can be grown, the fluence on a crystal can also be reduced by increasing the spot size on the crystal.

(iv) **Material absorption** Strong lattice resonances leading to absorption \( \alpha_T(\omega) \) in spectral regions of the generated THz radiation will strongly suppress the THz output. Moreover, strong absorption over the bandwidth of the laser pulse also reduces the generated field strength. Strong absorption of the pump pulses can also lead to damage for high pump fluences.

In Tab. 5.2 the most common materials used for generation of low frequency THz (1 – 5 THz) pulses are summarized, focusing on the discussed properties. It is evident that the organic crystals DAST, DSTMS and OH1 possess the largest EO coefficient. The phase matching region in these crystals, however, does not extend to the fundamental output of a Ti:sapphire laser, requiring further frequency conversion of pump pulses for high field generation.
5.2 Generation of terahertz pulses

### Material | EO coefficient (pm/V) | phonon modes (THz) | velocity matching wl. (nm)
---|---|---|---
GaP | $r_{41} = 0.88$ | 11 | 800
ZnTe | $r_{41} = 3.9$ | 5.3 | 800
LiNbO$_3$ | $r_{33} = 30.8$ | 7.7 | *(–)*
DAST | $r_{11} = 47$ | 1.1 | 1500
DSTMS | $r_{11} = 50$ | 1 | 1500
OH1 | $r_{11} = 52$ | 2.6 | 1300

Table 5.2: Comparison of commonly used material for optical rectification. The EO coefficient $r_{ijk}$ is related to $\chi^{(2)}_{ijk}$ via $\chi^{(2)}_{ijk} = -\frac{1}{2} n_j^2 (\omega_0) r_{jki}(\omega_0; \omega)$ where $n_j$ and $n_k$ are the refractive indices along the axes $j$ and $k$ [129]. It is typically reported in literature. Only the largest elements of $r_{ijk}$ are given in the table. The values of $r_{ijk}$ correspond to the given wavelengths, were velocity matching is fulfilled. Only phonon modes with a large associated oscillator strength are given. Material constants as published in [133, 129, 134, 135].

*–*: Velocity matching can only be achieved via pulse-front tilting.

5.2.2 High-field terahertz generation in organic crystals

As demonstrated in the previous section, organic crystals show great promise for high field THz generation in the range of 1 – 5 THz, covering a lot of low-lying phonons in different solid state materials. The organic crystal DAST (4-N,N-dimethylamino-4’-N'-methyl-stilbazolium tosylate) was first optically characterized in 1996 [136] and immediately sparked interest for electro-optic applications owing to its large nonlinear coefficients. DSTMS$_2$ and OH1$_3$ were synthesized and characterized later [133, 134]. The different organic crystals are similar in the value of the largest electro-optic (EO) coefficient and differ in the absorption spectrum and phase-matching conditions (see Tab. 5.2).

To achieve phase-matching in a collinear geometry, typically pulses from a Ti:sapphire laser are converted to wavelengths between 1200 nm and 1500 nm in an optical parametric amplifier (OPA). Since good phase-matching can be achieved over a quite broad range using DAST and DSTMS, the OPA can be operated at the wavelength with the highest power output or the best stability in this wavelength range without losing conversion efficiency. Figure 5.3 shows the transient electric field of a THz pulse generated with 1450 nm pulses with a duration of 80 fs and the corresponding spectrum. Figure 5.3 (b) shows the basic generation setup. Using a $\lambda/2$ waveplate to control the polarization of the OPA beam, the THz polarization can be set arbitrarily by rotating the crystallographic $a$-axis of the crystal and adjusting the OPA polarization accordingly. The simple collinear generation scheme and the complete control of the THz polarization presents a tremendous advantage over generation schemes where pulse-front tilting has to be applied to achieve velocity matching.

Crystallization of these organic crystals is mainly based on solution growth and it is possible...

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24-N,N-dimethylamino-4’-N'-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate
32-[3-(4-hydroxystyryl-5,5-dimethylcyclohex-2-enylidene)malononitrile
Figure 5.3: Generation of THz pulses in the organic crystal DSTMS. Pulses were generated with 1450 nm pulses with a pulse energy of 1.2 mJ in a 590 µm thick DSTMS crystal in the ETH laser laboratory. (a) Transient electric field measured with EO sampling in GaP (see Sec. 5.3.1). (b) Spectral amplitude of the THz pulse. Absorption due to a TO phonon is clearly visible as a dip in the spectral amplitude around 1 THz. (c) Schematics of the collinear generation geometry that allows for full control of the linear THz polarization.

5.2.3 Other pulsed sources

Photoconductive (PC) switches or PC antennas are mostly used for the generation of THz pulses for applications in THz time-domain spectroscopy.

A femtosecond laser pulse hits a semiconductor between two electrodes to which a DC bias is applied. Since the photon energy is larger than the semiconductor band gap, electron-hole pairs are generated between the electrodes and the conductivity is rapidly switched on. The current arising from accelerated free carriers in the DC field as well as their decay by scattering events result in the radiation of a sub-picosecond THz pulse. Terahertz pulses can be efficiently generated already with small laser pulse energies, making PC switches the most widely-used pulsed THz source for oscillators and high-repetition rate laser systems. However, the usable...
5.3 Detection of terahertz pulses

The energy of a 1 THz photon corresponds to 4.1 meV and is thus smaller than the kinetic energy given to a degree of freedom at room temperature. Detectors relying on the creation of electron-hole pairs in a semiconductor can therefore not be used in the THz range, and thermal detectors operate close to the thermal noise floor and typically only work well with intense THz

These quantities depend on the pulse energy and duration as well as intrinsic timescales of the PC switch material.

bandwidth is typically limited to below $3 - 4$ THz, peaking at around 1 THz.\footnote{These quantities depend on the pulse energy and duration as well as intrinsic timescales of the PC switch material.} Figure 5.4 shows a THz pulse generated in a GaAs PC switch. Although there exist schemes to use large-aperture

![Figure 5.4: Example of the (a) the electric field and (b) the corresponding spectrum of a THz pulse generated in a PC switch made of GaAs. Taken from [137].](image)

PC switches or arrays of PC switches [125], scaling up the THz field strength is difficult and PC switches are rarely used for high field applications.

One of the main disadvantages of all generation methods described up to now lies in the fact that they all rely on solid state generation media, in which lattice resonances often lie in or close to the emitted THz spectrum. This problem can be evaded by generating THz pulses from air plasma [138]: Focusing a laser pulse and its second harmonic into air creates a plasma filament that emits sub-picosecond, extremely broadband THz pulses. The underlying mechanism is still not fully understood, but using 1850 nm pulses from a high-energy OPA, field strengths of up to 4.4 MV/cm could be generated, making it a viable alternative for spectroscopic and high-field applications [126].

5.3 Detection of terahertz pulses

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radiation. The most widely-used method for the characterization of sub-picosecond THz pulses is electro-optic (EO) sampling, which furthermore especially stands out for its capabilities to detect amplitude and phase of the transient field of a THz pulse $E_{\text{THz}}$ in the time domain as well as the possibility to calibrate the measured field strength.

### 5.3.1 Electro-optic sampling of terahertz pulses

The basic idea behind EO sampling is to characterize the transient change in birefringence created by the electric field of a THz pulse in a nonlinear crystal with a femtosecond laser pulse. The change in birefringence is based on the Pockels effect: putting aside anisotropy and polarization effects for the moment, an applied electric field $E$ can change the refractive index $n$ of a medium by

$$\Delta n = n^3 r E$$ (5.9)

where $r$ is the effective electro-optic coefficient for a certain geometry. If a transient field $E(t)$ is applied to the crystal, the change of birefringence can be measured by copropagating a probe pulse through the nonlinear crystal and detecting changes in polarization. Figure 5.5 shows a standard setup for EO sampling in a transmission geometry.

![Figure 5.5: Schematics of EO sampling in transmission geometry with co-propagating THz pulse $E_{\text{THz}}(t)$ and probe pulse with a corresponding intensity $I_p$. PBS: polarizing beam splitter.](image)

A THz pulse and the probe pulse (intensity $I_p$) propagate through the EO crystal. After the crystal, the probe pulse is split into two orthogonal polarization channels by a polarizing beamsplitter. The difference in intensity of the two polarizations is measured by a balanced photodiode. The $\lambda/4$ waveplate is rotated such that when there is no temporal overlap between probe and $E_{\text{THz}}$, the balanced detector measures zero output ($\Delta I_p = 0$). When the probe pulse and $E_{\text{THz}}$ are spatially and temporally overlapped in the crystal, the transient birefringence induced by $E_{\text{THz}}$ causes a change in polarization of the probe beam. The balanced detector then has a nonzero output $\Delta I_p$.

---

5EO sampling can be explained more rigorously as a frequency mixing process between gate-pulse photons and THz photons, an approach which furthermore better highlights the close connection between EO sampling and THz generation via OR [139][140]. The simple Pockels picture is however fully sufficient to derive the results needed for field calibration of low-frequency THz pulses.
In order to connect the measured $\Delta I_P$ to the actual field amplitude $E_{\text{THz}}(t)$ equation, Eq. 5.9 is not sufficient and we have to take the anisotropy of the nonlinear medium and the polarization of the applied electric field into account. The refractive-index ellipsoid is given by [141]

$$\left(\frac{1}{n^2}\right)_1 x^2 + \left(\frac{1}{n^2}\right)_2 y^2 + \left(\frac{1}{n^2}\right)_3 z^2 + 2 \left(\frac{1}{n^2}\right)_4 yz + 2 \left(\frac{1}{n^2}\right)_5 xz + 2 \left(\frac{1}{n^2}\right)_6 xy = 1 \quad (5.10)$$

where $x, y$ and $z$ define a cartesian system in the crystal and are in the following chosen to coincide with the (100), (010) and (001) axes. The change of the refractive index along one of the axis when a field is applied is given by [141]

$$\Delta \left(\frac{1}{n^2}\right)_i = \sum_{j=1}^3 r_{ij} E_j \quad (5.11)$$

where the electric field and the changes in refractive index are now connected by a second-rank tensor $r_{ij}$. The most widely used crystals for EO sampling, (110)-ZnTe and (110)-GaP, have only one nonzero element of $r_{ij}$, resulting in [142]:

$$\Delta \left(\frac{1}{n^2}\right)_i = 2 E_x(t) r_{41} yz + 2 E_y(t) r_{41} xz + 2 E_z(t) r_{41} xy \quad (5.12)$$

It is evident that the index ellipsoid does not coincide with the coordinate axes. Planken et al. [142] used this equation as a starting point to calculate the intensity difference in the probe beam after passing through a crystal of length $L$ for small electric field strengths:

$$\Delta I(\alpha, \phi) = \frac{I_p \pi n_0^3 E_{\text{THz}} r_{41} L}{\lambda L} \left(\cos \alpha \sin 2\phi + 2 \sin \alpha \cos 2\phi\right) \quad (5.13)$$

The angles $\alpha$ between $E_{\text{THz}}$ and the $z$-axis and $\phi$ between the field of the probe pulse $E_P$ and the $z$-axis that are defined as shown in Fig. 5.6. The probe wavelength is $\lambda$, $n_0$ corresponds to the probe refractive index. The maximum modulation amplitude $\Delta I_P$ is measured for $E_P \perp E_{\text{THz}}$ and $E_P || E_{\text{THz}}$. Assuming such a geometry and taking the THz transmissivity $t$ into account, the measured field strength can be written as:

$$E_{\text{THz}} = \frac{\Delta I_P}{I_P} \frac{\pi \lambda_L}{L r_{41} n_0^3 t} \quad (5.14)$$

Table 5.3 lists all material constants necessary for quantifying $E_{\text{THz}}$ via EO sampling in ZnTe and GaP for $\lambda_L = 800$ nm. Typical crystal thicknesses used for EO detection lie in the range 50 – 500 µm. While ZnTe has a roughly four times higher $r_{41}$, the absence of a lower lying TO phonon often makes GaP a better choice for detection in the range of 1–5 THz. The refractive index in ZnTe in this range shows some dispersion related to the 5.3 THz TO mode.
<table>
<thead>
<tr>
<th>Material</th>
<th>$r_{41}$ (pm/V)</th>
<th>$n_0$</th>
<th>$t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>0.88</td>
<td>3.2</td>
<td>0.46</td>
</tr>
<tr>
<td>ZnTe</td>
<td>3.9</td>
<td>2.8</td>
<td>0.52</td>
</tr>
</tbody>
</table>

**Table 5.3:** Constants necessary for characterizing THz field strengths using GaP or ZnTe. The THz field transmittivity $t$ is given for normal incidence at 1 THz. For a more precise field reconstruction, dispersion of the listed quantities has to be taken into account.

For larger field strengths, usually the expression

$$E_{\text{THz}} = \sin^{-1} \left( \frac{\Delta I_P}{I_P} \right) \frac{\lambda_L}{2\pi L r_{41} n_0^3 t}$$  \hspace{1cm} (5.15)

is used. If field strengths get too high, it becomes necessary to attenuate the THz pulses before EO sampling or to use a thinner EO crystal to avoid saturation. There are several other factors making a thinner detection crystal more desirable: First, Velocity mismatch between the probe pulse and the THz electric field decreases the effective interaction volume. The interaction volume can further be decreased by different beam divergences of THz and probe pulse. Moreover, absorption in the THz range can distort the measured spectrum.

These effects are usually not taken into account when field strengths are reported in the literature, and reported values should typically be used as a lower bound of the actual field amplitude at the sampling position. An extensive analysis of dispersion effects and the associated observed field distortions is given in [147].

**Figure 5.6:** Relative orientation of the $z$-axis, the electric field of the THz-pulse $E_{\text{THz}}$ and the field of the probe pulse $E_P$ on a (110)-cut EO crystal.

### 5.3.2 Time-averaged detection

There are several different detection schemes based on the time-averaged energy deposited by THz radiation into an absorbing element of a detector. The change in temperature of the absorbing element induces a change in a certain measurable quantity like resistivity or pressure. The nature of these detectors makes their response time quite slow, with timescales associated with heat transport in the active volume being the limiting factor. These detectors are therefore best suited for continuous-wave THz radiation, but using lock-in methods, they can also be utilized to detect
5.4 Terahertz time-domain spectroscopy

THz pulses at lower repetition rates.

In bolometers, temperature changes in the absorbing element are measured as a change in resistivity. Bolometers typically have to be cooled to low temperatures for increased sensitivity [148]. In a Golay cell, the heat of the absorbing element is transferred to a gas and the change in pressure is measured [149].

A pyroelectric detector can observe changes in absorbed radiation levels by measuring changes in polarization of a pyroelectric material coupled to the absorbing element. Combined with a chopper and lock-in detection, it is the most flexible detector for the characterization of ultrafast THz pulses.

In principle, the peak field strength of a THz pulse can be calculated from the output of one of these detectors, using the repetition rate of the source and the connection between pulse energy $W_P$ and the electric field $E_{\text{THz}}$.

$$W_P = c\varepsilon_0 A \int |E_{\text{THz}}(t)|^2 dt$$  \hspace{1cm} (5.16)

where $A$ is the THz spot size, $c$ is the vacuum speed of light and $\varepsilon_0$ is the vacuum permittivity. It is, however, difficult to precisely calibrate thermal detectors in the THz spectral range. They often show nonlinear and frequency dependent behavior, which is especially problematic when characterizing intense broadband THz pulses [150].

5.4 Terahertz time-domain spectroscopy

The advances in THz sources and detectors have made THz radiation an important and often unique tool for imaging and spectroscopic applications in numerous areas of science and technology. A review detailing applications in areas ranging from biological sensing to homeland security can be found in [151]. Terahertz time-domain spectroscopy has become one of the most widely used tools to study infrared active elementary excitations in the solid state.

With THz time-domain spectroscopy (THz-TDS), the spectral changes of a broadband, phase-stable THz pulse after interaction with a sample are measured and compared to a reference pulse. Since both amplitude and phase information of the spectrum can be evaluated, the method in principle allows for a model-independent determination of the refractive index of a material in the THz range. This presents a great advantage to approaches based on Kramers-Kronig modelling [152] like Fourier-Transform spectroscopy. THz-TDS has become a widely used technique for the study of solid state systems, in correlated systems especially the possibility to introduce a pump pulse and study the spectral changes in the nonequilibrium state have produced intriguing results [153, 55]. The spectral contents of typical broadband THz pulses also make it an ideal tool to study low-lying phonon modes in solids.

The schematics of a typical THz-TDS setup are shown in Fig. 5.7. Depending on the required bandwidth and the available laser system, THz pulses are typically generated employing
a photoconductive switch or optical rectification in a nonlinear crystal. They are then focused
on a sample and, depending on the chosen geometry, either the reflected or the transmitted part
of the THz spectrum is detected employing EO sampling or a photoconductive switch.

The measured THz spectrum is then compared to a reference spectrum. In transmission
geometry, this is simply the detected THz pulse after taking the sample out of the beam path. In
reflection geometry, the sample has to be replaced by a reference material with known refractive
index (usually an uncoated metal mirror) in order to acquire a reference signal. In reflection

\[ \frac{E_{\text{sam}}(\omega)}{E_{\text{ref}}(\omega)} = \frac{\sqrt{R(\omega)}}{\sqrt{R_{\text{ref}}(\omega)}} \exp(-i\Delta \phi(\omega)) \]

(5.17)

Here, \( R \) and \( R_{\text{ref}} \) are the amplitude of the reflection coefficient of sample and reference, \( \Delta \phi \) and
\( \Delta \phi_{\text{ref}} \) are the change in phase for sample and reference, \( n \) and \( n_{\text{ref}} \) correspond to the refractive
index for sample and reference. In this description, internal reflections are neglected.\(^6\) A similar
expression can be derived for transmission geometry \(^7\) Measurements in transmission
geometry become increasingly difficult for materials that are strongly absorbing in the THz range,
which is an inherent characteristic of systems featuring strong THz resonances. This often makes
the reflection geometry necessary, which introduces several experimental difficulties.\(^8\)

- For a reliable measurement, sample and reference surface need to be positioned with an
  error of less than < 1 µm to avoid phase errors and changes in reflectivity due to alignment
  changes. In \(^9\) uncertainties in the refractive index due to positioning uncertainties are

---

\(^6\)This is usually a good approximation, since typically only strongly absorbing materials are studied in a
reflection geometry.

\(^7\)In transmission, multiple reflections usually have to be treated in detail in order to achieve reliable results.

\(^8\)Some of the introduced experimental difficulties like aperture effects and instabilities are also relevant in
transmission geometry.
5.4 Terahertz time-domain spectroscopy

calculated. Furthermore, steps in the sample surface or a non-flat surface will distort the results as well.

- The focus spot sizes in the low THz range can be larger than a millimeter (see Sec. \[5.1\]). The sample surface needs to be homogeneous over a comparable area. Even slight clipping of the beam or unstable apertures will distort the measurement.

- Since the sample and the reference mirror have to be exchanged during measurements, the THz spectrum, the setup and ambient conditions have to be kept absolutely stable over an extended period of time. Quick modulations between sample and reference as they are possible in a pump-probe measurement cannot be achieved in THz-TDS measurements.

The listed experimental difficulties make THz-TDS in reflection a challenging experiment. An alternative to study THz phonons in strongly absorbing solids that are both infrared and Raman active is presented in Chap. 6. For these measurements, a THz pump pulse is used to coherently excite a lattice vibration in a solid, which can then be studied phase-resolved with a near-infrared probe.
Coherent phonon spectroscopy using resonant terahertz excitation

The excitation of coherent phonons by femtosecond light pulses has become an important tool in the investigation of the solid state. The fundamentals of the generation and detection of coherent phonons are explained in detail in Chap. 2. Time-resolved coherent phonon spectroscopy based on ultrafast Raman scattering has for example been used to investigate the spectrum of $q = 0$ Raman active modes in the ground state in various broken symmetry compounds (see for example [42, 156, 30, 68]) and can, in some cases, yield spectroscopic information far superior to traditional static Raman spectroscopy. Spectroscopic studies typically are carried out with small excitation fluences in order to study a system as close to thermal equilibrium as possible. Nevertheless, an above-bandgap excitation pump pulse will always deposit a significant amount of energy into the electronic system in addition to driving a coherent lattice motion via an ISRS process.

