Nonlinear electromagnetic probes for the study of ultrafast processes in condensed matter

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Nonlinear electromagnetic probes for the study of ultrafast processes in condensed matter

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presented by

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Abstract

This thesis is dedicated to improving the understanding of nonlinear electromagnetic probes of solid-state properties in the ultrafast temporal domain. Nonlinear methods are able to provide an unparalleled sensitivity in the search for new physics in solid-state science. They can yield insight into the material symmetry and potentially induced changes thereof, which enables e.g. to track the inversion of polarization in a ferroelectric material\(^1\). The latter is of great interest in the search for novel and fast electronic gates and storage devices. More fundamentally, nonlinear probes can reveal coupling between various degrees of freedom and hence can give insight into the interplay and causal relations between electronic, magnetic and lattice excitations of a material. As switching processes are inherently time-dependent, it is crucial to fully comprehend the mechanism that generates such a nonlinear signal in the space and time-domain in order to make definite statements about the time-evolution of ordering based on these techniques. Here, we present two major studies focusing on improving the understanding of ultrafast nonlinear probes in the optical and the terahertz (THz) range of frequencies.

The first part of this thesis examines previous observations made in the prototypical antiferromagnet nickel(II) oxide (NiO) with the time-resolved nonlinear method of magnetic-dipole sensitive second-harmonic generation (SHG). These findings suggested that the material provides a coherent gateway to a non-thermal state of magnetic ordering via an ultrafast change in magnetic anisotropy. Using a complementary direct probe of antiferromagnetic order, i.e. picosecond-time-resolved non-resonant magnetic x-ray diffraction, we study the sublattice magnetism after ultrafast optical excitation and our findings suggest that the previously observed dynamics in the second-harmonic response of NiO do not directly reflect dynamics of the antiferromagnetic order parameter.

Our re-investigation of the experimental observations using SHG supplement the prior experiments and reveal inconsistencies with the current explanation for the ultrafast response of SHG in NiO which can instead be reconciled with an acoustic origin of the dynamics. The simulations of this process are likely to present the first treatment of second-order stimulated Brillouin scattering in non-ideally phase-matched crystals. Consistent with the experimental observations, the simulation gives rise to two signature frequencies \(\omega_{+,-} = \text{Re}(2k_\omega \pm k_2\omega)v_s\) leading to oscillations at frequencies that are different by orders of magnitude. The higher of these frequencies resembles linear stimulated Brillouin scattering but is shifted by phase mismatch.

In the second part of this work, we investigate the novel method of broadband 2D THz-spectroscopy. The technique combines the process of driving intrinsic infrared active material excitations, while at the same time probing the very same and associated, i.e. coupled, modes. Even in an excitation regime far away from driving permanent changes, the method can provide

\(^1\)Ferroelectric materials present a spontaneous electric polarization that can be reversed in an external field.
information about the curvature and symmetry of the energy landscape in which the modes reside. To improve the understanding of this means of spectroscopy, we perform reflective 2D THz measurements accompanied by time-domain simulations on low band gap III-V semiconductors. These materials represent well-understood polaron systems with an early onset of electric field-
nonlinearity. Experimentally, we observe in indium antimonide and indium arsenide on timescales on the order of 7.5 ps inter and intraband changes of carrier population. Interestingly, for excitation fields below 80 kV/cm we find that the nonlinear response observed at very early times is composed of a multitude of combination tones of the material’s intrinsic excitations, i.e. the plasmon and phonon modes, in the 2D frequency spectrum. Observing the full phase information and having control over the polarity of the excitation fields allowed us to further differentiate between the parity of these spectral features.

To understand this coherent response in more detail, we simulate field-driven ballistic carrier transport using realistic band structures in the time domain. For this, we solve Maxwell’s equations in the presence of a polaronic medium using Yee’s algorithm. The calculated ballistic transport leads the mean conduction band population into regions distant from the equilibrium position at the Γ-point by as far as 3% of the zone-boundary. The simulations are able to reproduce the approximate magnitude as well as all observed spectral features and their correct parity. The nonlinear 2D spectra, including features at phonon frequencies, can thus be assigned to be solely based on plasmonic anharmonicity and their explanation does not require additional coupling between the material’s intrinsic excitations.

Our studies show that nonlinear probes can lead to rather complex results when used under conditions of low absorption and non-ideal phase matching. The latter can be transiently altered by pulsed laser excitation, which is here discussed for the case of acoustic perturbation of SHG, and hence for extended sample volumes the assignment of the detected intensity to the nonlinear susceptibility cannot readily be made on ultrafast timescales.

In addition, we find that 2D THz-spectroscopy provides a sensitive tool to study electric field nonlinearities, in which e.g. purely plasmonic excitations can lead to a manifold of spectral features observed in the nonlinear response. Nonetheless, we can show that these spectra can be qualitatively and quantitatively understood using suitable simulation techniques.