This fact becomes especially problematic when a large-amplitude coherent motion is desired: While with above-bandgap excitation a strong coupling to coherent motion through a change in deformation-coupling can be achieved, the coherent motion is accompanied by high concentrations of excited free carriers and consecutive changes in the lattice potential. This can in some cases be desired, for example when coherent phonons are studied during an ultrafast photoinduced transition triggered by the pump pulse [109, 37], or when studying pump-induced softening of the frequency of the coherent motion. It prevents, however, the possibility to scale up the amplitude of the coherent motion, as raising the pump fluence will lead to a highly nonequilibrium electronic system and even sample damage. Phenomena like phonon-phonon coupling in the large-amplitude limit can therefore in most cases not be accessed with above-bandgap excitation.

An alternative to using above-bandgap excitation to drive large-amplitude coherent lattice motion lies in the resonant excitation of IR active phonons in solids as described in Sec. 2.2.2. Resonant coupling to a polar lattice mode allows the efficient transfer of energy into the coherent motion without exciting the electronic system when absorption features are only determined by
lattice resonances. In the past, experiments based on the resonant excitation of zone-center IR active optical phonons were hampered by the lack of sources of intense THz radiation with spectral content covering the typical range of frequencies of optical phonon modes in solids. Advances in THz generation methods like optical rectification in organic crystals (see Sec. 5.2.1) can now generate significant electric field strengths at frequencies covering low-lying phonons (1–5 THz) in solids. Terahertz pulses in this frequency range have been used to excite various other elementary excitations in solids, for example electromagnons in a multiferroic [96] and antiferromagnetic spin waves [157]. While with mid-IR pumping the off-resonant coherent excitation of a 5.8 THz mode via ionic Raman scattering has been demonstrated in a manganite [24], so far there exists no work on resonant excitation and coherent detection of a polar lattice mode.

In this chapter, the resonant excitation of large-amplitude non-fully symmetric modes using resonant THz excitation of single-crystal tellurium (Te) is demonstrated. The experiments were performed using intense THz pulses generated in an organic crystal in combination with an anisotropic detection scheme that allows to phase-resolve the coherent motion associated with the excited modes by measuring the polarization changes of laser pulses reflected from the sample surface.

The chapter begins with a discussion of relevant material properties of Te as well as a summary of previous time-resolved experiments focusing on the structural dynamics in Te. Following a detailed description of the experimental setup for the resonant THz excitation measurements, anisotropic reflectivity traces showcasing a resonant excitation of lattice modes are presented and polarization control of the coherent motion is demonstrated. A model based on the sum of damped harmonic oscillators driven by the electric field of the THz pulse inside the crystal is presented in Sec. 6.2.4. To complete the picture of the energy transfer from the THz electric field into the lattice, results on THz induced strain waves are discussed in Sec. 6.2.5.

Finally, preliminary time-resolved x-ray diffraction measurements are presented. In these measurements, no signal could be observed, but the methodology is still useful for possible experiments in the future. The chapter concludes with an outlook into further opportunities given by coherent phonon spectroscopy employing THz excitation.

Parts of the results presented in this chapter have been published in the following manuscript:

**T. Huber, M. Ranke, A. Ferrer, L. Huber, and S. L. Johnson,**

*Coherent phonon spectroscopy of non-fully symmetric modes using resonant terahertz excitation.*


### 6.1 Coherent phonons in tellurium

There are a number of reasons why Te presents an ideal model system to test the idea of resonant excitation of coherent phonons using intense THz pulses: (i) tellurium lacks inversion symmetry
and can therefore support phonon modes that are both infrared (IR) and Raman active, (ii)
tellurium is a narrow-bandgap semiconductor with a bandgap of 0.33 eV, which ensures that
THz photons will not excite electron-hole pairs and absorption features in the low THz range
are exclusively determined by phonon modes, and (iii) coherent phonons in tellurium have been
studied extensively using above-bandgap excitation, making it possible to compare the observed
dynamics to results from a number of different experiments.

In the following, material properties relevant to the experiment are discussed and an overview of
previously conducted time-resolved measurements in Te is given. An excellent book summarizing
the properties of tellurium, that to this day remains the definitive work on its equilibrium solid
state physics was written by P. Grosse [8]. It was apparently he who once said that to really
gain a deep understanding of general solid state physics, at least once in your life you have to
have studied the physics of Te.

Tellurium crystallizes with trigonal symmetry and has spacegroup $P3_121$ (or the enantiomor-
phic $P3_221$, depending on the helicity of the helical chains of atoms along the $c$-axis). The
primitive unit cell contains three atoms, which are arranged in a helix around the $c$-axis of the
system [159]. A depiction of the crystal structure of Te is shown in Fig. 6.1. In a hexagonal cell,
the cell parameters are given by $a = 4.456$ Å and $c = 5.921$ Å [159]. To assign lattice planes in a
hexagonal system, in the literature a notation with an additional Miller index is widely used.
Following this notation, a plane is described by $(hkil)$, with the third index $i = (-h + k)$ being
redundant. In this work, lattice planes in Te are just labeled using the conventional $(hkl)$ indices.

![Figure 6.1: Crystal structure of tellurium. The box corresponds to the trigonal unit cell. (a)
Side view revealing the helical chains of atoms along the $c$-axis. (b) View along the $c$-axis. Figures are based on unit cell data published in [159].](image)

The optical $q = 0$ optical eigenmodes of Te can be best understood when looking along
the crystallographic $c$-axis at a projection of three atoms in the helical chain. From this angle
of view they constitute an equilateral triangle. A depiction of the atomic movements in the

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1Private communication with T. Dekorsy.
plane perpendicular to the $c$-axis associated with each mode is shown in Fig. 6.2. One of these modes is a fully symmetric, Raman active $A_1$ mode (3.6 THz), the so called breathing mode of the structure. The crystal structure of Te only slightly deviates from a cubic structure and the $A_1$ mode connects its trigonal structure to the higher symmetry cubic structure [8]. The degenerate $A_2$ mode is IR active only and splits into a TO and an LO mode with internal polarization $\vec{E} \parallel \vec{c}$ and frequencies $A_{2,\text{TO/LO}} : 2.6/2.82$ THz. Finally, and most importantly for this work, there are two degenerate non-fully symmetric modes that are both IR and Raman active. The frequencies of these modes are $E'_{\text{TO/LO}} : 2.76/3.09$ THz and $E''_{\text{TO/LO}} : 4.22/4.26$ THz and the internal polarization of the associated dipole moment is $\vec{E} \parallel \vec{c}$. The atomic displacement associated with the LO modes is along the $c$-axis, while the atomic displacement associated with the TO modes lies in a plane perpendicular to the $c$-axis. Lattice modes in Te were first characterized via the Restrahlen effect and Raman spectroscopy (see for example [8, 160]).

It is interesting to note that elemental Te with its three identical atoms per unit cell in fact presents the simplest structure that still supports polar modes. The occurrence of IR active modes can be explained by a rearrangement of electronic charge during vibration, an in detail description of the properties of the dynamic charge is given in [161].

Tellurium was one of the first solid state systems in which coherent phonons generated by femtosecond laser pulses where studied. The fully symmetric $A_1$ mode can be excited using above-bandgap excitation and exploiting deformation potential coupling (see [162] and Sec. 2.2.1), while the $E$ modes can be excited via the ultrafast buildup of a photo-Dember field [23]. Using high excitation fluences, it was furthermore observed that the frequency of the excited mode softens, a consequence of changes in electronic bond strengths after excitation of large numbers of carriers above the bandgap [12].

A complete reconstruction of the unit cell after femtosecond excitation using time-resolved x-ray diffraction showed that only the $A_1$ mode is excited to significant amplitude after pho-
to excitation with a fluence that already leads to considerable $A_1$ mode softening. No signature of $E$ modes could be observed in these experiments. Figure 6.3 shows the isotropic transient reflectivity change associated with the $A_1$ coherent phonon after excitation with an above-bandgap femtosecond laser pulse, details on the experimental setup are given in the caption of the figure. The coherent oscillation is superimposed on a background that relaxes on a picosecond timescale and then remains at a level of around $\Delta R/R_0 = 4 \times 10^{-3}$ for a delay $t = 10$ ps. This background is related to electronic relaxation processes initiated by electrons that are promoted above the bandgap by photons of the pump pulse.

The modulation of reflectivity after excitation of a coherent motion of atoms $Q(t)$ along a certain phonon eigenvector is based on the dependence of the electronic susceptibility $\chi$ on $Q(t)$ for Raman active modes, as explained in detail in sec 2.2.1. The resulting reflectivity change $\Delta R$ can be calculated using Eq. 2.9. The $A_1$ mode has a fully symmetric Raman tensor $(\partial \chi/\partial Q)_{uv}$ with nonzero elements on the diagonal only. If the reflectivity changes of two orthogonal polarization channels are subtracted, transient changes associated with the $A_1$ mode and isotropic electronic relaxation processes are canceled out. Since the Raman tensor associated with the $E$ modes has off-diagonal elements (see Eq. 2.8), subtraction of orthogonal polarization channels does not cancel out the respective reflectivity modulation and the $E$-modes can be accessed with almost no background signal.

Figure 6.4 shows a comparison of isotropic and anisotropic reflectivity changes after above-bandgap photoexcitation taken from [23]. The applied excitation fluences are much lower than those used for Fig. 6.3, resulting in a much smaller isotropic reflectivity change and a smaller
contribution related to electronic relaxation processes to the signal. The measured change in anisotropic reflectivity associated with the $E$ modes is nearly two orders of magnitude smaller than the isotropic reflectivity change. In the vicinity of time zero, there is a fast component of the signal much larger than the beating structure associated with the $E$ modes. It originates from electronic processes that are not completely canceled in the anisotropic detection channel.

![Figure 6.4: Comparison of the isotropic and anisotropic reflectivity change in an all-optical pump probe experiment. Taken from [23].](image)

### 6.2 Optical probing of resonantly excited structural dynamics

The fundamental idea of the experiments presented in the following is the resonant excitation of large-amplitude, non-fully symmetric coherent phonons in Te. Owing to the below-bandgap excitation pulses, negligible perturbations of the electronic system can be expected. Since $E$ modes in Te are both Raman and IR active, the changes in anisotropic reflectivity after resonant THz excitation can be accessed with near-infrared laser pulses.

#### 6.2.1 Experimental setup

For the experiments, a 1 kHz laser system based on a mode-locked Ti:Sapphire oscillator and several amplification stages was used. The laser system and the high-energy optic parametric amplifier (OPA) used for wavelength conversion is described in detail in the appendix A.1. The output pulses of the system can have pulse energies up to 20 mJ and a FWHM pulse duration of around 90 fs at a wavelength of 800 nm. The high pulse energies are required for the generation of intense THz pulses via optical rectification in an organic crystal as described in Sec. 5.2.1. The setup for the measurements is detailed in Fig. 6.5.
For the generation of THz pump pulses, 1.4 mJ pulses with a pulse duration $t_{\text{OPA}} = 80$ fs from the OPA that is driven with 8 mJ pulses from the laser are sent into the setup. As a generation crystal, a 590 µm thick DSTMS crystal with a 6 mm diameter is used. The OPA beam is collimated onto the DSTMS crystal with a spot size slightly smaller than the diameter of the generation crystal. In combination with a $\lambda/2$ wave plate right before the crystal mounted in a rotation mount, the linear polarization of the generated THz pulses can be arbitrarily set. In front of the generation crystal, a mechanical chopper modulates the pump beam at a frequency of 500 Hz. The beam modulation allows for pump on / pump off subtraction. In addition, chopping the OPA beam reduces the thermal load on the organic generation crystal, which can quickly develop cracks for too high excitation fluences [120]. To rapidly estimate the pulse energy of the generated THz pulses, a pyroelectric detector with an active area of 9 mm can be placed right after the generation crystal. After the generation crystal, a lowpass filter made of Polytetrafluorethylen (Teflon) blocks residual infrared radiation. A wiregrid polarizer (a grooved polyethylene wafer with a metal coating) is used to set the THz polarization. Finally, the THz radiation is focused by an off-axis parabolic gold mirror with a focal length of 101.6 mm onto the sample. The resulting $1/e^2$-spot size at the sample position is 600 µm, as measured with an uncooled microbolometer array camera. The entire THz beam path is enclosed in a chamber.
purged with $N_2$ to reduce the effects of water absorption on the spectrum of the THz pulses.

For the probe pulses, a fraction (about 1 µJ pulse energy) of the fundamental output of the laser is branched off before the remaining part enters the OPA for wavelength conversion. The probe pulses first pass a motorized delay stage before they are focused onto the sample through a 1.5 mm-diameter hole in the parabolic mirror, resulting in a $1/e^2$ spot size of 150 µm. The polarization of the probe pulses is set by a thin film polarizer before the beam passes the hole in the parabolic mirror.

The experimental setup is constructed in a way so that two measurement modes can be realized with minimal changes to the setup: (1) characterization of the electric field of the THz pulses via EO sampling in transmission and (2) THz pump measurements with the probe beam being transmitted or reflected by the sample. The pump beam does not have to be changed at all switching from mode (1) to mode (2), ensuring that the electric field of the THz pulses measured via EO sampling closely resembles the field used for THz pump measurements. After the sample or the detection crystal, respectively, probe pulses are split into two orthogonal polarization channels by a Wollaston prism. The intensities associated with the different polarizations are measured with a balanced photodiode. To change between EO sampling and a THz pump measurement, the detection crystal has to be replaced by the sample and a mirror has to be inserted into the detection arm on a prepositioned magnetic mount.

The balanced photodiode is fed into a voltage preamplifier which is connected to a data acquisition card. The data acquisition scheme is described in detail in the appendix (Sec. A.2).

Electro-optic sampling measurements in transmission were carried out with a (110)-GaP crystal with a thickness $L = 100$ µm. Figure 6.6 shows a time trace of the transient electric field of the THz pulse and the corresponding spectrum. The field strength calibration was done according to Eq. 5.15 using material constants as listed in Tab. 5.3 for GaP. The measured peak modulation was $(I_1 - I_2)/(I_1 + I_2) = 0.63 \pm 0.02$. Here, $I_1$ and $I_2$ are the intensity of the two orthogonal polarization channels separated by the Wollaston prism. The corresponding peak field strength is given by $E_{\text{THz}}^{\text{peak}} = 0.64 \pm 0.02$ MV/cm. The error is calculated from pump and probe fluctuations, and it is important to keep in mind that the reported value presents a lower boundary of the field (see also Sec. 5.3.1). The spectrum of the THz pulses is centered around $\nu = 2.6$ THz and has a FWHM bandwidth $\Delta \nu = 2.4$ THz. There are therefore significant spectral components at the frequencies of the IR active lattice modes in Te.

Resonant THz pump measurements were conducted using 1 mm thick (100)-Te and (001)-Te single-crystal samples. The different surface orientations allow to vary the polarization of $E_{\text{THz}}$ with respect to the crystallographic c-axis in the samples. The probe pulses reflected off the sample are picked up by a mirror in front of the off-axis parabolic mirror used for focusing the THz beam. The mirror is moved into the beam as far as possible without clipping the THz cone in order to nearly align the sample surface normal with the collinear probe and THz pump beams. Eventually, the incidence angle of the beams could be set to $5^\circ$, ensuring only a small deviation
from the condition \( E \perp c \) for excitation of the \( E \)-modes when using the (001)-Te sample. Tighter focusing of the THz beam would in principle be possible using a parabolic mirror with a smaller focal length. This would, however, also lead to a larger incident angle of the beams on the sample.

In the following, the typical procedure for a measurement with the setup is quickly described.

The electric field of the THz pulses is first characterized at the sample position using EO sampling in transmission. This includes ensuring spatial overlap of pump and probe beam and adjusting the DSTMS crystal rotation for the required \( E_{\text{THz}} \) polarization. Although a measurement of the spectrum of the OPA pulses is usually a good indicator for the alignment of the OPA for a certain output wavelength (see Sec. A.1), the second and third amplification stages of the OPA can be tweaked while observing the peak signal of \( E_{\text{THz}} \) to maximize the amplitude of the driving field. The EO crystal is consequently replaced by the sample and the replaceable magnetic mirror mount is put into the detection arm. A CCD camera is used to monitor the spot of the 800 nm probe pulses on the sample. The position on the sample is chosen to minimize scattered light on the sample surface, which typically represents the sample spot that yields the lowest noise floor for the measurement.

### 6.2.2 Resonant excitation of non-fully symmetric modes

The anisotropic transient reflectivity change \( \Delta R/R_0 \) after excitation of (001)-Te single crystals with THz pulses as shown in Fig. 6.6 is presented in Fig. 6.7 (a). The relative polarization of \( E_{\text{THz}} \) and the probe pulses as well as the orientation of the crystallographic \( c \)-axis is shown in the inset of the figure. The data reveals a clear oscillatory modulation of the reflectivity, indicating
Figure 6.7: (a) Changes of the anisotropic reflectivity $\Delta R/R_0 = (R_1 - R_2)/R_0$ of a (001)-Te crystal after excitation with THz pulses as shown in Fig. 6.6. The oscillation corresponds to $E$ symmetry coherent phonons resonantly driven by the THz pulses. The inset shows the relative orientation of the electric field $E_{\text{THz}}$, the probe polarization and the crystallographic $c$-axis. (b) Spectral amplitude obtained via a fast Fourier transform (FFT) of the full time trace, showing peaks at the frequencies of $E$ modes with broad shoulders. (c) Spectral amplitude of the signal for delay times $t > 2$ ps, when the driving field $E_{\text{THz}} \approx 0$. 
the resonant excitation of coherent phonons by the THz pulses. Furthermore, the time trace
does not show any signature of relaxation processes related to electron-electron scattering or
electron-hole recombination. This indicates that the below-bandgap photons in the THz pulses
do not promote any carriers into the conduction band and the electronic system remains close to
equilibrium after excitation. It is important to note that the anisotropic detection scheme will
nearly completely cancel out any signal related to isotropic relaxation processes. For this reason,
we also conducted measurements of the isotropic reflectivity change after THz excitation and did
not observe any reflectivity change above the noise level $\sim 0.5 \times 10^{-3}$. The strong signal around
time zero observed after excitation with above-bandgap pulses (see Fig. 6.4), resulting from the
incomplete cancellation of isotropic relaxation processes in the anisotropic channel, is clearly not
present in the THz excitation data. For the model in the next section, we therefore do not take
into account any electronic background processes.

For a peak THz field $E_{\text{peak}}^{\text{THz}} \approx 0.6$ MV/cm, the anisotropic reflectivity change $\Delta R/R_0$
associated with $E$ symmetry coherent phonons is close to $3 \times 10^{-3}$. Utilizing above-bandgap
excitation of Te, obtaining a comparable signal level leads to a significant concentration of free
carriers, evidenced by considerable $A_1$ mode softening [12, 23].

The mode spectrum, obtained via an FFT of the full anisotropic reflectivity trace, is shown
in Fig. 6.7 (b). It displays strong peaks at the frequencies of the $E_{\text{TO}}$ modes. The spectrum
features broad shoulders that are not observed for an above-bandgap pump. These shoulders are
related to far-from-resonance contributions driven by the electric field of the broadband THz
pulse. Once the electric field of the pulses is close to 0 for delays around 1 ps, these contributions
quickly damp out. Figure 6.7 (c) shows the mode spectrum for time delays $t > 2$ ps, revealing
the linenshape of the undriven vibrational motion. The frequencies extracted from the undriven
mode spectrum are $E'_{\text{TO}} = 2.77 \pm 0.01$ THz and $E''_{\text{TO}} = 4.22 \pm 0.01$ THz. These values are in
good agreement with frequencies obtained in above-bandgap ISRS and Raman measurements [8]
[23]. The extracted damping times $t_{\text{damp}}(E'_{\text{TO}}) \approx 5$ ps and $t_{\text{damp}}(E''_{\text{TO}}) \approx 8$ ps are slightly lower
than damping times measured with above-bandgap pump-probe spectroscopy [23].

6.2.3 Control of the coherent lattice motion

The possibility to rotate the phase of the electric field of the THz pulse by $180^\circ$ by simply
rotating the generation crystal makes it possible to control the phase of the resonantly excited
lattice modes. This kind of phase control is not possible in an ISRS experiment, where the phase
of the excited coherent lattice motion is essentially determined by the lifetime of the excited
electronic states (see Sec. 2.2.1). The anisotropic reflectivity change after pumping with two
THz polarizations different by $180^\circ$ is shown in Fig. 6.8.

In (100)-Te crystals, the crystallographic $c$-axis lies within the surface plane. Rotating the
polarization of the THz electric field therefore allows to control the relative angle of $E_{\text{THz}}$ with
respect to the $c$-axis. The effective driving field of the coherent motion associated with the $E$
modes (internal polarization $E \perp c$), defined as $E'_{\text{THz}}$, is given by

$$E'_{\text{THz}} = \cos(90^\circ + \varphi)E_{\text{THz}}$$

Here, $\varphi$ is the angle between $E_{\text{THz}}$ and the $c$-axis. Figure 6.9 shows the anisotropic reflectivity change after THz excitation of a (100)-Te crystal when varying $\varphi$. For these measurements, two wiregrid polarizers are placed into the THz beam. This allows for more flexibility to keep the THz field strength constant when changing the polarization. Since the DSTMS generation crystal is not fully homogeneous, rotating it in the OPA pump beam can change the THz output power. These power changes are compensated for with the first wiregrid polarizer, while the second one is used to control the polarization before the sample. The inset shows the peak field for different values of $\varphi$ and a fit to the data according to Eq. 6.1.
Figure 6.9: Anisotropic reflectivity change after THz excitation of a (100)-Te crystal for different values of $\varphi$ as introduced in Eq. 6.1. The inset shows the dependence of the peak signal for a specific angle $\varphi$ normalized to the peak signal at $\varphi = 0^\circ$. The solid blue line is a fit to Eq. 6.1. Since the polarization can be set with a precision around $\pm 5^\circ$, the measured $\varphi = 0^\circ$ value does not necessarily correspond precisely to the $E \perp c$ condition. This offset in $\varphi$ is a fitting parameter.
6.2.4 Model of the resonantly driven coherent motion

To fully test the concept of the coherent motion being resonantly driven by the intense THz pulses and to understand the complete structure of the mode spectrum of the full time traces presented in Fig. 6.7, we can model the anisotropic reflectivity change as a sum of damped oscillators driven by the electric field of the THz pulses. The presented model relies on the following basic assumptions:

- Electronic background processes can be neglected and it is assumed that only the coherent motion of atoms after THz excitation contributes to the anisotropic reflectivity change.

- In the presented geometry, exciting a (001)-Te crystal, we expect strong coupling of the driving electric field only to TO-modes, specifically the $E''_{TO}$ and the $E'_{TO}$ modes. The IR active $A_2$ mode will not be excited as it has internal polarization $E \parallel c$. Since it is not Raman active, in any event a signal from the $A_2$ mode is not expected.

- We assume a homogeneous excitation of the probed volume. This is a reasonable assumption since the penetration depth of the 800 nm probe pulses lies below 50 nm, much smaller than the penetration depth of the THz frequency electric field. Even directly at the $E''_{TO}$ resonance, the THz penetration depth is around 2 $\mu$m. The THz spot size on the sample is around a factor of 4 larger than the probe spot size, furthermore ensuring a laterally homogeneous excitation.

- In the model, anharmonic coupling of phonon modes is neglected. In the large-amplitude limit of the coherent motion, phonon-phonon coupling effects can become important. With the applied field strength, however, no coupling effects could be observed. Varying the THz field strength by an order of magnitude using two wiregrid polarizer did not reveal any changes in the mode spectrum.

- As a driving force, the electric field measured via EO sampling in GaP at the sample position is used, assuming a flat frequency response of the detection systems in the low THz range.

Following these assumptions, we can write down the equation of motion for the displacement $Q_i(t)$ along the eigenvectors of the TO modes as damped harmonic oscillators driven by the electric field of the THz pulses (see also Sec. 2.2.2):

$$\frac{\partial^2 Q_i(t)}{\partial t^2} + 2\gamma_i \frac{\partial Q_i(t)}{\partial t} + \omega_i^2 Q_i(t) = \frac{q_i^*}{m_i^*} E_{THz}^T(t)$$  \hspace{1cm} (6.2)

Here, $i = E'_TO/E''_{TO}$ labels the non-fully symmetric TO lattice modes. The damping is described by $\gamma_i$ and the angular frequencies of the modes are given by $\omega_i = 2\pi \nu_i$. The driving field is given by the electric field inside the Te crystal, $E_{THz}^T = T(\nu)E_{THz}$, with the transmission coefficient.
6.2 Optical probing of resonantly excited structural dynamics

Finally, the coupling of lattice modes to $E_{\text{THz}}^T$ is determined by the effective charge $q^*_i$ and the effective mass $m^*_i$ of mode $i$.

In the vicinity of lattice modes, the transmission coefficient $T(\nu)$ is strongly frequency-dependent. To estimate $T(\nu)$, we use an approach based on treating the vibrational modes as Lorentz oscillators. The Lorentz model allows to connect properties of resonances in a solid, specifically damping time, frequency and oscillator strength, to its refractive index in the vicinity of these resonances (see for example chapter six of [163]). The transmission coefficient for normal incidence can then be calculated from the refractive index from the following relations [164]:

\[
\begin{align*}
n^2(\nu) - k^2(\nu) &= \varepsilon_0 + \sum_i 4\pi \rho_i \nu_i^2 \left( \frac{\nu_i^2 - \nu^2}{(\nu_i^2 - \nu^2)^2 + (\gamma_i \nu_i/(2\pi))^2} \right) & (6.3) \\
n(\nu)k(\nu) &= \sum_i \rho_i \nu_i^2 \left( \frac{\gamma_i \nu_i}{(\nu_i^2 - \nu^2)^2 + (\gamma_i \nu_i/(2\pi))^2} \right) & (6.4) \\
T(\nu) &= \frac{2}{1 + n(\nu) + ik(\nu)} & (6.5)
\end{align*}
\]

Here, $\rho_i$ is related to the oscillator strength of mode $i$ and $\varepsilon_0$ is the high-frequency dielectric constant.

The magnitude of the measured anisotropic reflectivity change after THz excitation associated with the coherent motion will be determined by two factors: (1) The field strength of the THz field as well as the coupling strength determined by $q^*_i$ and $m^*_i$, (2) the elements of the Raman tensor (Eq. 2.8) and the relative orientation of THz and probe polarization as well as the crystallographic c-axis. Within the framework of the model, with knowledge of the effective mass and charge $q^*_i$ and $m^*_i$ one can therefore estimate elements of the Raman tensor for a certain experimental geometry. To compare the model to the measured transient reflectivity after THz excitation, we introduce a constant for each mode that determines the magnitude of the anisotropic reflectivity change and therefore combines factors (1) and (2).

Fitting the model to the data is accomplished in the following way: For a set of fit parameters (damping times $\gamma_i$ and resonance frequencies $\nu_i$, as well as coupling constants for each mode) the transmission coefficient $T(\nu)$ is calculated using Eq. 6.5. The calculated transmission coefficient is then used to calculate the THz field inside the crystal $E_{\text{THz}}^T$, based on the actual field $E_{\text{THz}}$ measured via EO sampling. Using $E_{\text{THz}}^T$ as a driving field, the equation of motion is solved using a numerical solver based on the Runge-Kutta method. After a convolution of the signal to account for the experimental time resolution (given by the probe pulse duration $\tau_{\text{probe}} = 90$ fs), the simulated reflectivity is compared to the measured data, resulting in refined fitting parameters for the following iteration.

Figure 6.10 shows a comparison of the spectrum of the simulated and the measured reflectivity changes. The retrieved values from the fit are: $\nu_{E_{\text{TO}}^T} = 2.78 \pm 0.02$ THz, $\nu_{E_{\text{TO}}''} = 4.23 \pm 0.03$ THz, $\gamma_{E_{\text{TO}}^T} = 0.36 \pm 0.07$ THz and $\gamma_{E_{\text{TO}}''} = 0.34 \pm 0.1$ THz. These values are in close agreement with values retrieved from the undriven motion (for delays $t > 2$ ps) and Raman measurements [165].
The model agrees very well with the measured reflectivity changes for the $E'_{\text{TO}}$ mode, reproducing the shape of the spectral amplitude including the broad low frequency shoulder. In the measured spectrum, there is a broad feature around 3.6 THz that is not reproduced by the model. It could be related to an extraordinary phonon mode \cite{166} or background signal associated to a linear EO effect \cite{167}, things that are not included in the model. The ratio of the Raman detection sensitivity for the two $E$ modes in this geometry can be estimated using effective dynamic charges from Lucovsky \cite{165} and assuming an equal effective mass for both modes to be $E''_{\text{TO}}/E'_{\text{TO}} \approx 14$.

![Figure 6.10: Comparison of the spectrum of the measured anisotropic reflectivity (blue line) and the harmonic oscillator model as presented in the text (dashed black line).](image)

### 6.2.5 Strain dynamics induced by a terahertz pulse

The THz excitation measurements on tellurium offer an opportunity to study relaxation dynamics of a nonequilibrium structure with the electronic system being close to equilibrium. One interesting question concerns the problem of energy transfer into acoustic modes following the resonant excitation of coherent optical phonons.

After THz excitation of a (100)-Te crystal with a THz polarization $E_{\text{THz}} \perp c$, a slow oscillation can be observed in the anisotropic detection channel, see Fig. \ref{fig:6.11}. Furthermore, there is a small constant offset in $\Delta R/R_0$ after excitation that is most likely related to heating of the sample with the THz pulse.
Figure 6.11: Anisotropic reflectivity change after THz excitation of (100)-Te associated with a strain wave propagating through the sample. The blue line corresponds to a fit as explained in the text. The uncertainty for each data point, calculated as one standard deviation of the intensity fluctuation of all probe pulses collected for a specific delay point, corresponds to a change in anisotropic reflectivity of around $10^{-5}$.

The period of around 40 ps makes it seem likely that the oscillation is related to a strain wave generated by the THz pulse. The refractive index of a particular sample volume depends on the magnitude of the strain, resulting in a modified reflectivity when a strain wave is close to the sample surface. An in depth discussion of the phenomenon of strain waves generated by picosecond light pulses in solids can be found in the work of Thomsen et al. [39]. In this work, they also derive an expression for the reflectivity change associated with a strain wave propagating into the material:

$$\Delta R(t) \propto \cos\left(\frac{2\pi t}{\tau} - \phi\right) \exp(-z/\delta_P)$$  \hspace{1cm} (6.6)

The period of the oscillation is determined by $\tau = \lambda/(2nv)$, where $\lambda$ is the probe wavelength, $n$ is the refractive index for the probe wavelength and $v$ is the longitudinal sound velocity along $z$. The damping of the oscillation is determined by the absorption length $\delta_P$ of the probe pulse. The constant $\phi$ corresponds to some phase shift.

The solid line in Fig. 6.11 corresponds to a fit to the reflectivity data using Eq. 6.6 with an added background level to account for the thermal offset. For the fit, the fast dynamics associated with the resonant excitation of coherent phonons have been excluded.
The values retrieved from the fit are $\tau = 46.7 \pm 2$ ps and $\delta_P = 21.2 \pm 1.7$ nm. The values determined by the fit agree reasonably well with values calculated using literature values: Assuming reported values for the refractive index [168] and the sound velocity [169] yields $\tau = 33$ ps and the calculated absorption length from reflectivity data [168] is $\delta_P = 27$ nm.

Strain waves induced by laser pulses are of course a widely studied phenomenon. In most cases, however, the dynamics are launched through the electronic system, which is heated by the laser pulse and passes on energy to the lattice via electron-phonon coupling.

With THz pumping, the energy is directly deposited into the lattice, allowing for different initial generation mechanisms of strain. When using THz excitation, so that electron-phonon coupling as a generation method of strain waves can be excluded, there can be two other possible mechanisms of strain-wave-generation [170]: (i) Thermoelasticity: The THz pulse deposits a certain amount of energy into the surface layers of the sample, leading to a transient increase in temperature $\Delta T$. The thermal expansion of the excited volume in combination with the boundary condition given by the sample surface launches a strain wave along the surface normal $z$ into the sample. In this particular experiment, the temperature increase could originate from anharmonic decay of the coherent motion, transferring energy into acoustic modes and launching a strain wave. (ii) Inverse piezoelectric process: In systems lacking inversion symmetry, there exists a coupling between strain and the electric field inside the crystal, implying that the system acts as a THz-driven piezo-transducer.

Strain dynamics typically lead to an isotropic reflectivity change and can most likely be only observed in the anisotropic channel due to incomplete cancellation of the corresponding signal. A systematic study that can also help to shed light on the coupling mechanism leading to the strain wave would require more experiments using a sensitive isotropic detection scheme.

### 6.3 X-ray probing of resonantly excited structural dynamics

As demonstrated in this chapter, an optical probe can be used to measure transient reflectivity changes associated with a resonant excitation of coherent phonons. A direct, model-independent quantification of the amplitude of the coherent motion is however only possible using a probe directly sensitive to the structure. In the presented model, a coupling constant comprising a number of mode-specific quantities like effective charge and effective mass as well as elements of the Raman tensor has to be introduced. Utilizing time-resolved x-ray diffraction, the real-space oscillation amplitude and the effective coupling to the THz electric field of each mode can in principle be measured.

In the following, time-resolved x-ray diffraction measurements on Te after THz excitation, carried out at the FEMTO slicing source, are presented. In these measurements, no change in diffraction intensity after THz excitation could be observed. Furthermore, it was difficult to quantify the actual THz electric field at the frequencies of the $E$ modes during the experiments for an estimate of upper bounds of coupling constants. An upper bound of approximately 0.5 pm
can be calculated for the amplitude of resonantly $E$-symmetry coherent phonons, details on the calculation are given in the following experimental section.

A time-resolved x-ray diffraction experiment at the FEMTO slicing source using THz excitation is extremely challenging for a number of reasons: In addition to low sliced x-ray flux available for diffraction, the generated field strength in the x-ray hutch was nearly an order of magnitude lower than for the THz pulse shown in Fig. 6.6. Furthermore, the THz pump arm greatly complicates the experimental setup and expected signal levels are hard to estimate. Below, the experimental setup and details regarding material parameters and their significance for a THz-pump x-ray-probe experiment are given. This section mainly serves as a documentation of the experiment, as with the emergence of more intense ultrafast pulsed THz and x-ray sources, a THz-pump x-ray-probe measurement on Te in a very similar experimental setting should become feasible in the future.

### 6.3.1 Experimental setup

The basic idea of the experiment was to measure changes in the intensity of a diffraction peak with an associated structure factor that shows a big change when the $E$-TO modes are resonantly excited. As an example, using a (001)-Te crystal and looking at the (013)-reflection, a coherent motion along the eigenvector of the $E$ modes with an amplitude of 1 pm is expected to result in a change of diffraction intensity of at least $\Delta I/I_0 \approx 2\%$. This can be calculated using the eigenvector of the $E$-TO-modes, which for example can be found in [8] (see Fig. 6.2), and comparing the structure factors of the equilibrium unit cell and the structure factor of the unit cell when the atoms are shifted along that eigenvector. During the diffraction measurements, no signal above a noise floor of around $\Delta I/I_0 = 1\%$ could be observed, putting an upper bound of approximately 0.5 pm on the amplitude of the coherent motion.

The setup in detail is shown in Fig. 6.12. An in-depth description of the FEMTO slicing source is given in Sec. 4.1.1.

For the x-ray probe pulses, the 7 keV x-ray beam was focused vertically by an elliptically bent mirror that is part of a Kirkpatrick-Baez system to a spot size of 10 µm, the horizontal spot size was around 250 µm. The x-ray pulse duration was around 120 fs.

As for the optical probe measurements, THz pulses were generated in a DSTMS crystal utilizing optical rectification of an OPA beam. The OPA was placed in the x-ray hutch and fed by $\lambda = 800$ nm pulses with a pulse energy of around 1.4 mJ pulses and a pulse duration of around 120 fs. The 1350 nm output of the OPA had pulse energies around 0.25 mJ. The OPA pulses were collimated onto a DSTMS crystal with a diameter of around 3 mm. After passing an

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2It is not a priori clear which of the eigenvectors shown in Fig. 6.2 can be assigned to the $E'_{TO}$ mode and which eigenvector can be assigned to the $E''_{TO}$. In the example, the respective change in $\Delta I/I_0$ is however similar (2% compared to 3.5%). In the actual experiment, the contribution of the higher frequency mode can be neglected because of its much lower dynamic charge and the smaller spectral contributions around 4 THz when utilizing pump pulses generated in DSTMS with around 100 fs pulses.
Figure 6.12: Experimental setup for time-resolved x-ray diffraction measurements on Te after THz excitation. THz pulses are generated via optical rectification of an OPA beam. The lower inset shows a close-up of the sample geometry. KB mirror: Kirkpatrick-Baez mirror. ML: Multilayer mirror. APD: Avalanche Photodiode.

IR filter, the THz radiation was collimated by a first off-axis parabolic mirror and focused to the sample position with a second off-axis parabolic mirror.

Terahertz pulses were characterized at the sample position using transmission EO sampling in a (110)-GaP crystal with a small fraction of the 800 nm beam that was branched off before it entered the OPA. A delay stage after the beam splitter allowed for a variation of the relative time delay between THz pulses and the EO probe beam. The measured peak field strength was around 120 kV/cm².

With the chosen experimental geometry, THz pulses are focused onto the sample at near-normal incidence, resulting in a not-too-large THz spot size on the sample (a close-up of the sample geometry is shown in the inset of Fig. 6.12). To avoid significant time smearing, the incidence angle of the x-ray pulses cannot be chosen too small, and the vertical beam size of the x-rays becomes critical. For the experiment, an x-ray incidence angle $\alpha = 20^\circ$ was selected, resulting in a geometrical lower bound of the experimental time resolution of around 100 fs for a 10 μm vertical beam size of the x-rays, which is comparable to the pulse duration of the x-ray probe pulses. The attenuation length of 7 keV x-rays at this incidence angle calculates to around 1.5 μm [113], which is comparable to the field attenuation length of THz radiation at the $E_{TO}'$ resonance for an internal polarization $E_\perp c$. Away from the resonance, the THz penetration depth quickly increases, ensuring a homogeneous excitation of the probed sample volume.

A major difficulty in using a THz pump and x-ray probe lies in ensuring spatial and temporal overlap of the two beams at the sample position. The employed method for Te, that is well
characterized using optical excitation and x-ray probe [108] is described in the following. The delay stages controlling the delays between different beams (800 nm, THz and x-rays) are labeled as in the figure: Delay stage 1 controls the delay between x-ray pulses and the complete 800 nm branch, delay stage 2 controls the delay between a fraction of the 800 nm light and the THz pulses.