In the light of the findings presented in this thesis, we propose that evaluation of nonlinear probes should always be accompanied by considerations of the signal’s generation process with the implications of inhomogeneous ultrafast excitation. It appears essential to develop comprehensive time-dependent analysis tools in order to achieve a solid understanding of these signals.
Zusammenfassung


Unsere fortführenden Untersuchungen unter Verwendung von SHG ergänzen die bisherigen Experimente und offenbaren Widersprüche zur bisherigen Erklärung der ultraschnellen SHG-Dynamik in NiO. Stattdessen können diese konsistent durch einen akustischen Ursprung erklärt werden. Die hier gezeigten Simulationen dieses Prozesses präsentieren möglicherweise die erste Behandlung von Brillouin-Streuung zweiter Ordnung in nicht ideal phasenangepassten Kristallen. In Übereinstimmung mit den experimentellen Beobachtungen führen diese Berechnungen zu zwei charakteristischen Frequenzen $\omega_{\pm} = \text{Re}(2\omega \pm k_{2}\nu_s)$, welche typischerweise um

Ein Ferroelektrikum ist ein Material, das eine spontane elektrische Polarisation aufweist, die sich in einem externen Feld umkehren lässt.
Größenordnungen verschieden sind. Die positiven Lösungen ähneln dabei linearer stimulierter Brillouin-Streuung, sind jedoch durch Phasenfehlpassung leicht verschoben.


Um dieses kohärente Signal genauer zu verstehen, simulieren wir feldgetriebenen ballistischen Ladungsträgertransport in realistischen Bandstrukturen in der Zeitdomäne. Dazu lösen wir die Maxwell-Gleichungen in einem Polaronmedium mittels des Yee-Algorithmus. Die berechneten ballistischen Bahnen lenken die Ladungsträgerpopulation um bis zu 3% des Brillouin-Zonenrandes vom $\Gamma$-Punkt aus. Die Simulationen reproduzieren die ungefähre Grösse sowie alle beobachteten spektralen Signaturen und deren korrekte Parität. Die nichtlinearen 2D Spektren, einschliesslich der Signale bei Phononenfrequenzen, können damit ohne zusätzliche Kopplungen rein basierend auf Plasmonanharmonizität erklärt werden.

Unsere Studien zeigen, dass nichtlineare Messmethoden zu komplexen Resultaten führen können, wenn man diese unter Bedingungen mit niedriger Absorption und nicht idealer Phasenpassung verwendet. Letztere kann durch ultrakurze Laserpulse modifiziert werden, was hier für den Fall von akustischer Modifikation der SHG in NiO diskutiert wird. Für ausgedehnte Probenvolumina kann daher die Zuordnung der gemessenen Intensität zur nichtlinearen Suszeptibilität nicht ohne weiteres auf ultraschnellen Zeitskalen vorgenommen werden.

Darüber hinaus finden wir, dass 2D THz-Spektroskopie ein empfindliches Werkzeug darstellt um elektrische Nichtlinearitäten zu detektieren, in denen beispielsweise reine plasmonische Anregungen zu einer Vielzahl an spektralen Signaturen im nichtlinearen Signal führen. Dennoch können wir zeigen, dass diese Spektren mittels geeigneter Simulationstechniken qualitativ und quantitativ verstanden werden können. Aufgrund der Ergebnisse dieser Arbeit schlagen wir vor,
dass die Auswertung nichtlinearer Messmethoden immer auch mit Simulationen des Erzeugungspotenzialer einhergehen sollte, welche die Auswirkungen inhomogener ultraschwerer Anregung miteinbeziehen. Es erscheint unerlässlich, umfassende Analysewerkzeuge in der Zeitdomäne zu entwickeln, um ein solides Verständnis von nichtlinearen Signalen zu erreichen.
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Introduction

Electromagnetic spectroscopy has likely been the most successful tool of natural science to this date. Nearly every major breakthrough in physics and chemistry is in some way connected to the development of a spectroscopic method. From the cosmic microwave background to the recent potential discovery of the Higgs-Boson, almost any physical phenomenon leaves its electromagnetic fingerprint. This renders to be particularly true in molecular and solid-state matter. All relevant interactions in these systems, apart from the cohesion of the atomic nuclei, are mediated by the electromagnetic force. Thus interaction with electromagnetic fields can yield comprehensive information about their structure and elementary excitations.

The development of the ultrafast mode-locked laser, where ultrafast is loosely defined as occurring on femto- \((10^{-15} \text{ s})\) to picoseconds \((10^{-12} \text{ s})\), allows us to once more develop novel spectroscopic tools. These ultrafast timescales coincide with many of the elementary excitations found in the solid-state, such as lattice vibrations, excitations of the magnetic ordering of spins and even of composite degrees of freedom that form quasi-particles such as Cooper-pairs in superconductors. Ultrafast laser spectroscopy therefore allows to excite and observe their dynamical evolution in the time domain. A schematic overview of relevant time and energy scales is sketched in figure 1.

Inherent to ultrafast laser light is that the overall power is delivered in extremely short pulses. This also implies that unprecedented intensities can be achieved which allow to efficiently convert light to other wavelengths using nonlinear processes and to even manipulate macroscopic states of matter on a femtosecond timescale. These nonlinearities do not only reflect the strength of the impinging electromagnetic field, but also reveal insight into the symmetry and energy landscape the material’s excitations reside in. One can therefore use nonlinear spectroscopy as a tool to classify crystal symmetry, where in particular second-harmonic generation (SHG) was found to yield stringent information about the centrosymmetry, or rather its absence, of a material.

Here, we present two studies that aim to improve the understanding of nonlinear spectroscopic methods for investigating the solid-state in the ultrafast temporal regime. The first study, presented in part I, addresses a particular type of SHG that is sensitive to the magnetic structure
Figure 1: Overview of relevant time- and energy-scales in ultrafast nonlinear optics and the solid-state excitations that can be probed or directly excited with them. Here, the electromagnetic pulses that can be generated by conversion from an amplified ultrafast laser of a typical pulse-length of 100 fs are shown in red. The gray-shaded area marks the temporal domain that cannot be resolved by the laser pulse in the time domain. This implies, however, that THz electric fields, many optical phonon modes and virtually all acoustic and magnetic excitations can be observed phase-resolved.

of the prototypical antiferromagnet nickel(II) oxide (NiO), which will be introduced in chapter 1. We continue and extend previous studies on the time-evolution of the nonlinear signal after strong optical excitation of this compound, where the authors observed a large-magnitude change in SHG intensity that was related to a redistribution of magnetic spin orientation in this material. The bulk of this work is presented in chapter 5. The techniques applied in these experiments are introduced in chapters 2 and 3. We also perform complimentary direct measurements of detecting the time-evolution of the antiferromagnetic order using magnetic x-ray diffraction in chapter 4. In addition we carry out simulations of the generation process of SHG where we find a self-consistent description of the phenomenon that is incompatible with the previously given explanation.

Part II investigates a novel two-dimensional spectroscopy technique in a considerably different spectral range, i.e. the terahertz range (THz). We first review some of the most abundant high-field effects that can occur in semiconductors in chapter 6 and introduce the low band gap semiconductors indium antimonide (InSb) and indium arsenide (InAs) in chapter 7, which provide the testing ground for our investigations of nonlinear THz probes in chapter 9. There, we start by discussing linear broadband THz time-domain spectroscopy in reflection which is able to simultaneously observe the electronic as well as lattice modes of polar semiconductors. Quasi-static spectroscopy measurements are accompanied by time-resolved experiments following the observed dielectric function after optical excitation. The methods used there are introduced in
chapter 8. Phase-resolved 2D THz-spectroscopy can excite and detect elementary material modes directly at the same time and can give detailed insight into the coupling between different degrees of freedom in various materials. It could enable to observe arbitrary orders of nonlinear interaction, yet, the method is still in its infancy and here we intend to contribute to its understanding by carrying out measurements on basic nonlinear electron systems, i.e. InSb and InAs, that are supported by semi-classical simulations in the time-domain.

We hope that our findings can clarify the origin of observations in the past literature as well as open up new opportunities to gain understanding of ultrafast solid-state processes using nonlinear optical probes.
Part I

The ultrafast nonlinear response of nickel oxide
Chapter 1

Antiferromagnetic nickel oxide (NiO)

Discussing the electronic structure of NiO and related transition metal oxides has been at the heart of condensed matter physics since the early days of band-structure theory. In 1937, DeBoer, Verwey, Mott and Peierls came to realize that models that neglect electron-electron interaction fail to describe the conduction (i.e. the non-conduction) properties of these systems [1, 2]. This means that in order to describe the electronic properties of NiO it is not sufficient to consider the average, or mean field, effect of its fellow electrons but it becomes necessary to treat correlations between them.

A satisfying explanation why in particular NiO is an insulator instead of a metal with partially filled 3d-bands was given by Mott some 12 years later [3]. Nonetheless, discussion went on, as finding a model that appropriately describes the electronic energies of these materials in a quantitative manner remained a difficult task. It was later pointed out that a suitable description not only requires an on-site electronic exchange interaction $U$ between different nickel ion sites $\text{Ni}^{2+}$, as introduced by the Mott-Hubbard model [4], but also the possibility of transferring charge to the valence band of neighboring oxygen $\text{O}^{2-}$ anions [5]. This introduced the differentiation of correlated insulators into Mott-insulators and charge-transfer insulators and NiO is often named as the prototypical example of the latter due to its hybridization between the transition metal 3d-states and oxygen 2p-bands [6]. Unlike Mott-insulators, where charge is transferred between unit cells, the charge in charge-transfer insulators moves within the unit cell.