To ensure temporal and spatial overlap between THz-pump and x-ray-probe pulses on the sample, the GaP crystal was first positioned in the x-ray beam by half-clipping the transmitted x-ray intensity with it. Subsequently, the position of the THz focal spot radiation was adjusted to coincide with the x-ray beam position. After ensuring temporal and spatial overlap of the 800 nm pulses with the THz pulses via EO sampling (varying delay stage 2), delay stage 2 is kept constant to preserve temporal overlap between 800 nm pulses and THz pulses. The GaP crystal was then replaced by the Te sample. Spatial overlap between 800 nm pulses and x-ray pulses was verified with the Te sample by increasing the 800 nm beam pulse energy and using it as a pump to trigger the $A_1$ coherent phonon, which was measured as a transient change in the x-ray intensity on an APD (varying delay stage 2). Finally, the 800 nm beam was blocked before the THz-pump x-ray-probe measurement and delay stage 1 is used to vary the time delay between THz-pump and x-ray-probe pulses.

As mentioned before, the low available laser power in the near-infrared and the low photon count severely restrict a THz pump experiment at the FEMTO slicing source. With the laser system at the free electron laser LCLS, higher field strengths for time-resolved x-ray measurements have already been reported [96] and the much higher x-ray flux allows to measure comparable changes in structure factor in much less time. More intense x-ray pulses also greatly simplify procedures to ensure spatial and temporal overlap, as for example a quick cross-correlation of laser pulses and x-ray pulses in an EO crystal due to the excitation of free carriers by intense x-ray pulses becomes possible.

6.4 Summary and outlook

In this chapter, we demonstrated the resonant excitation of large-amplitude non-fully symmetric coherent phonons in single-crystal Te. Anisotropic reflectivity changes associated with the coherent vibrational motion were detected with optical laser pulses. The presented approach allows to study coherent phonons while the electronic system is essentially in equilibrium, since no free carriers are promoted into the conduction band by the THz radiation. The measured temporal evolution of reflectivity could well be reproduced by a model based on the sum of damped harmonic oscillators driven by the electric field of the THz pulse, and the phase of the coherent lattice motion could be controlled via the polarization of the THz field.

The interaction of THz pulses with polar lattice modes has so far been predominantly investigated using THz time domain spectroscopy (see Sec. 5.4). In the vicinity of lattice resonances, the THz penetration depth can be as small as a few µm, requiring very thin samples...
for transmission measurements. This in turn leads to multiple internal reflections that overlap in time, obscuring the measured signals. An alternative when strongly absorbing samples are studied is to carry out the measurement in a reflection geometry, resulting in a host of challenges connected to the problem of maintaining a reliable reference for the phase of the THz electric field (see Sec. 5.4).

The demonstrated approach allows the study of coherent modes using optical probing, which in most cases presents a more stable and flexible probing method. For example, the spot size can be easily reduced to values below 10 µm, making sample surface inhomogeneities a much smaller problem. Furthermore, using the fundamental wavelength of a laser typically allows for a superior signal-to-noise ratio. Choosing a suitable, highly absorbed wavelength for probing can also make the presented method a highly surface-sensitive probing technique.

The presented self-consistent modeling approach makes it possible to extract material parameters from the recorded reflectivity traces. Even in the presence of strongly damped modes, when the lattice response essentially overlaps with the driving THz field, it is possible to quantify mode properties, provided that the waveform of the THz electric field is well-known.

One of the main limitations of the presented spectroscopic method lies in the strict requirements it poses on the sample under study: Only materials lacking inversion symmetry support modes that are both Raman and IR active. Furthermore, the band-gap has to be large enough so that the THz radiation is not absorbed by free carrier excitation. For high field strengths at higher-frequency spectral components exceeding 10 THz, even a band-gap below around 100 meV could be problematic, as multi-photon absorption process might start to dominate the material response.

While resonant excitation of elementary excitations in a solid and optical probing can be a viable alternative to traditional THz time domain spectroscopy for certain systems, one of its biggest strengths lies in the possibility to scale up the THz field and access regimes where nonlinear interactions between phonon modes become important. At peak field strengths of around 0.6 MV/cm², no coupling effects could be observed. Very recently, THz pulses with field strengths exceeding 1 MV/cm² by far have been reported using similar generation methods at repetition rates below 100 Hz. With these field strengths, anharmonic phonon coupling could be studied in a similar experimental setting.
Chapter 7

Structural dynamics of the ultrafast CDW-to-metal transition in $\text{K}_{0.3}\text{MoO}_3$

Inducing an ultrafast phase transitions in a broken symmetry ground has become an important tool to study and transiently manipulate broken symmetry ground states in different classes of correlated systems (see also Sec. 1.2). In most of the studied systems, a femtosecond laser pulse destroys correlations in the electronic system, which in turn leads to a melting of order in other subsystems like the lattice or the spin system. To fully characterize an ultrafast phase transition and the associated timescales, all subsystems relevant to the transition need to be completely described after photoexcitation.

In thermal equilibrium, the CDW ground state is fully characterized by a multicomponent complex order parameter that combines the periodic modulation of the charge density and the associated periodic lattice distortion. After excitation with a femtosecond laser pulse, however, electronic and lattice subsystem cannot necessarily be described by a common order parameter anymore. Timescales of lattice modes associated with the change of symmetry from the low-temperature ground state to the high-temperature phase are typically much slower than timescales connected to the melting of order in the electronic system. The disconnection of electronic and lattice parts of the order parameter was investigated with all-optical pump-probe spectroscopy: Excitation of $\text{K}_{0.3}\text{MoO}_3$ resulted in melting of electronic order, while zone-folded lattice modes where observed to persist at much higher fluences, leading to the conclusion that the lattice initially remains unperturbed after photoexcitation [3]. These considerations were refined by all-optical pump-probe spectroscopy in the low-fluence regime. Temperature-dependent damping times and frequencies obtained from these measurements could be explained by a linear coupling of lattice modes to an overdamped electronic amplitude mode in a nonadiabatic regime [30, 68].

All the reported measurements, however, rely on indirect access to the structural dynamics of the system, as only changes of the reflectivity associated with atomic movements are measurable.
The complete characterization of the structure during the ultrafast melting of the CDW requires a direct probe of the lattice with a time resolution good enough to access structural dynamics associated with elementary excitations of the broken symmetry ground state. Only then can questions concerning the ultimate timescale of the change of symmetry of the system and the details of the coherent motion during the ultrafast transition be thoroughly answered.

Direct time-resolved probing of the lattice during a photoinduced melting of CDW systems have been performed using time-resolved x-ray [44, 77] and electron diffraction [5]. The time resolution and sensitivity of these measurements did however not yet allow to observe the coherent structural dynamics of the systems during a CDw-to-metal transition. Moreover, all these measurements were conducted on two-dimensional CDW systems, where the origin of CDW formation is not fully understood (see Sec. 3.3).

In this chapter, results on the coherent structural dynamics during the CDW-to-metal transition of the prototypical one-dimensional CDW compound $K_{0.3}MoO_3$ are presented. The time-resolved x-ray diffraction experiments were carried out at the hard x-ray slicing source FEMTO, simultaneously providing the spatial and temporal resolution needed to follow the coherent dynamics of the structure during the photoinduced transition. By measuring the diffraction intensity of a superlattice peak of the periodic lattice distortion and thus being directly sensitive to the structural symmetry of the system, a complete picture of the coherent structural dynamics during the photoinduced transition could be obtained.

The chapter is structured as follows. At first, the experimental setup is described in detail and some of the preparatory time-resolved diffraction measurements are presented and explained. This section can also serve as a reference for potential time-resolved diffraction measurements on $K_{0.3}MoO_3$ in the future. The following Sec. 7.2 focuses on the dynamics in the low fluence regime, establishing the observed structural dynamics as a motion along the coordinate of the Peierls distortion. The complete picture of the symmetry-changing transition is presented in Sec. 7.3 and modeled in Sec. 7.4. Finally, the results are discussed and compared to previous measurements reported in the literature. In Chap. 8 results of double-pump excitation measurements on $K_{0.3}MoO_3$ are reported as a continuation of the single-pump measurements presented in this chapter, confirming and building on the concepts introduced in the following.

Parts of the work presented in this chapter have been published in the following manuscripts:


and S. L. Johnson, *Coherent dynamics of structural symmetry during the ultrafast melting of a charge density wave*, 

### 7.1 Experimental

Time-resolved x-ray diffraction measurements were carried out at the hard x-ray slicing source FEMTO in a grazing incidence geometry (for a detailed description of the source see section 4.1.1). A sketch of the most important elements of the experimental setup in the x-ray hutch is presented in Fig. 7.1. The sample was a cleaved K$_{0.3}$MoO$_3$ single crystal previously characterized with grazing incidence measurements at the Material Science beamline at the Swiss Light Source [173]. The cleavage plane of the sample corresponds to the (2 0 1) plane. The sample was cooled well below $T_c = 183$ K to $T = 95$ K using a cryogenic nitrogen blower. Lower temperatures are in principle possible at FEMTO using a cryogenic vacuum chamber, however the chamber does not allow the level of accessibility that is possible with the nitrogen blower. In fact, preliminary time-resolved x-ray diffraction measurements were carried out at $T = 45$ K using a vacuum chamber, but sample instabilities proved to be a serious problem. Since the efficiency of the superlattice peaks in the CDW phase of K$_{0.3}$MoO$_3$ hardly changes below $T = 100$ K, a cryogenic nitrogen blower is by far the superior alternative.

The crystal was excited by 800 nm (1.55 eV) laser pulses with a FWHM duration of 100 fs. The polarization of the pump pulses was set with a Brewster plate to $p$ polarization. The incident fluence could be varied using a motorized waveplate before the Brewster plate. To calibrate the incident laser fluence, the laser power was measured at the sample position with a thermal detector. The beam was focused onto the sample using a focusing telescope to a FWHM spot size around 650 µm × 650 µm, as measured with a beam profiler (*Dataray WinCam D*). The laser pulses hit the sample at an angle of $\beta = 10^\circ$, resulting in a penetration depth of roughly 650 µm.
$\delta_L = 80 \text{ nm}$

The 7 keV x-ray probe pulses were focused vertically with an elliptically bent mirror that is part of a Kirkpatrick-Baez system to 10 $\mu m$, horizontally they were only loosely focused by a toroidal mirror to 300 $\mu m$. The duration of the x-ray pulses was estimated using fits to high fluence data to be around 80 fs. The bandwidth of the x-rays was set by a multilayer mirror. The grazing angle of the x-rays was set to $\alpha \approx 0.4^\circ$, resulting in a penetration depth around $\delta_x = 100 \text{ nm}$ \[174\]. Since no clear-cut total reflection for grazing incidence x-rays of the sample surface could be observed, the incidence angle could not be determined with high precision. Surface irregularities also lead to different effective incident angles for different parts of the sample, implying that for some parts of the x-ray spot the penetration depth can be larger than the stated $\delta_x$.

An avalanche photodiode (APD) was positioned to measure the intensity of the strongest superlattice reflection accessible in a grazing geometry, the $(1 (4 - q_b) 0.5)$ reflection, for varying time delays between the pump and the x-ray probe. To reduce the effects of scattered x-rays, a lead aperture with a diameter of around 2 mm was mounted in front of the active area of the APD. Between the exit window of the KB-mirror box and the sample, a helium tube was mounted to limit the x-ray path through air and consequently reduce air absorption of the 7 keV x-rays\[2\]. Due to the low scattering efficiency of the superlattice reflection (around $10^{-6}$ at the grazing angle $\alpha \approx 0.4^\circ$), on average count rates around only 2 photons/second could be achieved at the detector position. For low-fluence excitation, a single delay trace with sufficient signal-to-noise ratio required more than 12 hours integration time.

To prevent x-ray induced sample degradation, the sample was never exposed to the full power of the unsliced synchrotron radiation and care was taken to aperture as much remaining core beam as possible. Sample degradation resulted in a reduced count rate, but the time-resolved signal seemed to remain consistent even when the count rate reduced during longer scans. Partial recovery of the count rate could be achieved after cycling the sample through the phase transition. Figure 7.2 (a) shows a sample rotation scan of the $(1 (4 - q_b) 0.5)$ reflection recorded directly after a heating cycle through the phase transition. The figure also allows to compare the signal level and the halo background. All delay traces reported in the following are recorded with the sample rotation adjusted to measure the peak diffraction intensity.

Rough temporal and spatial overlap of pump and probe beams was achieved observing photoinduced changes of the Bi-(1 1 1) diffraction peak. Overlap on the sample was ensured looking directly at the photoinduced changes of the $(1 (4 - q_b) 0.5)$ superlattice peak. Figure 7.2 (b) shows an overlap scan, where an axis of a motorized mirror that determines the beam position on the sample is moved at an incident laser fluence of around 3 mJ/cm\(^2\).

During the experiments, we also recorded time traces of the regular lattice $(4 4 3)$-peak. The

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1 Calculated with optical data from \[59\].
2 The helium filled tube increased the measured photon count by around 20%.  

7.2 Structural dynamics associated with the amplitude mode

For excitation fluences below the melting threshold of the CDW condensate, the time-resolved x-ray diffraction signal allows to directly observe the structural dynamics associated with the collective amplitude mode of CDW ground state. Figure 7.3 shows the time evolution of the diffraction intensity $I(t)$ of the $(1 \ (4-q_b) \ \bar{0} \ 5)$ superlattice peak after photoexcitation, normalized to the equilibrium diffraction intensity $I_0 = I(t < 0)$ for an absorbed pump fluence $F = 0.3$ mJ/cm$^2$. The time trace shows (i) a clear signature of a damped oscillation (ii) an overall reduction in superlattice diffraction for $t > 0$ that relaxes back to the equilibrium value $I_0$ on a picosecond timescale. In the following, we assume that the observed coherent motion of lattice atoms occurs mainly along the structural coordinate of the Peierls distortion and contributions of other phonon modes can be neglected. All-optical pump-probe data (see Sec. 3.3.2 and [3, 30]) showed that numerous zone-folded modes can be excited after optical excitation,
Figure 7.3: Time evolution of the normalized diffraction peak intensity of the $(1 \ 4 - q_b \ 0 \ 5)$ superlattice reflection for an absorbed pump fluence $F = 0.3 \, \text{mJ/cm}^2$. The solid line is a fit to the data using a displacive excitation model (see Eq. 7.3) but signatures of these modes could not be observed in the time-resolved diffraction signal. We label the coherent movement along the distortion coordinate $X(t)$.

To model the data, several approximations that allow to establish a connection between the measured intensity $I(t)$, the structure factor of the superlattice reflection $F_{\text{SL}}$ and the magnitude of the coherent motion $X(t)$ can be made:

- The small diffraction efficiency of the superlattice reflection allows us to apply the kinematic approximation (see Sec. A.3)

\[ I(t) \propto |F_{\text{SL}}(t)|^2 \quad (7.1) \]

- The amplitude of the equilibrium periodic lattice distortion is small \cite{58}, to leading order we can therefore estimate

\[ F_{\text{SL}} \propto X(t) \quad (7.2) \]

These approximations are also used in Sec. 7.3 to model the coherent structural dynamics for higher excitation fluences. For low excitation fluences, it can furthermore be assumed that the dynamics in an inhomogeneously excited solid are qualitatively similar in all excited layers. This assumption does not hold any longer for the high fluence excitation measurements discussed in Sec. 7.3. Since the amplitude mode corresponds to the atomic movement $X(t)$ along the distortion coordinate, we model it in the displacive limit of an ultrafast stimulated Raman scattering process (see Sec. 2.2.1). The displacive excitation model yields the following expression
7.3 Structural dynamics through the ultrafast CDW-to-metal transition

for the movement along \( x(t) = X(t)/X_T \), normalized to the equilibrium distortion \( X_T \) \[21\]:

\[
x(t) = A_{\text{disp}} \left( \cos(2\pi\nu_{\text{AM}} t) \exp \left( -\frac{t}{\tau_{\text{AM}}} \right) - \exp \left( -\frac{t}{\tau_{\text{disp}}} \right) \right) + 1 \quad (7.3)
\]

Here, \( A_{\text{disp}} \) is a fluence dependent constant, \( \nu_{\text{AM}} \) is the frequency of the amplitude mode, \( \tau_{\text{AM}} \) is the damping time of the amplitude mode. The time constant \( \tau_{\text{disp}} \) describes the relaxation of the quasiequilibrium position \( X_T(t) \) after excitation. Equation 7.3 can be derived from the DECP expression given in \[21\] assuming \( 1/\tau_{\text{disp}} < 2\pi\nu_{\text{AM}} \) and \( 1/\tau_{\text{AM}} < 2\pi\nu_{\text{AM}} \). The solid line in Fig. 7.3 corresponds to a fit to the normalized diffraction intensity \( I(t)/I_0 = |x(t)|^2 \). For absorbed excitation fluences of \( F = 0.15 \text{ mJ/cm}^2 \) and \( F = 0.3 \text{ mJ/cm}^2 \), the fitting parameters are given in table 7.1. The values for \( \nu_{\text{AM}} \) and \( \tau_{\text{AM}} \) are in close agreement to values obtained from all-optical pump-probe spectroscopy at \( T = 100 \text{ K} \). For a small perturbation, the lattice relaxes back to the equilibrium position in a few picoseconds. This relaxation time \( \tau_{\text{disp}} \) cannot be accessed with all-optical pump-probe spectroscopy or other time-resolved methods that are not directly sensitive to the structure of a system.

The clear observation of coherent structural dynamics associated with the amplitude mode in the time-resolved diffraction signal greatly simplifies the interpretation of the data taken with high excitation fluences presented in the next section: The signal can be clearly attributed to a coherent motion along the coordinate of the Peierls distortion. This fact will also become important later when comparing the presented measurements to time-resolved measurements interpreted using arguments concerning domain creation after photoexcitation.

### Table 7.1: Fitting parameters of the displacive excitation model (Eq. 7.3) for fluences below the CDW melting threshold.

<table>
<thead>
<tr>
<th>( F ) (mJ/cm(^2))</th>
<th>( A_{\text{disp}} )</th>
<th>( \nu_{\text{AM}} ) (THz)</th>
<th>( \tau_{\text{AM}} ) (ps)</th>
<th>( \tau_{\text{disp}} ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>-0.17</td>
<td>1.65 ± 0.1</td>
<td>0.8 ± 0.4</td>
<td>1.8 ± 0.6</td>
</tr>
<tr>
<td>0.3</td>
<td>-0.28</td>
<td>1.62 ± 0.1</td>
<td>0.6 ± 0.15</td>
<td>2.3 ± 0.4</td>
</tr>
</tbody>
</table>

#### 7.3 Structural dynamics through the ultrafast CDW-to-metal transition

The time evolution of the \((1 - q_b) \frac{0.5}{2q_b}\) superlattice peak after photoexcitation over a wide range of absorbed fluences is shown in Fig. 7.4. As explained in the following, the data provides a complete picture of the coherent structural dynamics associated with the ultrafast melting of the CDW.

The amplitude of the coherent motion associated with the amplitude mode increases with increasing fluence from \( F = 0.15 \text{ mJ/cm}^2 \) to \( F = 0.3 \text{ mJ/cm}^2 \). The relaxation time \( \tau_{\text{disp}} \) increases
Figure 7.4: Time evolution of the $\langle 1 (4 - q_b) \frac{\mu}{5} \rangle$ superlattice peak after photoexcitation over a wide range of absorbed fluences. The horizontal dashed line in the higher fluence scans corresponds to a saturation background. The vertical bar indicates the time delay of the transient recovery $t = 350$ fs. The solid lines correspond to fits to the model as described in the text and in Fig. 7.7.
as well, as was also made evident by the fitting parameters of the DECP model in Tab. 7.1.