The most compact approach to describe these systems is given by the ionic Hubbard Hamiltonian [7, 8, 9, 4, 10, 11]

$$\mathcal{H} = - \sum_{i \neq j, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{\Delta}{2} \sum_{i, \sigma} n_{i\sigma},$$

(1.1)

with number operator $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$, where $\sigma$ denotes the spin $\uparrow$ or $\downarrow$, $U$ the effective $\text{Ni}^{2+}$-site Coulomb repulsion, $\Delta$ the charge-transfer energy to $\text{O}^{2-}$-sites and $t_{ij}$ is representing the hopping amplitude between site $i$ and $j$. If $U < \Delta$, the Mott-Hubbard transition determines the gap,
while $\Delta < U$ leads to charge-transfer character. For NiO, $\Delta$ is theoretically estimated to lie between 4 to 6 eV and $U$ is expected around 7 to 10.5 eV, thus defining NiO as charge-transfer insulator [12]. Eder gives a Hamiltonian based on the electronic population of Ni $d$-states and oxygen $p$-states that is better suited for the actual description of NiO [13], but less instructive than the one given in equation 1.1. Such electron-electron interactions have consequences for a wide range of electronic excitations in NiO which we will investigate in the following sections 1.1 and 1.2.

## 1.1 Structural, magnetic and domain properties

We are first interested in the implication of the Hamiltonian in equation 1.1 on the material’s magnetic moments. In the limit of low-energy excitations of the Mott-insulating phase, only the collective excitations of the spin degrees of freedom play a role and perturbation in terms of $t_{ij}/U$ or $t_{ij}/\Delta$ result in the well known Heisenberg model [10, 14]

$$H_{\text{Heis}} = -\sum_{i,j} J_{ij} S_i S_j,$$

(1.2)

where $J_{ij}$ represents the magnetic exchange interaction and $S_i$ is the spin vector of the $i$-th Ni$^{2+}$-ion. Thus, if the temperature is low enough, magnetic order is established throughout the crystal. The magnetic exchange interaction mediates the interaction between sites $i$ and $j$ and can in transition metal oxides be well approximated by the interaction between nearest neighboring Ni$^{2+}$ ions via $J_1$ and next nearest-neighbors via $J_2$, as depicted in figure 1.1.

![Figure 1.1: Nearest- $J_1$ and next-nearest-neighbor interaction $J_2$ in the approximately cubic antiferromagnet NiO. The nearest neighbor interaction is evidently frustrated.](image)

For NiO, the nearest neighbor interaction leads to ferromagnetic coupling due to the positive sign of $J_1$ [15, 14], while the negative $J_2$, that is mediated via a single oxygen $p$-orbital, prefers
1.1 Structural, magnetic and domain properties

alternating spins along the connecting coordinate. In cubic transition metal oxide crystals, this leads to frustration and the dominant $J_2$ forms planes of alternating spins that are internally ferromagnetically aligned, see figure 1.2. For this, the non-dominant $J_1$ coupling is of minor importance, nonetheless, it influences the spin direction within the ferromagnetic planes and leads to splitting of the zone-center optical phonons [16]. The next nearest-neighbor interaction is particularly strong in NiO with an experimentally estimated value of -19.01 meV [15] (-17.32 meV in reference [17]). This is the main reason for its high Néel temperature of $T_N = 523$ K [16], which is the highest among all binary transition metal oxides. For comparison, MnO has a $T_N = 118$ K, for FeO $T_N = 192$ K and CoO has a $T_N = 289$ K [14].

![Figure 1.2](image)

**Figure 1.2:** a) Orientation of magnetic Ni$^{2+}$-spins along $(112)$. Reprinted from Sänger et al. [18] with permission from the American Physical Society. b) Antiferromagnetically aligned planes form in NiO along $(111)$ due to next nearest-neighbor coupling. The oxygen ions are omitted in this depiction.

As we have seen from the discussion above, NiO is a frustrated antiferromagnet (AFM) that is derived from the cubic phase. To be more precise, above its Néel temperature NiO is paramagnetic and shows the rock-salt crystal structure consisting of two interpenetrating face-centered cubic lattices of Ni$^{2+}$-cations and O$^{2-}$-anions. The high symmetry of the cubic phase implies that an emerging order along one crystal direction may as well form along any of the equivalent lattice vectors of the cubic crystal structure. Thus, the antiferromagnetic stacking along the $(111)$-coordinate can happen along 4 equivalent directions as shown in figure 1.3.

However, not only the magnetic order is influenced by the transition, but magnetostriction [19, 20] leads to small structural contractions along the stacking coordinate, making the antiferromagnetic $T_i$’s, introduced in figure 1.3, also structural domains that show deviations from cubic symmetry. We can observe these structural domains using birefringence microscopy in section 1.3 and will discuss the implications of this for the crystal symmetry in more detail in section 2.1.3 and 2.2.2. Within the $(111)$-planes, the spins align ferromagnetically, pointing along one of three equivalent $\{11\bar{2}\}$ directions [21, 22, 15], as shown in figure 1.3. This leads to, in total, 12
Chapter 1: Antiferromagnetic nickel oxide (NiO)

Figure 1.3: The antiferromagnetic twin domains are derived from the cubic structure. The four equivalent \{111\}-domains are shown in black (\(T_1\), in the (111)-plane), blue (\(T_2\)), yellow (\(T_3\)) and red (\(T_4\)). Inside these domains, spins may align along another set of 3 equivalent directions along \{11\bar{2}\} forming the spin domains \(S_1(T_1)\), \(S_2(T_1)\) and \(S_3(T_1)\). This leads to 12 distinguishable domains in total. In the \(T_1\) domain, depicted in black, the spin pointing upwards is the \((11\bar{2})\), which is equivalent to \((11\bar{2})\) up to a translation along the stacking direction.

distinguishable domains that can be observed with methods that are sensitive to magnetic order, such as magnetic x-ray diffraction, in section 2.1 and magnetic second-harmonic generation in section 2.2.

The Heisenberg model in equation 1.2 can account for the antiferromagnetic stacking along (111) and restricts the spins to align in this plane but does not specify a preferred direction of the spins along the experimentally found (11\bar{2}). For this the Hamiltonian can be adjusted to cover the in-plane anisotropy arising from dipolar interactions in the distorted crystal and the influence of the crystal potential due to spin-orbit coupling. The formulation for NiO given by Hutchings and Samuelsen was adapted by Kampfrath et al. for separated sublattice spins \(S_1\) and \(S_2\) to read [23]

\[
H = -J'S_1S_2 + \sum_i \left[D_x S_{1x}^2 + D_y S_{iy}^2\right],
\]

with an effective exchange interaction \(J'\). Here, the coordinate system was chosen such that \(x\) points along the ordering plane vector (111), \(y\) along (1\bar{1}0) and \(D_x\) and \(D_y\) represent the out-of-plane and in-plane anisotropy, respectively [15]. Thus, for positive anisotropy energies, the spins align along \(z\), i.e. (11\bar{2}). Using neutron diffraction, Hutchings and Samuelsen found experimental values for the anisotropy energies \(D_x = (0.997 \pm 0.003)\) meV and \(D_y = (0.005 \pm 0.004)\) meV.

Solving the equation of motion for an electromagnetically driven system based on equation 1.3 leads to high frequency antiferromagnetic modes around 1 THz (4.1 meV) [24, 23, 25] which is shown in figure 1.4. In reality, more magnetic eigenmodes due to dipolar exchange and the lifted crystal symmetry arise in NiO and can be observed using Raman scattering [26, 27, 28].
1.2 Optical properties and electronic states

The most prominent characteristic of NiO as a charge-transfer insulator is found in its charge-transfer gap at 4 eV which is shown for a recent ellipsometric measurement of the dielectric function in figure 1.5. Below this value, NiO shows only little conductivity and behaves as an insulator, although there are indications for a direct gap transition at 0.85 eV which has been pointed out recently by Ghosh et al. [29].

The macroscopic dielectric response in the infrared to ultraviolet range is defined by this charge-transfer excitation, while the far infrared dielectric function is governed by the strong polar optical phonon with transverse frequency 10.6 THz (44 meV) that is shown in figure 1.6 a). Below $T_N$, one can additionally find the infrared active antiferromagnetic excitation around 1 THz as the relatively weak absorption feature discussed in section 1.1. Between optical phonon and band gap excitations, a rich fine structure can be observed in transmission which is shown in figure 1.6 b).

As pointed out by Fromme [12], the strong correlation between electrons in the partially filled 3$d$-bands of NiO is not only responsible for the opening of the large insulating gap, but also leads to localization of electrons at the Ni$^{2+}$ sites. Thus, these electronic states behave much less like bands but rather like $d$-electron states of free ions. Still, the ions are exposed to the octahedral crystal environment which lifts their state degeneracies. These 3$d$-states then form the ground state at the valence band energy and a set of localized states inside the charge-transfer gap.

Such excitations within this crystal-field multiplet are transitions between 3$d$-states and are
Chapter 1: Antiferromagnetic nickel oxide (NiO)

Figure 1.5: a) The pseudo-dielectric function of NiO as measured in reflection by ellipsometry at room temperature. The data shown here was taken from reference [29]. The *pseudo-dielectric function* is often given in ellipsometric measurements and includes effects due to surface imperfections [29]. b) The refractive index deduced from (a) as function of wavelength.