For a fluence \( F = 1 \text{ mJ/cm}^2 \), no clear signature of the amplitude mode can be observed in the time trace. The relaxation time of the superlattice reflection intensity increases to \( \tau_{\text{disp}} \approx 10 \text{ ps} \). Moreover, the timescale of the initial drop reduces to around \( \tau_{\text{drop}} \approx 100 \text{ fs} \), which is faster than dynamics that could be associated with the amplitude mode of the system. The measured superlattice intensity immediately after the initial drop at a delay time \( t = 100 \text{ fs} \) corresponds to \( 0.5 I_0 \). Remarkably, the measured intensity at this time delay stays constant for even higher excitation fluences (\( F = 2.1 \text{ mJ/cm}^2 \) and \( F = 3.7 \text{ mJ/cm}^2 \)). At the fluence \( F = 2.1 \text{ mJ/cm}^2 \), the superlattice intensity does not show any signs of relaxation on the measured timescale. The remaining diffraction intensity at \( t = 3 \text{ ps} \) stays at a value of approximately \( 0.4 I_0 \). At nearly twice the fluence, \( F = 3.7 \text{ mJ/cm}^2 \), the time evolution of the diffraction signal remains essentially unchanged, showing the same remaining signal at a time delay around \( t = 3 \text{ ps} \) and no relaxation in the measurement window can be observed.

A striking feature in the data is observable for high fluences (\( F = 2.1 \text{ mJ/cm}^2 \) and \( F = 3.7 \text{ mJ/cm}^2 \)): After the initial suppression at \( t \approx 100 \text{ fs} \), the superlattice diffraction intensity transiently recovers, peaking at a time delay \( t = 350 \text{ fs} \). Afterwards, it rapidly drops to the saturation background value \( 0.4I_0 \).

The saturation background, that for the highest fluence \( F = 3.7 \text{ mJ/cm}^2 \) remains at around \( 0.4I_0 \) for more than 100 ps, is a clear indication of a complete melting of the CDW and the associated periodic lattice distortion for high excitation fluences. We attribute the remaining background to contributions coming from unexcited volumes of the sample. As mentioned in the experimental Sec. 7.1, the cleaved surface of the \( K_{0.3} \text{MoO}_3 \) single crystal has surface irregularities and step heights up to \( 1 \mu \text{m} \) were measured on the sample after the experiment using white light interferometry. Consequently, the incidence angle for parts of the sample was much larger than the set angle \( \alpha \approx 0.4^\circ \). This is furthermore supported by measurements at grazing angles below the critical angle, where still considerable diffraction from the superlattice peak was observed. The fluences for which the saturation background level is reached agree well with fluences for which zone-folded modes where observed to disappear in all-optical pump-probe spectroscopy [3], confirming the applicability of all-optical coherent phonon spectroscopy to investigate photoinduced symmetry-breaking transitions [3, 42].

A more detailed view of the relaxation dynamics on a longer timescale can be obtained by examining sample rotation scans of the \((1 \ (4-q_b) \ 0.5)\)-reflection for fluences high enough to reach the saturation background. For longer delays \( t \), there can be shifts in the position of the superlattice peak related to strain waves or sample heating and it is not sufficient to just measure the peak diffraction intensity.

As mentioned before, no relaxation dynamics can be observed for \( F = 3.7 \text{ mJ/cm}^2 \), where the residual diffraction intensity stays constant up to a delay \( t = 100 \text{ ps} \). Figure 7.5 shows sample rotation scans for several time delays after photoexcitation with \( F = 2.1 \text{ mJ/cm}^2 \) pulses. In Fig.
Figure 7.5: Sample rotation scans of the $(1 (4 - q_b) \bar{q})$ for $F = 2.1 \text{ mJ/cm}^2$, corresponding to a fluence where the transient recovery is present in the sub-picosecond structural dynamics transient. (a) Measured normalized diffraction intensity $I/I_0$ for an unpumped sample (black) and photoexcitation with a time delay $t = 1 \text{ ps}$ (red). The fits correspond to Gaussians. (b) Gaussian fits to the normalized diffraction intensity for varying time delays. The inset shows the evolution of the peak value of the fits, the error bars correspond to the uncertainty of the fit parameter for the peak value.

(a), Gaussian fits to the unpumped signal and to a pumped signal at a delay $t = 1 \text{ ps}$ are presented. Figure 7.5 (b) shows fits for several time delays, revealing a clear relaxation within the first 100 ps. At $t = 100 \text{ ps}$, the signal has reached a level of around $0.6I_0$. The inset of Fig. 7.5 (b) shows the evolution of normalized peak diffraction intensity.

The position of the diffraction peak and its width do not show any changes larger than the uncertainties of the Gaussian fit. This behavior can be expected, since the residual diffraction intensity corresponds to signal from unexcited volumes of the sample. From these experiments, it is therefore not possible to draw conclusions on the evolution of the modulation vector of the periodic lattice distortion or the correlation length after photoexcitation, since the signal in a sample rotation scan is dominated by contributions from unexcited sample volume.

### 7.4 Model of the structural dynamics

The most noteworthy characteristics of the sub-picosecond time-resolved diffraction data are the change of the timescale of the initial drop $\tau_{\text{drop}}$ and the transient recovery of the periodic lattice distortion on a sub-picosecond timescale, and a model describing the coherent structural dynamics must capture these features. The phenomenological model we propose in the following
relies on two major assumptions:

- The measured structural dynamics through the ultrafast symmetry-breaking transition can be described as a coherent atomic motion along the coordinate of the Peierls transition.

- The CDW in $K_{0.3}MoO_3$ is driven by Fermi surface nesting (see 3.3.1) and the melting of the electronic order and consequently the interatomic potential leading to a periodic lattice modulation occurs instantaneously compared to the coherent lattice motion.

Based on these assumptions, we can introduce a fluence dependent double-well potential describing the displacement along the coordinate of the Peierls distortion after photoexcitation ($t > 0$). Similar approaches inspired by Landau theory (see Eqs. 3.8) have been used to describe the dynamics of the order parameter after photoexcitation before [30, 175].

$$V(x) = \frac{1}{2} \left( \eta \exp \left( -\frac{t}{\tau_{\text{disp}}} \right) - 1 \right) x^2 + \frac{1}{4} x^4$$  \hspace{1cm} (7.4)

The fluence dependent parameter $\eta \propto F$ describes the suppression of electronic order just after excitation. It is assumed to relax exponentially with a time constant $\tau_{\text{disp}}$. In thermal equilibrium (for $t < 0$), the parameter $\eta = 0$, and the potential takes the form of a double-well potential with a Peierls barrier partitioning two equivalent equilibrium positions. In equilibrium, the system resides in one of these minimum positions, the atom positions correspond to the equilibrium displacement along the structural coordinate of the Peierls distortion.

After photoexcitation, $\eta > 0$ and the Peierls barrier will be reduced. In the low perturbation regime $\eta \approx 0$, the Peierls barrier only slightly reduces, resulting in a small shift of the equilibrium position and coherent oscillations around the transient equilibrium position corresponding to the amplitude mode. For fluences above the melting threshold of the CDW condensate, $\eta \geq 1$, the Peierls barrier collapses almost instantaneously, resulting in coherent oscillations in a high-symmetry potential and the system overshoots into the opposite side of the potential, corresponding to a transient periodic lattice distortion with different phase. The evolution of the potential for different excitation fluences is shown in Fig. 7.6. Based on the fluence dependent potential (Eq. 7.4), the equation of motion for the coherent motion after photoexcitation is given by:

$$\frac{1}{\omega_{\text{DW}}^2} \frac{\partial^2}{\partial t^2} x - (1 - \eta \exp \left( -\frac{t}{\tau_{\text{disp}}} \right)) x + x^3 + \frac{2\gamma(t)}{\omega_{\text{DW}}^2} \frac{\partial}{\partial t} x = 0$$  \hspace{1cm} (7.5)

Here, $\omega_{\text{DW}} = 2\pi\nu_{\text{DW}}$ corresponds to the angular frequency of the motion in the double-well potential. In the equation of motion, a phenomenological time-dependent damping parameter $\gamma(t)$ is introduced. This parameter is needed to accurately reproduce the measured diffraction signal and will be explained in detail later. To be able to compare the model to the measured delay traces, we have to take into account the inhomogeneous excitation profile of the $K_{0.3}MoO_3$ single crystal. Since the laser penetration depth $\delta_L$ is comparable to the x-ray penetration depth
\[ I(t) \propto \sum_{j} \Delta_j \left| F_{Sj}^{\text{SL}}(t) \right|^2 \] (7.6)

with weights \( \Delta_j = \exp \left( -\frac{2j d}{\delta_X} \right) \). The signal of a single layer with a distinct excitation parameter is shown in Fig. 7.7 (a) for several fluences. For the phenomenological damping parameter in the equation of motion, an expression as simple as possible that still allows to capture the main features of the data is chosen:

\[ \gamma(t) = \gamma_{\text{asym}} \left( 1 - \exp \left( -\frac{t}{\tau_\gamma} \right) \right) \] (7.7)

For long delay times after photoexcitation, the damping is set to take an asymptotic value \( \gamma_{\text{asym}} = 2 \text{ ps}^{-1} \) which is close to the damping constant measured with neutron diffraction near the thermal phase transition [65]. The assumed timescale of the damping \( \tau_\gamma = 300 \text{ fs} \) is close to the fast relaxation timescale measured with optical pump-probe spectroscopy [3]. Without a time-dependent damping that assumes small values immediately after photoexcitation, the near complete transient recovery of the periodic lattice distortion at \( t = 350 \text{ fs} \) cannot be explained. Moreover, there are no further oscillations after the recovery, requiring that the damping has to be rapidly increasing during the motion associated with the overshoot in the high symmetry.
potential. The full fitting procedure includes a convolution with a Gaussian to account for the

![Diagram](image)

Figure 7.7: (a): Simulated normalized diffraction intensity from individual layers for selected values of $\eta$. Low values of $\eta$ lead to a signal associated with the amplitude mode, while $\eta \geq 1$ leads to overshoot dynamics associated with the motion in a high-symmetry potential. (b) Excitation profile of the crystal. The value of $\eta$ at the surface is defined as $\eta_0$. The parameter $\eta$ for layer deeper into the crystal is scaled along the surface normal $z$ due to linear absorption in the crystal. (c) Flow diagram of the fitting procedure.

experimental time resolution and is illustrated in Fig. 7.7 (c). The only fitting parameters needed to fit the complete fluence dependence are $\eta_0(F)$, the excitation parameter at the uppermost layer, and $\tau_{\text{disp}}$, the relaxation time averaged over all layers. Fits according to the model are shown as solid lines in Fig. 7.4. The frequency $\nu_{\text{DW}}$ was determined by fits to low fluence traces to be $\nu_{\text{DW}} = 1.53$ THz, which is in close agreement with the frequency of the high temperature bare phonon frequency of the phonon branch displaying the Kohn anomaly [65]. For the comparison to the data, the model is rescaled by the same saturation background level 0.4$I_0$ for all fluences.

Fits based on model simulations are shown as solid lines in Fig. 7.4. The model simulations agree well with the measured data and capture all main features of the different fluence regime:

- Excitation of the amplitude mode for fluences below the melting threshold ($\eta < 1$)
- No clear oscillatory signature of the amplitude mode or the transient recovery for intermediate fluences ($F = 1$ mJ). In this regime, significant contributions of $\eta < 1$ layers as well as $\eta > 1$ layers are added, effectively canceling out a clear oscillatory signal. For fluences
that are close to the threshold for a complete suppression of the periodic lattice distortion, the decrease of the initial drop time to $\tau_{\text{drop}} = 100$ fs is well reproduced by the model.

- Transient recovery of the periodic lattice distortion, which corresponds to the overshoot in a high-symmetry potential after photoexcitation. The transient recovery is followed by a complete suppression of the periodic lattice distortion. The peculiar shape of the overshoot corresponding to a half oscillation in the high symmetry potential is reproduced after introduction of a time-dependent damping parameter $\gamma(t)$.

For the intermediate fluence $F = 1$ mJ/cm$^2$, the agreement of the model with the data is not as good as in the low and high fluence regime. This is most likely related to the fact that layers with qualitatively very different dynamics add up to form the full signal, which thus depends crucially on the precise excitation profile of the sample. In the model, no possible nonlinear components of the initial absorption process were considered. Furthermore, as discussed earlier, variations of the grazing angle $\alpha$ allow for a range of x-ray absorption lengths, which is also not considered in the model. If most layers are excited below or above the melting threshold, the dynamics of different layers are qualitatively similar and the overall signal does not depend as critically on the precise absorption profile.

The introduced phenomenological time-dependent damping can have several origins. In the highly nonequilibrium state after photoexcitation, it is not clear which scattering channels are primarily determining the damping of the coherent motion along the distortion coordinate. Possibilities include (i) excited quasiparticles that relax back to the Fermi surface via electron-electron scattering and then strongly couple to the amplitude mode and (ii) anharmonic coupling of the coherent motion in the transient high-symmetry potential with other phonon modes.

7.5 Discussion and outlook

In summary, the coherent structural dynamics associated with the ultrafast melting of the CDW in $K_{0.3}$MoO$_3$ were observed using time-resolved x-ray diffraction. The experimental time resolution at the FEMTO slicing source as well as its spatial and temporal stability over many hours made it possible to acquire a complete picture of the structural dynamics through the symmetry breaking transition. In the low fluence regime, coherent oscillations could be unambiguously assigned to the collective amplitude mode of the system. For fluences above the melting threshold of the CDW condensate, we observed a transient recovery of the periodic lattice distortion and can directly quantify timescales of the change of the structural symmetry in the system.

The phenomenological model of a fluence-dependent double-well potential captures all important features of the measured time-resolved diffraction data. Using the model, the change of structural symmetry on a sub-picosecond timescale during the ultrafast transition can be naturally explained as a coherent motion along the structural coordinate of the Peierls distortion. The agreement with the model indicates that in fact the shape of the transient high-symmetry
potential determines the dynamics through the ultrafast transition and not the lattice modes of the initial state.

This finding should prove to be universal for ultrafast symmetry-breaking transitions in other materials where the periodic lattice distortion is a consequence of an instability in the electronic system. The details of the coherent structural dynamics will of course depend on the specific system. Whether a transient recovery of the periodic lattice distortion can be observed depends crucially on the evolution of transient scattering channels for the coherent motion in the nonequilibrium state after photoexcitation.

On a more fundamental level, the results contribute to answer the question how the change of structural symmetry during a photoinduced transition can happen on a sub-picosecond timescale for a macroscopically large excited volume of a sample. Domain growth occurring on much slower timescales does not present a limitation since the change of structural symmetry is promoted coherently in all parts of the sample that are excited above the melting threshold. In fact, no dynamics associated with domain creation or changes in Debye-Waller factor (see Sec. 2.4) needed to be included to fully explain the observed dynamics. This stands in contrast to results from all-optical pump-probe spectroscopy investigating the changes of electronic symmetry in CDW systems, utilizing double-pump excitation [175]. Here, the creation and annihilation of domains had to be included to explain the dynamics observed after melting of the CDW.

A big question mark remains with regard to the origin of the time dependent damping. As mentioned earlier, the time dependence could either be related to anharmonic coupling of the coherently excited amplitude mode to other modes, or be caused by coupling of quasiparticles to the coherent motion. Since in the transient regime after excitation eigenmodes in the crystal are not well-defined and the transient potential can be highly anharmonic, phonon-phonon coupling is likely to significantly determine the transient damping. On the other hand, the evolution of the damping of the amplitude mode in the CDW ground state could be fully explained by coupling of $2k_f$ modes to the electronic order parameter [30]. Consequently, electron-phonon coupling cannot be ruled out completely.

A promising new experimental technique made possible by FELs that could be helpful to shed light on the damping mechanism is time-resolved diffuse scattering [25]. Utilizing time-resolved diffuse scattering, the nonequilibrium phonon population after photoexcitation can be observed, allowing for a study anharmonic decay paths. It has, however, been proven difficult to conduct these measurements on CDW compounds due to the generally bad surface quality of cleaved CDW crystals. Results gathered from time- and angle-resolved photoemission spectroscopy lead to the hypothesis of anharmonic decay of the coherently excited $q = 0$ amplitude mode into two phasons with opposite wave vector [28], a mechanism that could also contribute to the anomalous damping in the presented measurements.

In Sec. 3.3, the question of how CDW formation in a solid state system can be classified was discussed. In a lot of systems, the important question is whether the main driving force of CDW formation is based on (i) an instability in the electronic system and a dispersionless electron-
phonon coupling constant (Peierls transition) or (ii) a $q$-dependent electron-phonon coupling constant [see Sec. 3.3]. Recently, time-dependent techniques like angle-resolved photoemission and broadband THz spectroscopy have contributed to help solve this question in some systems [176, 55]. A transient recovery as observed in the Peierls system $K_{0.3}$MoO$_3$ is only expected to occur if CDW formation is based on an electronic instability. Similar measurements could therefore help to elucidate the origins of CDWs in more complicated systems.

Recently, we could observe a similar overshoot in a transient high-symmetry potential in the perovskite manganite Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ after melting of charge and orbital order by a femtosecond laser pulse with x-ray pulses from an FEL [37], already showcasing the universality of the phenomenon observed in $K_{0.3}$MoO$_3$. The results of the x-ray diffraction measurements on the manganite could however be explained without having to assume any time-dependent damping of the coherent motion.

The emergence of FELs will certainly play an important role in the study of structural dynamics in CDW compounds and other strongly correlated electron systems in the future. The sensitivity of $K_{0.3}$MoO$_3$ to x-ray induced sample damage could however make FEL measurements difficult, making synchrotron slicing an almost ideal source for these types of measurements in this specific compound.

An experimental technique that allows to gain more information about the structural dynamics in the transient state is explored in chapter 8. Using double-pump optical excitation and x-ray probe, different questions can be addressed: Can we actively modify the damping of the coherent motion using a second excitation pulse? Can a second pump pulse help to distinguish between different damping mechanisms?
Chapter 8

Double-pump excitation in K$_{0.3}$MoO$_3$

In this chapter, results of time-resolved x-ray diffraction measurements of the periodic lattice distortion in K$_{0.3}$MoO$_3$ after double-pump excitation are presented. First, the general idea behind time-resolved measurements with multiple excitation pulses and its usefulness for studying transient damping mechanisms in K$_{0.3}$MoO$_3$ are outlined. After giving details on the experimental setup, results of the double-pump measurements for varying pump-pump delays and fluence ratios are presented. The results are then discussed with regard to the possibility of exploring the observed time-dependent damping in the transient state after intense photoexcitation.

8.1 The double-pump approach

One of the most important questions in connection with the time-resolved x-ray diffraction experiments on K$_{0.3}$MoO$_3$ concerns the origin of the time-dependent damping of the coherent motion during the change of structural symmetry associated with the CDW-to-metal transition. To find out more about transient scattering channels of the coherent motion during the ultrafast transition, double-pump excitation studies provide a means to re-excite the system in the nonequilibrium state induced by the first pump pulse and test if and how a second pump pulse can change available scattering channels and consequently the damping of the coherent motion.

In the past, double-pump excitation studies of solid state systems have primarily been used as a means to control coherently excited $q = 0$ excitations. Using this method it was shown, for example, that the amplitude of a fully-symmetric coherent phonon in bismuth after double-pump excitation depends on the relative delay of the two pump pulses $\Delta t_{12}$ [177]. For in-phase excitation (when $\Delta t_{12}$ corresponds to the phonon period $T$), the amplitude of the coherent phonon is enhanced, while for out-of-phase excitation ($\Delta t_{12} = T/2$), the oscillation cancels out. Similar measurements showcasing coherent control of lattice vibrations where conducted in various systems, ranging from simple metals and semi-metals to superconductors [178, 35, 179].
Using resonant THz double-pump excitation, coherent control of antiferromagnetic spin waves was demonstrated \[157\].