Figure 1.6: a) Broadband reflectivity of NiO at 300 K measured by Newman and Chrenko [30] showing the charge-transfer peak at 4 eV, as well as the polar phonon at 44 meV. b) Absorption spectrum of NiO at 300 K measured in transmission. The measurement shows well defined fine structure peaks at energies of 240 meV, 1.13 eV, 1.75 eV, 1.95 eV, 2.75 eV, 2.95 eV, 3.25 eV, 3.52 eV and the charge-transfer edge at 4 eV [30]. The red diamonds indicate the measurement for a sample with high oxygen concentration induced by Lithium diffusion as shown in more detail in figure 1.7.
therefore forbidden by the parity selection rule $\Delta l = \pm 1$. Multiplicity changing transitions additionally violate spin conservation $\Delta S = 0$. Nonetheless, in the solid-state, in contrast to free molecules, the presence of lattice vibrations (phonons) can lead to an admixture of even and odd-parity wave functions which lifts these selection rules [12]. The necessity for an additional phonon nevertheless reduces the effective intensity of such transitions [30].

Transitions in the NiO spectrum that can be attributed to 3$d$-transitions were studied by Newman and Chrenko using absorption spectroscopy and are shown in figure 1.6 b). They identified all of the observed features with internal transitions of the Ni-ion, with exception of the low energy excitation at 240 meV that was assigned to a magnon-phonon combination mode. They also tentatively assigned the observed features to crystal symmetry representations of excited states, which was later refined by Hüfner [31]. We will discuss this in more detail in section 2.2.3 in the context of resonantly enhanced second-harmonic generation in NiO where the 3$d$-states play a central role.

Newman and Chrenko also found that absorption in this range strongly depends on oxygen content, such that increased concentrations lead to strong broadband absorption between 0.1 and 3.5 eV [30], see figure 1.7. We may add the remark that the Ti:sapphire laser that is commonly used in ultrafast measurements lases at a photon energy of about 1.55 eV, thus excitation of NiO would mainly act on these impurity states. The effect of deviations from stoichiometric composition may also be observed in the NiO samples used in this work that are described in section 1.3.

![Figure 1.7:](image)

*Figure 1.7:* The dependence of room temperature absorption in NiO on different treatments that are assumed to mainly increase the excess oxygen concentration. The figure is reprinted from Newman and Chrenko [30] with permission from the American Physical Society.
1.3 NiO samples and domain characterization

We investigated three different NiO specimens with (111)-surface orientation that underwent different annealing and polishing processes. Two of them were originally bought from MaTeck\(^1\) as (5 x 5 x 0.5) mm\(^3\) as-cut flame-fusion grown crystals with a surface orientation along (111), with orientation better than 2°. The third sample, a 50 µm thick NiO platelet, was kindly provided by Prof. Manfred Fiebig from the Material Science Department at ETH Zurich.

From the MaTeck bulk crystals, we prepared samples of 36 and 45 µm thickness using abrasive lapping on a lapping machine that provided a jig for application of evenly distributed pressure. The front-and backside were then treated using chemical and diamond polishing to obtain surfaces of optical quality.

Using the flame-fusion method, crystals are grown from NiO powder in an oxygen rich oxyhydrogen flame [30]. This procedure typically leads to a non-stoichiometric excess of oxygen which strongly reduces crystallinity [19, 20] and increases optical absorption due to the introduction of impurities [30]. This type of NiO sample is thus often referred to as black or brown NiO. To obtain green NiO of high crystallinity, the flame-fused specimen have to undergo high-temperature annealing in order to induce impurity emigration from the bulk crystal. We used a process similar to the one described in references [20, 32, 18] and heated the samples to 1400 K at a rate of 2 K/min in a gas stream of 90% argon and 10% oxygen flowing at 10 l/min. The two MaTeck samples underwent the same recipe but in two different runs, which resulted in an olive-green 36 µm thick sample and a bright-green 45 µm thick sample.

The small rhombohedral structural distortions of the \(T_i\)-domains lead to birefringence that can be observed using a crossed-polarization microscope. Images mapping the polarization rotation by the 36 µm, 45 µm and 50 µm thick NiO crystals are shown in figures 1.8, 1.9 and 1.10, respectively.

The 36 µm sample is likely to consist of evenly distributed structural domains smaller than 10 µm, which, accompanied by its brownish-green color, is hinting at a deviation from ideal stoichiometry [30]. The 45 µm sample shows birefringent domains of sizes between 10-100 µm, which could clearly be identified as such by rotating the incoming polarization and analyzer. The NiO sample provided by Prof. Fiebig was found to be of superior domain quality, showing even areas of 100-500 µm diameter. Nominally, all of these samples have the same origin and were treated using the same annealing recipe. However, the same annealing applied to the 36 µm and 45 µm sample was evidently not reproduced, thus we assign their poor domain quality to an improperly controlled annealing process. It was shown that additional straining and magnetic biasing while or after annealing [19, 20], can improve the domain sizes to 1 mm and larger, and single domain crystals were achieved in the 1960s.