In addition to being merely used to control coherent motion in a solid, double-pump excitation can be employed to contrast the effects of lattice anharmonicity and the generated electron-hole plasma after photoexcitation on a coherent phonon. For example, it could be shown that in highly photoexcited bismuth, lattice anharmonicity plays a minor role for the observed softening of the $A_{1g}$ coherent phonon \[181\]. Such a study is possible since double-pump excitation allows to separately control the amplitude of the coherent motion and the concentration of excited carriers.

A similar approach can now be employed to study the coherent motion associated with the change of structural symmetry in $K_{0.3}MoO_3$: The first pump pulse melts the CDW condensate and triggers a coherent motion, while the second pump pulse re-excites the electronic system. A schematic of the idea is presented in Fig. 8.1.

The response of the system to double-pump excitation then helps to answer questions concerning the time-dependent damping term introduced to model the structural dynamics after single-pump excitation. For example, if the structural dynamics and the transient recovery of the periodic lattice distortion do not significantly change after strong re-excitation of the electronic system, the electronic distribution at the Fermi surface cannot have a decisive impact on transient scattering channels for the coherent motion during the phase transition. If strong re-excitation however leads to a modification of the measured coherent structural dynamics, the existence of time-dependent scattering channels can be confirmed and the damping mechanism can potentially be clarified.

**Figure 8.1:** Schematic of the double-pump excitation experiment. The first pump pulse melts the electronic order and launches the coherent motion, as observed in the single-pump experiment presented in Chap. 7. The second pump pulse re-excites the electronic system while the atoms still coherently move along the coordinate of the Peierls distortion.
8.2 Experimental setup

The double-pump x-ray probe experiments were carried out at the FEMTO slicing source at the Swiss Light Source with an experimental geometry that closely resembles the setup for single-pump excitation measurements presented in Sec. 7.1. The x-ray probe branch was not modified, like in the single-pump experiments 7 keV sliced x-ray pulses were diffracted off the sample in a grazing incidence geometry with a comparable spot size and time duration. Again, an APD was positioned to measure the temporal evolution of the $\{(1 - q_b) \ 0.5\}$ reflection from a freshly cleaved $K_{0.3}MoO_3$ sample cooled to $T = 95$ K with a cryogenic nitrogen blower. A schematic of the experimental setup is shown in Fig. 8.2.

![Image of Experimental setup](image)

**Figure 8.2:** Experimental setup for the double-pump x-ray probe measurements at the FEMTO slicing source. Compared to the standard 800 nm pump setup, a Mach-Zehnder interferometer is inserted into the pump branch, allowing to create two successive pump pulses with an adjustable time delay $\Delta t_{12}$. The overall delay between pump and x-ray probe is set by the delay stage $Delay \ 1$, while the relative delay of the two pump pulses is set by delay stage $Delay \ 2$ inside the interferometer. BS: non-polarizing beam splitter. WP: $\lambda/2$ wave plate. ML: Multilayer mirror. KB mirror: Kirkpatrick-Baez mirror.

To create two 800 nm pump pulses with adjustable relative time delay $\Delta t_{12}$, a Mach-Zehnder interferometer was integrated into the pump branch. The beam is split by a non-polarizing beam splitter with a splitting ration close to 50/50 and one part is routed over a delay stage, while the other part travels through a fixed-length beam path. The two beams are then recombined with a second identical non-polarizing beam splitter. The relative time delay of the two pumps $\Delta t_{12}$ can be set by the interferometer delay stage, while the overall delay between the two pump pulses and the x-ray probe pulse is set by another delay stage before the interferometer. A $\lambda/2$ wave plate is placed into each of the two arms of the interferometer to allow for an independent adjustment of the fluence of the two pump pulses in combination with the Brewster plate in front of the sample. The zero delay position ($\Delta t_{12} = 0$ fs) of the stage in the interferometer was found using a cross-correlation of the pulses traveling through the two different arms in a Barium borate (BBO) crystal. Spatial overlap of the pump pulses at the sample position was verified by
imaging the leak of a mirror on a beam profiler placed at an equal distance from the mirror as the sample.

Preliminary double-pump measurements to ensure temporal and spatial overlap with x-ray pulses were carried out in a grazing incidence geometry using a bismuth sample. The final calibration of the delay stage in the Mach-Zehnder interferometer was achieved by overlaying delay traces of the time-dependent intensity of the Bi-(111) reflection after single pump excitation and alternate blocking of one of the two interferometer arms. Coherent control of the \( A_{1g} \) similar to results reported in [35] could be observed by measuring the time evolution of the Bi-(111) diffraction peak after double-pump excitation.

One of the main challenges of using double-pump excitation in a strong-excitation regime, where the fluence of both excitation pulses has to be high enough to solely photoinduce melting of the CDW as well as trigger the transient recovery in large parts of the excited sample volume, is degradation of the K\(_{0.3}\)MoO\(_3\) sample surface and a resultant drop in overall diffraction efficiency. For high-fluence double-pump measurements, the fluence for each pump pulse was chosen to be the lowest possible so that in single-pump time traces the transient recovery could still be observed with a magnitude close to its maximum value. As evident from Fig. 7.4, higher fluences do not result in different measured structural dynamics once the saturation fluence is reached.

### 8.3 Results

Figure 8.3 shows a comparison of single-pump and double-pump traces taken under identical conditions in direct succession. The two single-pump traces are recorded with one arm of the interferometer closed at a time. Time-zero with respect to the x-ray pulses of the second single-pump trace was shifted by \( \Delta t_{12} = 300 \text{ fs} \) with the delay stage in the interferometer. The absorbed fluence for both traces was \( F_1 = F_2 = 1.7 \text{ mJ/cm}^2 \). As expected, the two traces look very similar to the traces shown in Fig. 7.4 for an excitation fluence larger than the excitation threshold of the CDW condensate: There is a clear sub-picosecond transient recovery of the diffraction intensity and the saturation background assumes a similar value \( (I(t > 1 \text{ ps})/I_0 \approx 0.4I_0) \).

The double-pump trace recorded with both arms of the interferometer open and a relative time delay \( \Delta t_{12} = 300 \text{ fs} \) shows a clear second recovery peaking at a delay \( t = 650 \text{ fs} \). In this configuration, the second pump pulse hits the sample when the transient recovery induced by the first pump pulses reaches its maximum. After the second recovery, the diffraction intensity remains at a background level \( I(t > 1 \text{ ps})/I_0 \approx 0.35I_0 \), which is only slightly lower than the background level obtained in a single-pump experiment.

To learn more about the nature of the additional recovery induced by the second pump pulse and the nonequilibrium state after photoexcitation, we varied the time delay \( \Delta t_{12} \) between the two pump pulses. The time-resolved x-ray diffraction signals for varying pump-pump delays \( \Delta t_{12} \) are shown in Fig. 8.4. When the second pump pulse hits the sample while the atoms are still in a coherent motion \( (\Delta t_{12} = 180 \text{ fs and } \Delta t_{12} = 300 \text{ fs}) \), it induces a clear second transient recovery.
For larger delays between the two pump pulses ($\Delta t_{12} = 500$ fs and $\Delta t_{12} = 1$ ps), there is no second recovery and the delay scans closely resemble a single-pump delay scan. Notably, there is no change of the background level for a late arrival of the second pump pulse ($\Delta t_{12} = 1$ ps).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure83.png}
\caption{Normalized diffraction intensity of the (1 (4 − $q_b$) 0 5) SL reflection after single- and double-pump excitation. The black dots correspond to single pump traces taken at absorbed fluences $F_1 = F_2 = 1.7$ mJ/cm$^2$. The temporal delay of the lower single-pump curve was shifted by $\Delta t_{12} = 300$ fs with respect to the x-ray pulses compared to the upper single-pump trace. The data shows the same transient recovery and a comparable saturation background as the high-fluence data presented in Chap. \ref{chap:7}. The red dots show the evolution of the measured diffraction intensity for double-pump excitation when both pump arms in the interferometer are open. There is a clear additional second recovery with almost the same magnitude. For clarity, the double-pump trace is offset by +0.8 and the upper single pump trace is offset by +1.6.}
\end{figure}
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![Normalized diffraction intensity of the SL peak for double-pump excitation with varying pump-pump delays $\Delta t_{12}$.](image)

Figure 8.4: Normalized diffraction intensity of the SL peak for double-pump excitation with varying pump-pump delays $\Delta t_{12}$. The fluence for both pump pulses was set to $F_1 = F_2 = 1.7 \text{ mJ/cm}^2$ for all measurements. The red vertical line in the plots indicates the arrival of the second pump pulse.
Figure 8.5 shows the normalized diffraction intensity after double-pump excitation with varying fluence $F_2$ of the second pump pulse, while the fluence of the first pump pulse is kept constant at a value above the melting threshold of the CDW for large parts of the probed volume, $F_1 = 1.7 \text{ mJ/cm}^2$. The pump-pump delay for all traces is kept constant at $\Delta t_{12} = 300 \text{ fs}$. For a fluence $F_1 = F_2$, the results of the previously shown double-pump measurements recorded under identical conditions are reproduced. For lower fluences ($F_2 = 0.9 \text{ mJ/cm}^2$ and $F_2 = 0.5 \text{ mJ/cm}^2$), there is no clear second transient recovery. In a single-pump measurement, a fluence of around $1 \text{ mJ/cm}^2$ results in a melting of the periodic lattice distortion of large parts of the probed sample volume, but a transient recovery is not observed. An excitation fluence of around $0.5 \text{ mJ/cm}^2$ results in an excitation of the amplitude mode and no melting of the periodic lattice distortion.

The three different reported pump-pump delay traces (see Figs. 8.3, 8.4 and 8.5) with $t_{12} = 300 \text{ fs}$ where both fluences were chosen to be above the melting threshold of the periodic lattice distortion all show a clear second transient recovery that nearly assumes the same magnitude as the recovery induced by the first pump pulse.

It has to be noted, however, that two traces recorded under similar experimental conditions did not show a second transient recovery with a comparable magnitude. In one case, even the first transient recovery was significantly less pronounced, albeit all traces having the same saturation background. The traces with non-fully developed transient recoveries were recorded after different high-fluence measurements had been performed on the same sample spot. The difference in magnitude of the recoveries in diffraction intensity might therefore be related to sample degradation after prolonged exposure to intense femtosecond laser pulses. Non-ideal spatial overlap between x-ray probe and both 800 nm pump pulses can likely be excluded since the procedure of ensuring spatial overlap did not differ from other measurement series. It is not completely clear how the effects of sample degradation can be thoroughly explained, since the magnitude of the recoveries does not correlate with the diffraction intensity of a certain sample spot.
Figure 8.5: Normalized diffraction intensity of the SL peak for double-pump excitation with varying fluence $F_2$ of the second pump pulse. The pump-pump delay was kept constant at $t_{12} = 300$ fs and the fluence of the first pump pulse was $F_1 = 1.7$ mJ/cm$^2$ for all traces.
8.4 Discussion of the double-pump excitation results

The time-resolved x-ray diffraction signal after double-pump excitation clearly shows a second transient recovery when the second pump pulse hits the sample while, right after the ultrafast melting of the CDW, the atoms are still in a coherent motion ($\Delta t_{12} = 180$ fs and $\Delta t_{12} = 300$ fs). The measured data can be naturally described within the framework of the model introduced in Chap. 7. The first pump pulse melts the CDW condensate and triggers a coherent motion along the coordinate of the Peierls distortion in a high symmetry potential. The system overshoots into the other side of the transient high symmetry potential. The second pump pulse then modifies the shape of the potential or the effective damping of the coherent phonon, resulting in an additional overshoot into the initial side of the transient high-symmetry potential. The peak of the second recovery therefore corresponds to a periodic lattice distortion with the same phase as the equilibrium distortion, but with a reduced amplitude. After the second overshoot in the transient high symmetry potential, the system remains in the central point of the high symmetry potential without any further oscillations.

One of the main motivations of conducting the double-pump excitation measurements was to test whether the anomalous damping of the coherent motion during the ultrafast transition can be modified by a second pump pulse. This is clearly the case, as evidenced by the second overshoot followed by the abrupt stop to the coherent motion when the system again reaches the high-symmetry point. The temporal evolution of the damping triggered by the second pump pulse seems to closely resemble the one after single-pump excitation. A clear assignment of the main microscopic scattering channel dictating the damping of the coherent motion however still remains difficult, as both coupling of quasiparticles to the coherent motion and lattice anharmonicities cannot be ruled out as a main contributing factor to the damping:

- The second pump pulse re-excites the electronic system, which is assumed to relax on a timescale on the order of around 100 fs $[3]$. Changes of the population of the Fermi surface and the resulting change in coupling to the coherent motion along the amplitude-mode coordinate could change the damping of the coherent motion.

- The re-excited electronic system can also cause changes to the transient crystal eigenmodes and the anharmonic coupling between the coherent motion along the coordinate of the Peierls distortion and other phonons.

The two listed possible damping mechanisms are highly interconnected and cannot be easily disentangled. Additionally, dephasing of the coherent motion between layers with different excitation levels and consequently a different shape of the transient interatomic potential that dictates the coherent motion could contribute to the observed time-resolved diffraction signal.

A possible model of the double-pump experiments needs to be able to capture all features of the double-pump diffraction data for varying parameters. While a phenomenological approach with a simple exponential time-dependent damping (see Eq. 7.7) can explain parts of the
double-pump excitation data, it does not allow for an introduction of for example a varying fluence of the second pump pulse and will not give more insights into the damping mechanism.

A different approach to model the structural dynamics after double-pump excitation lies in the use of a two-temperature model, describing the electronic temperature $T_e$ after photoexcitation and the energy transfer to (a subsystem) of the lattice with temperature $T_l$. The system can then be described by the set of rate equations

$$C_e(T_e) \frac{\partial T_e}{\partial t} = -g(T_e - T_l)$$

$$C_l(T_l) \frac{\partial T_l}{\partial t} = g(T_e - T_l)$$

where $C_e$ is the electronic heat capacity, $C_l$ is the heat capacity of the subsystem of the lattice that couples most strongly to the electronic system, and $g$ is the electron-phonon coupling constant.

The electronic temperature after photoexcitation can then be employed to define the shape of a Landau-type double-well potential (see Eq. 3.8) and the damping of the coherent motion could be compared to the damping of the amplitude mode of the CDW ground state measured in thermal equilibrium, which shows a peaked increase around $T_c$.

Modeling the results in this way, however, introduces a large number of parameters that at this point are not sufficiently characterized, for example the temperature-dependent electronic heat capacity $C_e(T_e)$ and the electron-phonon coupling parameter $g(T_e)$, that depend on the density of states at the Fermi surface. To acquire meaningful results, for example a precise measurement of the time evolution of the electronic distribution around the Fermi surface with time-resolved angular photoemission would be extremely helpful. With good knowledge of these parameters, adapting the model to the data might allow to shed more light on the origin of transient scattering channels. Nevertheless, a model based on an effective transient temperature will in certain aspects always rely on the mapping of equilibrium properties to a highly nonequilibrium state after intense photoexcitation.

Preliminary attempts to model the data with simplified parameters can accurately describe a subset of the measured delay traces, but cannot consistently account for all experimentally observed features. Furthermore, the simulated results are highly sensitive to input parameters.

An important, model-independent insight from the double-pump measurements concerns the nature of the transient state after the coherent motion damps out ($t > 1$ ps). A second late excitation does not induce a change of the measured diffraction intensity. This fact has several important implications, for both the double- and the single-pump experiments: (i) the dynamics induced by the second pump pulse are not related to the destruction of the CDW state in previously unexcited parts of the probed volume. A scenario where the second pump pulse induces a transient recovery in unexcited parts of the sample, resulting in a similar double-pump signal with two transient recoveries, can thus be ruled out. (ii) The transient state after photoexcitation corresponds to a state with a completely melted periodic lattice distortion, which
is further evidence that the background level observed in all delay scans can be attributed to
diffraction from surface irregularities.

8.5 Summary and outlook

The double-pump measurements presented in this chapter confirm the presence of a time-depen-
dent damping in the transient state after intense photoexcitation of the quasi-one-dimensional
CDW compound $K_{0.3}MoO_3$. Moreover, they also reveal that the damping during the photoin-
duced CDW-to-metal transition can be actively modified by a second pump pulse. For a complete
understanding of the transient scattering channels after photoexcitation, the data however seems
insufficient, since no potential origin of the transient damping can be thoroughly ruled out,
as effects of lattice anharmonicity and electron-phonon coupling on the measured signal are
deply entangled. The damping mechanism determines whether the energy of the coherently
moving atoms is primarily transferred to the electronic system or the lattice as a first step of
relaxation. As mentioned earlier, (i) experiments directly accessing the occupation of electronic
states like time-resolved photoemission and (ii) time-resolved diffuse scattering experiments that
can directly measure the incoherent phonon population could therefore help solve the question of
the origin of the time-dependent damping. A precise knowledge of the electronic occupation of
the system after photoexcitation would also be needed to model the data in the framework of a
two-temperature model.

A more complete mapping of pump-pump delay times and fluence ratios could further help
to put tighter restrictions on a potential model that aims at discriminating different origins of
the damping. The mentioned problems regarding sample degradation could be circumvented
by choosing a different quasi-one-dimensional CDW compound that is expected to show similar
structural dynamics during the ultrafast CDW-to-metal transition. Possibilities include $(TaSe_4)_2I$
and NbSe$_3$, whose phase diagram is presented in Fig. 3.5. Surface irregularities will however
most likely also present a problem when working with these compounds in a grazing incidence
geometry necessary for time-resolved x-ray diffraction. For example, NbSe$_3$ grows in the form of
ribbon-like crystals with a width of only up to 100 $\mu$m.

Similar time-resolved x-ray diffraction measurements after double-pump excitation could help
to study ultrafast photoinduced transitions in other strongly correlated systems. For example,
the order parameter dynamics after photoexcitation in $Pr_{0.5}Ca_{0.5}MnO_3$, where a related coherent
motion in a transient high symmetry potential has been observed [37], could be refined using
double-pump excitation.

In systems with a more complicated phase diagram like 1T-TaS$_2$, double-pump excitation
allows to study the transient phase after photoexcitation in a new way. Starting in the nearly-
commensurate phase, the first pump pulse can trigger a transition to the incommensurate phase,
that nucleates on a timescale of several picoseconds [183]. The second pump pulse can now be
utilized to trigger dynamics in the transient incommensurate phase. In this scenario, different
pump-pump delays would allow to for example tune the correlation length in the incommensurate phase at the time of the arrival of the second pump.
Chapter 9

Ultrafast structural dynamics in the commensurate phase of 4H_b-TaSe_2

Transition metal dichalcogenides are a class of materials in which transitions to various CDW ground states cannot be adequately explained within the Peierls picture (see Sec. 3.3). Often, momentum-dependent electron-phonon coupling is assumed to be a significant factor in the formation of CDW in these systems [54, 73]. In 4H_b-TaSe_2, a CDW commensurate with the underlying lattice is present at room temperature, details on the compound and its structure are given in Sec. 3.3.3.

Quasi-two-dimensional compounds like 4H_b-TaSe_2 are easily cleaved between layers perpendicular to the crystallographic c-axis. Sample thicknesses below 100 nm can be achieved by cleaving sheets of bulk (001)-single crystals, making transition metal dichalcogenides ideal samples for studying the dynamics of CDW formation with ultrafast electron diffraction [44, 77]. Using this technique, the melting of commensurate order as well as its reformation dynamics in 4H_b-TaSe_2 have been directly observed [77]. The time resolution of these measurements was however not sufficient to fully access sub-picosecond coherent dynamics of the lattice during the melting of commensurate order, which is assumed to occur on the timescale of the soft modes of the system. As a result, for example the damping of the coherent motion during the melting of the CDW could not be quantified. In the context of this work it is particularly interesting to contrast the coherent dynamics after intense photoexcitation in 4H_b-TaSe_2 to the results obtained in the quasi-one-dimensional system K_{0.3}MoO_3 and to test whether qualitatively similar dynamics, specifically regarding the sub-picosecond transient recovery, can be observed. In the long run, a direct structural probe of the photoinduced melting of electronic order could help to classify different mechanisms of CDW formation by monitoring the coherent structural dynamics during ultrafast CDW-melting.

In this chapter, time-resolved x-ray diffraction measurements carried out in the commensurate phase of 4H_b-TaSe_2 are presented and compared to the results obtained in the quasi-one-dimensional system K_{0.3}MoO_3. A very similar excitation-dependent interatomic potential is
utilized to describe the coherent motion launched after photoexcitation. The classification of the results in the framework of the model is however not as far-reaching as for $K_0.3MoO_3$, as the observed structural dynamics are not as rich as in the quasi-one-dimensional system, posing less restrictions on potential models and in turn weakening possible conclusions. The results of the time-resolved x-ray diffraction measurements are then compared in detail to the ultrafast electron diffraction experiments [77] to highlight differences of the two methods.

9.1 Experimental setup

Preparatory static x-ray diffraction measurements in the commensurate phase of 4H$_b$-TaSe$_2$ at room temperature were carried out in a grazing geometry at the Material Science beam line at the Swiss Light Source [173] with 7 keV-energy x-rays. Figure 9.1 shows a cut through reciprocal space along a modulation vector of the charge density wave. Such a scan can be obtained with the 2+3 circle diffractometer at the beamline by moving the detector position and the sample rotation in unison with the control software of the diffractometer, at all times keeping a defined ($h \ k \ l$) position for a certain area of the 2D pixel detector. The scan in the figure goes along $(3/13 \ 1/13 \ 0)$, passing the regular lattice peak (1 1 4) and showing the commensurate superlattice reflections $(1 \ 1 \ 4) - (3/13 \ 1/13 \ 0)$ and $(1 \ 1 \ 4) + (3/13 \ 1/13 \ 0)$.

The grazing angle of the x-rays for the static diffraction measurements was set to $\alpha = 5^\circ$. The efficiency of the superlattice peaks at this grazing angle was measured to be approximately $1.5 \times 10^{-4}$. The inset of Fig. 9.1 shows an image of a superlattice peak taken with the pixel detector. Owing to the poor surface quality of the cleaved crystal that is typical for transition metal dichalcogenides [53], the diffraction peak has considerable internal structure.

Time-resolved x-ray diffraction measurements were conducted at the FEMTO slicing source at SLS in an experimental geometry very similar to the one presented for the measurements on $K_0.3MoO_3$ (see Fig. 7.1). Since the commensurate phase of 4H$_b$-TaSe$_2$ emerges below a transition temperature $T_c = 410$ K, no temperature control was employed for the measurements.

For pumping, the $\lambda = 1310$ nm output of an OPA in the x-ray hutch was used, hitting the sample at an angle $\beta = 10^\circ$. The parameters of the x-ray probe pulses were identical to those during the $K_0.3MoO_3$ measurements ($E = 7$ keV, focus size $(10 \times 250) \ \mu m^2$, 1.3% bandwidth set by a multilayer mirror). The grazing angle was set to approximately $\alpha = 1^\circ$, resulting in an x-ray penetration depth of around 100 nm. A precise determination of the grazing angle was again prohibited by the bad surface quality of the cleaved crystal.

An APD was positioned to measure the regular lattice reflection (1 0 8) as well as the superlattice reflection $(1 \ 0 \ 8) + (1/13 \ 3/13 \ 0)$, giving direct access to the structural symmetry of the system after photoexcitation. At the grazing angle $\alpha$ around 5 photons/second could be detected.
9.2 Results

Figure 9.1: Static diffraction intensity measured at the Material Science beamline at SLS in a grazing incidence geometry with an incidence angle $\alpha = 5^\circ$. The diffraction signal was measured with a Pilatus pixel detector and is normalized to the peak signal of the (1 1 4) regular lattice reflection. The $x$-axis corresponds to a cut through reciprocal space along one of the three modulation vectors of the CDW. The inset shows an image of a superlattice peak recorded with the 2D pixel detector.

9.2 Results

Figure 9.2 shows the sub-picosecond dynamics associated with the melting of the commensurate lattice order after photoexcitation with various fluences. For all fluences, the normalized diffraction intensity of the $(1 0 8) + (1/13 3/13 0)$ superlattice peak first drops rapidly on a timescale of around 150 fs and then recovers to a fluence dependent offset value. While for the lowest fluence, there seems to be a recovery on a 10 ps timescale, no clear recovery can be observed within the measurement window for higher fluences. The offset value persists at larger delay values (measured up to $t = 5$ ps), but with the limited range of recorded delay values, no definite statement about the relaxation timescale can be made.

The offset value increases when increasing the fluence from $F = 1.8 \text{ mJ/cm}^2$ to $F = 3.6 \text{ mJ/cm}^2$, but then saturates at a value of approximately $I = 0.7I_0$ for the highest fluence $F = 5.5 \text{ mJ/cm}^2$. This clear sign of saturation indicates that in parts of the probed volume the commensurate lattice modulation is fully melted, while the mismatch in penetration depths of
near-infrared pump and x-ray probe pulses results in a large contribution of diffraction signal from unexcited sample regions. As for the measurements on $K_{0.3}$MoO$_3$, additionally significant diffraction signal from unexcited sample volume due to surface irregularities can be expected.

Clear coherent oscillations associated with the amplitude mode ($\nu_A = 2.1$ THz) of the commensurate phase cannot be observed for any of the studied fluences. The time evolution of the superlattice peak diffraction intensity is very similar for all traces, first exhibiting a small dip before recovering and then remaining almost constant at a fluence-dependent offset value. This behavior indicates a highly damped motion along the coordinate of the commensurate distortion.

The time evolution of the diffraction intensity of the $(1\ 0\ 8)$-regular lattice peak measured for a fluence $F = 3.6$ mJ/cm$^2$ first increases on a timescale comparable to the timescale of the initial drop of superlattice peak intensity. It then decreases on a slightly slower timescale and drops below the equilibrium diffraction intensity. The changes in regular lattice diffraction intensity are much smaller than for the superlattice peak, with the largest change at around $t = 200$ fs being less than 1%.
Figure 9.2: Temporal evolution of the normalized diffraction intensity after photoexcitation in the room-temperature commensurate phase of 4H$_2$TaSe$_2$ for varying fluences. Upper plot: Dynamics of the (1 0 8) regular lattice reflection after photoexcitation with a fluence $F = 3.6$ mJ/cm$^2$. Lower plot: Dynamics of the (1 0 8)+(1/13 4/13 0) superlattice reflection for varying fluences.
9.3 Model of the coherent motion during the melting of commensurate order

The model introduced in the following describes the structural dynamics associated with the melting of commensurate order in 4H$_b$-TaSe$_2$ as a highly damped coherent motion along the coordinate of the commensurate lattice distortion. As in the case of the quasi-one-dimensional system K$_{0.3}$MoO$_3$, an excitation-dependent interatomic double-well potential is assumed to determine the coherent motion during the photoinduced transition. For the two-dimensional system 4H$_b$-TaSe$_2$, several limitations of the model concerning both the underlying physics of the system as well as the significance of the measured data have to be noted:

- For the quasi-one-dimensional system K$_{0.3}$MoO$_3$, the coherent motion can be assumed to be triggered by the collapse of the Peierls barrier in the double-well potential, induced by a sudden destruction of electronic order after intense photoexcitation. The mechanism of CDW formation in 4H$_b$-TaSe$_2$ is not as clear-cut and the Peierls picture may not be appropriate. However, a similar interatomic potential after photoexcitation may still be applied, as changes in electron distribution in the Ta 5$d$ band after photoexcitation can be assumed to result in a similar strong modification of the interatomic potential and a consequent coherent motion along the coordinate connecting the commensurate phase and the high-symmetry phase [77]. As momentum-dependent electron-phonon coupling effects most likely play a significant role in 4H$_b$-TaSe$_2$, the double-well potential can however not be considered to be of purely electronical origin.

- The model only describes the dynamics associated with the melting of commensurate order. The build-up of incommensurate order is assumed to occur as a second step on a timescale associated with domain creation. The timescale of the formation of incommensurate order after photoexcitation in the commensurate phase in the transition metal dichalcogenide 1T-TaS$_2$ could be observed during a different experiment conducted at FEMTO [183]. These experiments showed that the incommensurate order emerges from a diffuse scattering background, and a similar behavior can be expected in 4H$_b$-TaSe$_2$.

- The observed structural dynamics show a qualitatively similar evolution for all measured fluences. Contributions from different layers are therefore expected to be qualitatively similar, and the inhomogeneous excitation profile of the crystal is not taken into account. For lower fluences, coherent oscillations associated with the amplitude mode can be expected, but contributions from weakly excited layers seem to be insignificant even for the lowest measured fluence. No transient recovery for higher fluences can be observed, which could be related to the high damping constant of the coherent motion after photoexcitation. Owing to this fact, also for higher fluences the structural dynamics are qualitatively similar. Parameters in the model are therefore averages over the whole excited volume of the sample.
9.3 Model of the coherent motion during the melting of commensurate order

- A saturation background of $I/I_0 = 0.65$ is assumed in the model, implying that the residual signal stems from unexcited sample volume.

The normalized amplitude of the coherent structural motion $x(t)$ along the coordinate of the commensurate distortion can now be written as

$$\frac{1}{\omega^2} \frac{\partial^2 x}{\partial t^2} - \left(1 - \eta \exp \left(-\frac{t}{\tau_{\text{disp}}} \right) \right)x + x^3 + \frac{2\gamma}{\omega^2} \frac{\partial}{\partial t} x = 0$$

with the angular frequency $\omega_{\text{DW}} = 2\pi\nu_{\text{DW}}$ of the motion in the double-well potential, an excitation parameter $\eta$ (averaged over the whole excited volume), and the relaxation time $\tau_{\text{disp}}$ of the partition of the double-well potential. More information on the reasoning behind the equation of motion can be found in Chap. 7. In contrast to the time-dependent damping $\gamma(t)$ introduced for the coherent dynamics in $K_{0.3}\text{MoO}_3$, a damping constant $\gamma$ is assumed. The same approximations (see Eq. 7.1 and 7.2) are applied to connect the measured diffraction intensity and the amplitude of the coherent motion.

Fits to the data according to the model are shown in Fig. 9.2. The employed fitting procedure is described in Fig. 7.7 while as mentioned above, the inhomogeneous excitation profile is not taken into account. The model reproduces the main features of the temporal evolution of the measured superlattice diffraction intensity, namely the initial dip in diffraction intensity and the similar temporal evolution for all fluences. For all fluences, for the fits the frequency of the coherent motion in the double-well potential is kept constant at a value $\nu_{\text{DW}} = 1.5$ THz. The fitted value of the damping constant is similar for all traces, $\gamma \approx 5$ ps$^{-1}$. The relaxation time $\tau_{\text{disp}}$ is larger than 10 ps for all traces, but an accurate value cannot be assigned owing to the small measurement window.

The dynamics of the measured diffraction intensity of the $(1 0 8)$ regular lattice peak can now as well be treated within the same framework. In a kinematic approximation, the diffraction intensity integrated over the complete reciprocal space of the photoexcited structure and the structure with the fully developed commensurate lattice distortion is equivalent. According to Parseval’s theorem, this is however only strictly true on aggregate and not necessarily given for a singular regular lattice peak and its neighboring superlattice peaks. Nevertheless, the following estimate and a comparison to the relative changes of the measured superlattice and regular lattice peak in the commensurate phase indicate that it can be assumed as a good approximation for the measured relative changes.

As six superlattice peak emerge around every regular lattice Bragg peak in the commensurate phase of an untwinned 4H$_b$-TaSe$_2$ crystal and the intensity of superlattice peaks corresponds to roughly 1% of regular lattice peaks, a 30% change in superlattice peak intensity is, on average, expected to correspond to around a 2% change of a regular lattice peak. Single-crystal samples of 4H$_b$-TaSe$_2$ however always show twinning into so-called $\alpha$- and $\beta$-domains, that differ in the sense of rotation of the superlattice with respect to the underlying structure [53]. The exact domain distribution varies from crystal to crystal and while only one domain is measured at a time, the
suppressed intensities of $\alpha$- and $\beta$-superlattices are transferred to the regular lattice Bragg peaks. The expected overall value of the photoinduced change for a fluence $F = 3.6 \text{ mJ/cm}^2$ is therefore very close to the measured changes in the (1 0 8) peak.

To model the effect of the coherent motion connecting the commensurate structure and the transient photoexcited state, the simulated change of the superlattice peak due to the transient changes in the interatomic potential is scaled and reversed in sign. To account for the decay in diffraction intensity, an exponential decay $C \cdot (1 - \exp(t/\tau_{\text{coh}}))$ with a constant $C < 0$ is introduced as in [77] to account for changes in Debye-Waller factor after photoexcitation. The retrieved value from the fit for the timescale of these changes $\tau_{\text{coh}} = 400 \pm 60$ fs agrees well with the value presented in [77]: $\tau_{\text{coh}} = 500$ fs. In order to describe the temporal evolution of the superlattice diffraction intensity, changes in Debye-Waller evidently do not need to be taken into account, as changes in diffraction intensity due to the coherent motion fully account for the measured changes.

The structural dynamics of the CDW-to-metal transition in $K_{0.3}\text{MoO}_3$, which show various different regimes from amplitude mode excitation to the transient recovery, put a set of tight restrictions on possible models. By contrast, this is not the case for the measured structural dynamics in $4H_b$-TaSe$_2$. Nevertheless, it can be concluded that a similar approach to model the coherent motion during the melting of commensurate order can be used to describe the dynamics of superlattice and regular lattice diffraction intensity in the quasi-two-dimensional system $4H_b$-TaSe$_2$. For excitation fluences strong enough to melt the commensurate order in significant parts of the volume probed by x-rays, the coherent motion is highly damped.

## 9.4 Discussion and perspective

In summary, we observed the sub-picosecond dynamics of the structure of the transition metal dichalcogenide $4H_b$-TaSe$_2$ during the transient melting of the room-temperature commensurate phase. The change of structural symmetry takes place in around 150 fs and is promoted by a highly damped coherent motion of the lattice atoms. The data can be modeled within the framework of an excitation-dependent double-well potential presented in Chap. [7]. To accurately describe the dynamics of regular lattice peaks within the same framework, an exponential decay accounting for transient changes in the Debye-Waller factor has to be included.

The results of the time-resolved x-ray diffraction measurements can be compared to ultrafast electron diffraction experiments (UED) [77], highlighting the fundamental differences between the two methods for the study of CDW systems. The UED measurements were carried out at a different pump wavelength ($\lambda = 775$ nm). The pump wavelength should however not change the qualitative evolution of the measured time-dependent diffraction intensity, as the photon energy in both experiments was large enough to change the electron distribution in the Ta 5$d$ band. The UED measurements were conducted in a Laue transmission geometry with sample thicknesses comparable to the penetration depth of the pump pulses. For high excitation
fluences, the measured superlattice diffraction intensity was fully suppressed. Due to imperfect penetration depth matching and sample surface irregularities, significant residual diffraction can be observed for the highest excitation fluences in the x-ray measurements. In the x-ray diffraction measurements, a kinematic approximation could be applied. Owing to the large scattering cross-section of electrons in solids, a similar approach is not necessarily sufficient in a UED experiment. As mentioned before, the time resolution of a time-resolved x-ray diffraction measurement at a slicing source or an FEL is still superior to that of UED, in this example allowing to fully resolve the coherent motion during the melting of commensurate order. Apart from these apparent differences, the experimental results from both methods are consistent, illustrating the applicability of both methods to study the ultrafast structural dynamics in CDW systems.

Recently, we conducted similar time-resolved x-ray diffraction experiments observing the ultrafast structural dynamics of the commensurate-to-incommensurate transition in the transition metal dichalcogenide 1T-TaS$_2$ at the FEMTO slicing source [76, 183]. In 1T-TaS$_2$, the superlattice diffraction efficiency is generally much larger than in 4H$_b$-TaSe$_2$ and the emergence of incommensurate order after photoexcitation could be observed with the high-Q resolution provided by 7 keV x-rays.

A possible interpretation of the measurements on 1T-TaS$_2$ suggests that while the commensurate phase is destroyed coherently on a sub-picosecond timescale, the incommensurate phase emerges from a diffuse scattering background. It is likely that a similar temporal evolution occurs in the 4H$_b$-TaSe$_2$ compound, indicating that the measured sub-picosecond transition actually corresponds to the sub-picosecond transition from the commensurate phase to a transient high-symmetry state not identical to the incommensurate phase.
Chapter 9: Ultrafast structural dynamics in $4H_b$-$TaSe_2$
Chapter 10

Conclusions and Outlook

One of the most fascinating ideas facilitated by ultrafast pump-probe experiments is the concept of an ultrafast nonthermal phase transition in a solid driven by a femtosecond laser pulse. A system follows a trajectory that is not available in thermal equilibrium, allowing for changes in macroscopic properties on a femtosecond timescale. Since macroscopic material properties crucially depend on the structural symmetry of a system, it is of great interest to fully characterize the structure during a nonthermal transition.

In this thesis, it was shown that in CDW systems, the change of structural symmetry associated with a nonthermal phase transition occurs as a concerted, coherent atomic motion after the collapse of electronic order. These observations were made possible by the temporal and spatial resolution provided by a synchrotron-based hard x-ray slicing source.

Observing the coherent structural dynamics during the photoinduced melting of CDW-order furthermore allowed us to observe previously uncharted phenomena during an ultrafast phase transition, like a sub-picosecond transient recovery of the periodic lattice distortion and a time-dependent damping that can be modified by a second pump pulse. Remarkably, these features can be explained within the framework of simple models of the transient interatomic potential that determines the coherent motion along the coordinate connecting the broken symmetry ground state and the transient high-symmetry state.

In this work, as prototypical examples of CDW systems the textbook-Peierls system $K_{0.3}MoO_3$ and the quasi-two-dimensional compound $4H_b$-TaSe$_2$ were investigated. Charge-density-wave systems will continue to serve as model systems for correlated materials with coupled degrees of freedom. Especially the results obtained in $K_{0.3}MoO_3$ will help to understand the interplay of electronic and lattice order after intense photoexcitation in other correlated materials. In addition, the results allow to critically interpret experiments conducted with indirect time-resolved structural probes — for example by revealing, that domain growth can only be a second step in the observed ultrafast transitions, while the structural symmetry change is promoted coherently over a large sample volume.

A deeper understanding of transient states after photoexcitation will however also require an
in-depth look at the transient state created after intense photoexcitation on longer time scales. Only then can we determine how these often long-lived phases, that are reached via a concerted atomic motion, differ from thermodynamic states — answering the question whether not only the photoinduced transition occurs nonthermally, but also if the transient state has different properties from the thermodynamic state on longer timescales. This can for example be tested by observing changes of the CDW modulation vector in the transient states in detail. These questions also have a highly technological relevance, as femtosecond switching to transient states could have applications in electronic data processing.

In stark contrast to the experiments on the laser-induced melting of electronic order, the presented measurements utilizing resonant THz pumping in single-crystal Te present a spectroscopic method that allows to study coherent lattice vibrations with the electronic system being close to equilibrium. The method and the modeling approach based on Lorentz-oscillators can already be a useful alternative to linear THz time-domain spectroscopy in certain systems.

In the future, upscaling the THz field strength could open new fields of nonlinear phonon interactions. Since even for very high field strengths the electronic system after THz-excitation remains close to equilibrium in materials with a sufficiently large bandgap, the coupling mechanism can be unambiguously assigned to anharmonic coupling of other phonon modes to the resonantly driven coherent motion.