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1.3 NiO samples and domain characterization

**Figure 1.8:** Cross-polarized microscope image of the 36 $\mu$m NiO sample. The image shows the sample through a 28 mm wide aperture and was taken using an LED light source that was polarized with a nanoparticle linear film polarizer. The analyzer was a commercial film polarizer equipped in the Nikon SMZ800N microscope. The crystal appears dark, but shows non-vanishing polarization rotation. No structures can be observed in the 36 $\mu$m sample, thus we are led to assume that the domain sizes are well below 10 $\mu$m.

**Figure 1.9:** Cross-polarized microscope image of the 45 $\mu$m NiO sample. The black lines are assumed to be caused by surface reconstruction from the annealing process where residual oxygen accumulated [20]. The cloudy bright-green structures can be assigned to structural $T_i$ domains of sizes 10-100 $\mu$m.

**Figure 1.10:** Cross-polarized microscope image of the 50 $\mu$m NiO sample. This sample shows large structural domains of sizes between 100-500 $\mu$m. Such a sample allows to measure single structural domains in an experiment using focused laser beams.
1.4 Previous studies on dynamics observed in NiO

NiO has been a playground for theorists to test correlated electron models as well as for experimentalists to develop techniques to investigate magnetic order, thus extensive experimental work has been carried out on elementary excitations of its lattice, electronic and magnetic degrees of freedom. The recent development of the field of ultrafast science has also added some significant contributions to the understanding of this material. In particular, the magnetic excitations have been studied in time-resolved measurements.

Faraday rotation was applied as a tool to observe optically excited magnons, where coherent excitation of antiferromagnetic modes could be achieved via the inverse Faraday effect and the inverse Cotton-Mouton effect [28, 33, 34].

The same excitation mechanisms also lead to THz emission from the infrared active AFM resonance induced by excitation with ultrashort 800 nm Ti:sapphire laser pulses which can be detected using electro-optic sampling [35].

Kampfrath et al. proved the feasibility of driving the NiO antiferromagnetic resonance mode coherently, using the magnetic field component of a THz pulse where they detected the emerging oscillating magnetization using Faraday rotation of an ultrashort optical gate pulse [23]. Recently, they were able to observe nonlinearities arising in the spin response in strong magnetic driving fields by observation of the second-harmonic of the antiferromagnetic mode [36]. Even in this regime where spin nonlinearities could be observed, the maximum transient spin excursion from the equilibrium position was extracted to be only about 2° at a magnetic peak field of \( B = 0.4 \) T, and we can assume that the non-resonant excitation in references [28, 33, 35, 34] led to even lower deflection amplitudes.

It was thus remarkable that studies on NiO using a different detection technique, i.e. magnetic SHG of EH-type, were understood to show extremely nonlinear spin behavior [38, 37, 39]. Their interpretation was based on the observation that the static SHG intensity was found to be proportional to the 4th power of the antiferromagnetic order parameter \( l \) and thus the sublattice magnetization [40]. The data was therefore considered to be a direct measure of the order parameter also for non-equilibrium measurements. Figure 1.11 presents their observation of a large magnitude modulation of the SHG response after strong optical excitation with 800 nm laser pulses.

Figure 1.11 and 1.12 illustrate that optical excitation of NiO can lead to modulations of the SHG response at two quite different frequencies of very similar magnitude. In these measurements 55 and 1 GHz oscillations with peak modulations of the response of 18% were observed [38, 37, 39]. In addition, the authors of reference [38] found a significant onset behavior of the oscillations showing a threshold dependence on the excitation density, which is shown in figure 1.13. Subsequently, a dependence on pulse-length was observed in reference [39], where at a
1.4 Previous studies on dynamics observed in NiO

Figure 1.11: Change of the detected SHG intensity in reflection geometry of a (111) oriented NiO sample at room temperature for two incident pump pulses $1$ and $2$ at $t_0 = 0$ ps and $\Delta t = 19$ ps (a) and 9.5 ps (b). The frequency of the oscillation is 55 GHz. Reprinted from Satoh et al. [37] with permission from the American Physical Society.

Figure 1.12: Change of the SHG intensity in reflection geometry of a (111) oriented NiO sample for delays up to 12 ns. The inset shows the Fourier transform for frequencies given in $\mu$eV. The centroid position corresponds to about 1.09 GHz. Reprinted from Rubano et al. [39] with permission from the American Physical Society.
certain excitation density a response similar to figure 1.11 was observed for 110 fs long excitation pulses which transformed to a slow oscillation behavior, as shown in figure 1.12, by changing the excitation to slightly longer 130 fs pulses. The two frequencies have not been observed in the same measurement [39].