Both experimental methods utilized for this work aimed at studying the coherent structural dynamics — time-resolved diffraction and resonant excitation with intense THz pulses — are still in a rapid development phase.

The broader availability of hard x-ray free electron lasers and improved ultrafast electron sources with sub-phonon period time-resolution in the future will allow for characterizing the sub-picosecond structural dynamics during ultrafast phase transitions in much greater detail. Time-resolved x-ray diffraction measurements on K$_{0.3}$MoO$_3$ would in particular benefit from increased count rates, as a lot more data needs to be taken to be able to fully characterize the structural dynamics after double-pump excitation and put tight restrictions on potential models. Time-resolved diffuse x-ray diffraction measurements have proven to be difficult to conduct on CDW systems but would help tremendously in our understanding of transient scattering channels shortly after photoexcitation.

In addition to non-resonant diffraction experiments, new methods like time-resolved resonant x-ray diffraction can already directly probe other subsystems in materials with coupled degrees of freedom, for example the spin system. Concepts of the interplay between different types of order observed in model systems like CDWs after intense photoexcitation can then be compared to the behavior in materials with more relevant degrees of freedom.

With growing THz field strengths, it could eventually even become possible to routinely drive ultrafast phase transitions not by melting electronic order, but by selectively exciting a coherent phonon that connects two phases with different structural symmetry.
Appendix

A.1 Laser system at ETH

The laser at ETH outputs high energy, femtosecond pulses at a repetition rate of 1 kHz, making it an ideal system for experiments exploiting high-field THz pulses. A detailed schematic of the laser utilized for the coherent phonon spectroscopy experiments on tellurium is presented in Fig. A.1. For the following discussion, it is useful to conceptually divide the system into (i) the laser system containing several amplification stages seeded by a Ti:Sapphire oscillator (ii) the high-field THz generation set-up.

Figure A.1: Schematic of the laser system as explained in the main text. RGA: regenerative amplifier. SPA: single pass amplifier. OPA: optical parametric amplifier. FROG: frequency-resolved optical gating. HE1, HE2: high energy stage 1,2. Beam distribution into the OPA: (1) Pump beam for third amplification stage in HE1. (2) Pump beam for third amplification stage in HE1. (3) Beam for white light generation (which is split into two parts) and the first two amplification stages for both pulses (pulses sent to HE1 and pulses sent to HE2).
energy optical parametric amplifier used to convert the wavelength of the fundamental laser pulses to wavelengths for efficient THz generation in an organic crystal.

(i) Ti:Sapphire laser system. A Kerr lens-modelocked laser (Coherent Vitesse) produces $\lambda_0 = 800$ nm pulses at a repetition rate of 80 MHz. The pulses pass through a grating stretcher that introduces group velocity dispersion, lengthening the pulses to prevent high peak powers during the following amplification stages (an operation mode called chirped pulse amplification, CPA). The stretched pulses are sent into the cavity of a regenerative amplifier (RGA) where they undergo several roundtrips through a Ti:Sapphire crystal pumped by a frequency-doubled Nd:YLF diode laser (Coherent Evolution HE). In- and outcoupling of the cavity are controlled by Pockels cells synchronized to the oscillator. After the RGA, the repetition rate of the pulses has decreased to 1 kHz and the amplified pulses pass the first single pass amplifier (SPA), a Ti:Sapphire rod pumped by the same Nd:YLF diode laser.

The pulse energy after the first two amplification stages in normal operation mode lies around 9 mJ. The pulses now pass a third amplification stage, a Ti:Sapphire rod cryogenically cooled to around 65 K. The rod is pumped by two frequency-doubled Nd:YLF diode laser. The cryogenic cooling prevents crystal damage as well as thermal-lensing effects and strongly improves the mode quality of the output pulses. After the third amplification stage, the pulses are split into two compressors, where they are recompressed to pulse durations of around 100 fs. The total output pulse energy after compression can be as high as $E_p = 20$ mJ. For high-field THz experiments, a small fraction of the beam is split and sent to the setup as a probe beam. The major part of the two beams is distributed to the high energy OPAs. The probe pulse duration can be monitored via frequency-resolved optical gating (FROG) [184].

(ii) High energy optical parametric amplifier pulses with an energy $E_p = 1.4$ mJ are used as input for the TOPAS Twins OPA (Light conversion). A part of the pulses is used to generate white light pulses in a Sapphire plate. The white light pulses are split into two parts, each is sent to the first and second amplification stages. Here, the parametric amplification process takes place in BBO crystals pumped by the remaining parts of the input pulses (see Fig. A.1 for details on the beam distribution into the OPA). After the TOPAS Twins stage, two tunable near-infrared pulse trains with pulse energies around $E_p = 0.1$ mJ are sent into the third amplification stages, HE1 and HE2. Here, they are amplified to pulse energies larger than 1 mJ by around 7 mJ pulses from the fundamental laser. The HE1 and HE2 output pulses are derived from a common white light source, which is important for stability when used for difference frequency generation in a nonlinear crystal. For high-field THz generation in an organic crystal, only the output pulses of one of the two high-energy stages is used. Typically, pulse energies of around 1 mJ are used for THz generation. Pulse wavelengths are tunable between 1040 nm - 1600 nm (signal) and 1600 nm - 2700 nm (idler). When the OPA is working in optimal condition, the duration of the high energy pulses is around 80 fs. Figure A.2 shows spectra of OPA pulses measured with an Avantes near-infrared spectrometer with wavelengths relevant for

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1In normal operation mode, 15 roundtrips are passed.
THz generation in DSTMS. Since the input power into HE1 and HE2 can be almost arbitrarily set when split before compression, it is possible to use almost all of the pulse energy for just one high energy amplification stage. This in principle allows for signal pulse energies around 3 mJ.

Figure A.2: Spectra of OPA pulses relevant for THz generation in DAST/DSTMS. Taken from the Master thesis of Martin Ranke.

A.2 Data acquisition

The data acquisition (DAQ) scheme for the laser lab at ETH follows a concept proposed in [185]. In a nutshell, the readout of a diode measuring the intensity of probe laser pulses is bandpass-filtered and then fed into a DAQ card connected to a PC. Ultimately, the signal of every measured pulse is recorded and saved, allowing extensive noise analysis and simple integration of pump beam modulation. The DAQ scheme is described in detail in the following, starting with an overview of the electronic trigger distribution in the laser lab. A schematic of the DAQ scheme is presented in Fig. A.3 (a).

The main timing synchronization unit of the laser system (Coherent Signal Delay Generator (SDG)) receives a trigger based on the 80 MHz pulse train of the Vitesse oscillator and divides it into the 1 kHz repetition rate of the amplified laser pulses. The SDG feeds delayed versions of
this trigger to all *Evolution* pump lasers and the Pockels cells in the RGA. A delayed copy of the trigger is fed into a delay generator (*Stanford DG535*). The output triggers of this delay generator are therefore synchronized to the laser pulses and can be used to clock the data acquisition with a DAQ card.

In the lab, typically DAQ cards with a maximum sampling rate of 1.25 MHz and a resolution of 16 Bit are used (*National Instruments USB-6251*). These cards can operate in an external sampling clock mode, where they integrate for around 1 μs (the inverse maximum sampling rate) whenever they receive the external trigger. Using the laser trigger as an external sampling clock, the cards are thus intrinsically synchronized to the laser pulses. Adjusting the relative delay of the trigger with the *DG535*, the acquisition window of the cards can be positioned in time to coincide with the voltage readout of a diode. For the coherent phonon spectroscopy measurements, usually...
A low noise balanced photodiode (*Newport 2307*) with internal amplification was used. As typical readout rise and decay times of this and other diodes lie in the nanosecond range, the diode readout is filtered (and amplified) by a low noise voltage preamplifier (*Stanford SR560*) with a lowpass set to around 10 kHz before being fed into the DAQ card. This makes the acquisition much more stable as the slope of the signal is much smaller at the acquisition point. The DAQ card is controlled via *Matlab*, allowing real-time noise analysis (see A.4). A schematic of the output of the preamplifier and the trigger used as a sampling clock is shown in Fig. A.3 (b).

![Figure A.4: Screenshot of the acquisition software written in Matlab. (a) Intensity of the measured laser pulses, in this case for 1000 shots. (b) Histogram of the intensity of the measured laser pulses. (c) Noise spectrum of the measured laser pulses.](image)

To introduce pump beam modulation, a chopper (*Thorlabs MC2000 Optical Chopper*) can be placed into the pump beam. The chopper controller receives a trigger copy of the main laser trigger and an internal feedback loop ensures that it is phase-locked to the laser pulses. The frequency of the chopper is set to 500 Hz by an internal frequency divider and the phase of the rotating wheel can be set in a way that every second pulse completely passes the wheel while every other second pulses is completely blocked. To ensure that the phase of the chopper stays consistent over several measurements (i.e. the measurement for example always starts with the pump beam open), the chopper controller is connected to the DAQ card and provides a start trigger, after which the external sampling clock is used to time the acquisition windows.

The DAQ scheme also works with a higher repetition rate laser system, it was tested with a 250 kHz *Coherent RegA* system. While recording of each pulse in this scheme in principle still works, it is not feasible due to the large incoming data volume. Without an electro-optic modulator, pump-on pump-off modulation is not possible. Using a mechanical chopper, however, laser shots can be grouped into pump-on and pump-off groups to increase signal-to-noise.
Typically, mean values of groups containing around 1000 detected probe pulses are subtracted to acquire a background-free signal.

### A.3 Principles of x-ray diffraction

In this section, a short introduction to the principles of static x-ray diffraction as a means to study the periodic structure of a solid is given. This introduction is by no means supposed to be exhaustive, but rather serves as a basis for the chapters on time-resolved x-ray diffraction: Pulsed x-ray sources are discussed in Chap. 4 and their application to study ultrafast structural dynamics with x-rays are described in Chap. 2.

In a nutshell, x-ray diffraction and other diffraction-based structural investigation methods are based on the interference of scattered radiation by particles in a sample. To be sensitive to interatomic distances in a solid, the wavelength of the radiation must therefore be comparable to these distances. Since typical interatomic distances in a solid are on the order of 1 Å, x-ray energies in the hard x-ray regime (around 10 keV and more) are required.

The basic question of an idealized diffraction experiment (see Fig. A.5) can then be formulated as follows: If a plane wave \( E(\vec{r}, t) = E_0 \exp \left( i(\omega t - \vec{k} \cdot \vec{r}) \right) \) diffracts from a sample, how big is the measured intensity at an outgoing wave vector \( \vec{k}' \)? If the sample is a crystal, consisting of electrons and nuclei, the superposition of the scattered field of all electrons and nuclei has to be summed up and calculated at the detector position, which defines the outgoing wave vector \( \vec{k}' \). In the following, results of a kinematical approach are presents, which implies that multiple scattering and absorption effects can be ignored. Furthermore, only the elastic Thomsen scattering of electrons is included in the description, and inelastic Compton scattering, that

![Figure A.5: Schematics of a diffraction experiment on a crystal. To calculate the intensity at a certain detector position, the scattered field of all electrons in the solid has to be calculated. The figure shows the conceptual partition into (1) atoms, (2) unit cells and (3) the whole lattice (see Eq. 1).](image-url)
A.3 Principles of x-ray diffraction

can only be described quantum-mechanically and leads to an inelastically scattered background, is omitted. Using these assumptions and considering the translational symmetry of a periodic crystal, where the position \( \vec{r} \) of \( j \)-th atom in a unit cell at \( \vec{R}_n \) can be located via \( \vec{r} = \vec{R}_n + \vec{r}_j \), the scattering amplitude \( F(\vec{Q}) \) for a certain scattering vector \( \vec{Q} = \vec{k}' - \vec{k} \) can be written as:

\[
F(\vec{Q}) \propto \sum_j f_j(\vec{Q}) e^{i\vec{Q} \cdot \vec{r}_j} \cdot \sum_{\vec{R}_n} e^{i\vec{Q} \cdot \vec{R}_n}
\]

The contributions to the scattering amplitude can be conceptually divided as follows:

- **1. Atomic scattering factor** \( f_j(\vec{Q}) \).

  The atomic scattering factor includes the scattering contributions of all \( Z \) electrons of an atom. Using a probability density \( \rho_k(\vec{r}) \) to describe the \( k \)-th electron of an atom, it can be derived from Thomsen scattering of all electrons of an atom\(^2\) (see for example [186], Chap. 1):

  \[
f(\vec{Q}) = \int \rho(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d^3\vec{r}
  \]

  Assuming probability densities with spherical symmetry, \( \rho(\vec{r}) = \rho(r) \), the atomic scattering factor depends only on the magnitude of the scattering vector \( Q = |\vec{Q}| \). Values for \( f(Q) \) for most elements and significant ions are tabulated [187]. If the energy of the scattered x-rays is close to an absorption edge of the atom, additional energy-dependent corrections in the form of a real and an imaginary component have to be included [174]:

  \[
f^{\text{corrected}}(q) = f(q) + \Delta f' + i\Delta f''
  \]

  For x-ray diffraction in a solid, the atomic scattering factors are typically just used to be able to correctly calculate the measured overall diffraction signal.

- **2. Unit cell structure factor**

  The unit cell structure factor

  \[
  S(\vec{Q}) = \sum_j f_j(\vec{Q}) e^{i\vec{Q} \cdot \vec{r}_j}
  \]

  is calculated as the superposition of the scattered x-rays of all \( j \) atoms in the unit cell of a crystal. The unit cell of a crystal is the smallest volume of a crystal that, via translational symmetry, can generate the whole crystal lattice. The magnitude of the structure factor is determined by the atomic scattering factors and the positions of atoms in a unit cell.

- **3. Lattice sum over all unit cells**

\(^2\)Due to their much higher mass, contributions of nuclei to the overall measured intensity can be neglected.
To finally calculate the scattering amplitude for the whole crystal, the contributions of all unit cells have to be added up. This is an enormously large sum, and as a result only scattering vectors $\mathbf{Q}$ for which $e^{i\mathbf{Q} \cdot \mathbf{R}_n} = 1$ lead to nonzero scattering amplitudes, all other scattering vectors result in complete destructive interference. This implies

$$\mathbf{Q} \cdot \mathbf{R}_n = 2\pi m$$

with $m \in \mathbb{Z}$ for a nonzero scattering amplitude. The vector $\mathbf{R}_n$ can be expressed with its components, which are multiples of the edges of a unit cell:

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad n_1, n_2, n_3 \in \mathbb{Z}$$

This yields the Laue conditions for scattering vectors where diffraction intensity can be observed:

$$\mathbf{Q} \cdot \mathbf{a}_1 = 2\pi h$$
$$\mathbf{Q} \cdot \mathbf{a}_2 = 2\pi k$$
$$\mathbf{Q} \cdot \mathbf{a}_3 = 2\pi l$$

The integer numbers $h, k, l$ are the so-called Miller indices. Using the definition of reciprocal lattice vectors

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

The Laue condition can be written as

$$\mathbf{Q} = \mathbf{G}$$

where $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is a reciprocal lattice vector. An equivalent formulation can be given in form of the Bragg condition, that connects the spacing of lattice planes $d$ and the scattering angle $\theta$:

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

where $\lambda$ is the wavelength of the x-rays. An illustration of the Bragg condition is shown in Fig. A.6.

In the kinematic picture, the measured intensity is then proportional to the square of the
A.3 Principles of x-ray diffraction

Figure A.6: Illustration of the Bragg law for a symmetric diffraction geometry. The sample is oriented such that the surface normal corresponds to the normal vector of the lattice planes $\vec{G}$. For an incident angle $\theta$, whose value is given by Eq. (10) diffraction can be observed with a detector placed at the outgoing $\vec{k}'$. Non-symmetric diffraction geometries, where the lattice planes are not parallel to the sample surface and the sample rotation becomes crucial are of course also possible (see Sec. 4.2).

scattering amplitude:

$$I(\vec{Q}) \propto |F(\vec{Q})|^2$$  \hspace{1cm} (11)

These considerations of the intensity of diffracted light lead to two major conclusions:

- There are well defined diffraction peaks, whose position depends on the chosen experimental geometry and on the symmetry of the crystal. Their location can be calculated using the Laue condition or the equivalent Bragg law. As a consequence, a change in crystal symmetry due to a phase transition or propagation of strain waves will lead to new possible diffraction conditions or to a slight change in their position, which is crucial for time-resolved x-ray diffraction measurements.

- When kinematic theory is applicable, the measured intensity of a diffraction peak gives direct information about the positions of atoms in a unit cell. Consequently, changes in the position of atoms associated with a zone-center coherent phonon lead to changes in the measured intensity (see Chap. 2).

Besides the listed processes that lead to changes in the measured diffraction intensity, other corrections have to be taken into account:

**X-ray polarization** The measured diffraction intensity will depend on the relative polarization of the incoming x-rays and the direction of the scattered light. This is a consequence of the directional radiation characteristics of electrons accelerated in the electric field of the x-rays, which can be classically understood in the Thomsen picture of scattering. At a synchrotron, the x-ray radiation is polarized linearly in the plane of the ring\(^4\). If the x-ray polarization lies in the

\(^4\)Sliced radiation at a synchrotron consequently is also horizontally polarized.
The plane of scattering is defined by $\vec{k}$ and $\vec{k}'$. The diffraction intensity is scaled by a polarization factor \[ I \propto \cos^2 2\theta \] (12)

In a grazing incidence experiment, unlike in the symmetric geometry, the plane of scattering differs for different diffraction conditions. As a result, different diffraction peaks have to be scaled with different polarization factors.

**Diffuse scattering and the Debye-Waller factor** To this point, only a static lattice with atoms at the equilibrium positions was considered. Thermally excited phonons with wave vector $\vec{q}_{\text{phonon}}$ lead to new diffraction conditions

$$\vec{k} - \vec{k}' = \vec{G} + \vec{q}_{\text{phonon}}$$ (13)

that result in a diffuse background around the main diffraction peaks. At the same time, the intensity of the Bragg peaks is reduced by the Debye-Waller factor $e^{-2W}$. For a monoatomic lattice with small amplitudes of thermal vibration, the factor $W$ is proportional to the square of thermal vibration amplitude $\langle u^2 \rangle$ and the square of the scattering vector, $W \propto \langle u^2 \rangle Q^2$. The reduction of diffraction intensity associated with the Debye-Waller factor therefore gets stronger with increasing temperature and scattering angle $\theta$. 

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The plane of scattering is defined by $\vec{k}$ and $\vec{k}'$. 

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List of publications

• T. Huber, “Coupled degrees of freedom in quantum materials”. *Whitebook on FEL science*. Ed. by B. Patterson. *(to be published in 2016)*


Conference contributions

- Coherent structural dynamics of an ultrafast CDW-to-metal transition, Poster at the International Conference on Ultrafast Structural Dynamics, Zurich, Switzerland, June 2015. Awarded with a poster prize.


- Coherent dynamics of structural symmetry during the ultrafast melting of a charge density wave, Talk at Ultrafast Phenomena XIX, Okinawa, Japan, July 2014.

- Terahertz driven dynamics in Tellurium, Poster at the annual NCCR-MUST meeting, Engelberg, Switzerland, January 2014.

- Femtosecond structural Dynamics of a quasi one-dimensional charge density wave, Poster at the annual NCCR-MUST meeting, Engelberg, Switzerland, January 2013.

- High-field THz applications to solid state structural dynamics, Poster at the annual NCCR-MUST meeting, Lenk, Switzerland, January 2012.

- Time-resolved diffuse x-ray scattering, Talk at the SwissFEL workshop: Scattering and diffraction experiments, Bern, Switzerland, November 2011.

- Order parameter dynamics in the quasi two-dimensional charge density wave system 2H-TaSe$_2$, Talk at the DPG Frühjahrstagung, Dresden, Germany March 2011.
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