This set of observations thus prominently stands out from other studies on NiO and presents the foundation for our investigations in the first part of this thesis, where we apply a quantitative measure to the change in magnetization and try to get more insight into the method of SHG as a probe to study ultrafast phenomena.
Chapter 2

Methods for detecting antiferromagnetic order

Antiferromagnetic materials show several obvious properties revealing their antiferromagnetic nature. The magnetic susceptibility typically peaks at the Néel temperature and similar observations can be made in specific heat measurements that also show clear indications of the antiferromagnetic phase transition. Yet, in the absence of a net magnetization, the absolute value of the antiferromagnetic order parameter remains an elusive experimental observable. Neutron diffraction can offer direct access to this information [15], but does not at this time allow for time-resolved measurements on timescales relevant for the processes we intend to study. For this reason we chose to use ultrafast magnetic x-ray diffraction which is able to provide quantitative information about the AFM order parameter on ultrafast timescales. The method will be discussed in section 2.1. Furthermore, in section 2.2 we are going to introduce time-resolved SHG of EH-type which was found to indicate the AFM order parameter under equilibrium conditions [40] and can be applied for ultrafast measurements in a laboratory environment.

2.1 Magnetic x-ray diffraction

Magnetic x-ray diffraction represents one of the few linear techniques employed in this work. Here, we use it to access the value of magnetic order in a quantitative manner which is often difficult using nonlinear optical probes. In x-ray diffraction this is possible as the method has a rather direct relationship between measured intensity and magnetization. However, to get there, a few considerations have to be made first. We start with a general discussion of the interaction of photons and electronic spins in section 2.1.1, briefly introduce the fundamentals of x-ray diffraction in section 2.1.2 and show how we can quantitatively probe antiferromagnetic order using this technique in section 2.1.3.
2.1.1 Electromagnetic interaction of photons and electrons

The by far dominant contribution to scattering of photons and electrons is the interaction of the photon’s electric field with electronic charge. For free electrons this can be described by Compton scattering which further reduces to Thomson scattering in the extreme non-relativistic limit. Since the early works on x-ray diffraction by Laue and Bragg more than a hundred years ago, diffraction was primarily used as a tool to study the electronic density distribution in solids. Hence, for a long time neutrons have been the only probe in order to study magnetic structure in solid-state systems. However, the interaction between light and matter is electro-magnetic in nature, implying that magnetic moments and fields can also lead to contributions to scattering.

The cross section for the scattering of photons by free charges in the energy range that is relevant for x-ray diffraction can be derived including magnetic effects by taking the non-relativistic limit of the Compton cross section and using perturbation theory as was done in the early 1950s by Low and Gell-Mann as well as by Goldberger [41, 42]. Later, Blume added extensions in order to account for electron binding effects, paving the way for resonant diffraction [43].

Following Blume and Gibbs in the limit of high photon energies [44] the differential scattering cross section can be written as follows

\[
\frac{d^2\sigma}{d\Omega' dE'} \bigg|_{\lambda \rightarrow \lambda', \ a \rightarrow b} = \left( \frac{e^2}{mc^2} \right) \left[ \langle b | \sum_j e^{i\mathbf{Q} \cdot \mathbf{r}_j} | a \rangle \hat{\epsilon} \cdot \hat{\epsilon}' \right. \\
- \frac{i\hbar \omega}{mc^2} \langle b | \sum_j e^{i\mathbf{Q} \cdot \mathbf{r}_j} \cdot \left[ \frac{i\mathbf{Q} \times \mathbf{p}_j}{\hbar k^2} \cdot \mathbf{A} + \mathbf{s}_j \cdot \mathbf{B} \right] | a \rangle \left. \right] \left[ \delta \left( E_a - E_b - (\hbar \omega'_k - \hbar \omega_k) \right) \right]^2 \tag{2.1}
\]

The geometric conventions are given in figure 2.1 and the abbreviations \( \mathbf{A}, \mathbf{B} \) correspond to \( \mathbf{A} = \hat{\epsilon}' \times \hat{\epsilon} \) and \( \mathbf{B} = \hat{\epsilon}' \times \hat{\epsilon} + (\hat{\mathbf{k}}' \times \hat{\epsilon}') (\hat{\mathbf{k}} \times \hat{\epsilon}) - (\hat{\mathbf{k}} \times \hat{\epsilon}') (\hat{\mathbf{k}}' \times \hat{\epsilon}) + (\hat{\mathbf{k}} \times \hat{\epsilon}') \times (\hat{\mathbf{k}} \times \hat{\epsilon}) \), the sum is taken over all electrons \( j \) and the momentum transfer is given by \( \mathbf{Q} = \mathbf{k} - \mathbf{k}' \). The photon energy and polarization are given by \( \hbar \omega \) and \( \hat{\epsilon} \), with \( \mathbf{p}_j \) being the electronic momentum before the scattering event and \( \mathbf{s}_j \) its spin. The unprimed and primed characters refer to the incident and scattered quantities, respectively. Here, \( | a \rangle \) and \( | b \rangle \) represent the initial and final state of the scatterer [44]. The \( \delta \) term ensures energy conservation. For the scope of this work it is sufficient to study the case of elastic scattering. For inelastic scattering and its application in condensed matter the reader is referred to references [43, 45, 46, 47]. For the elastic case we have \( | b \rangle = | a \rangle \)
2.1 Magnetic x-ray diffraction

Figure 2.1: Geometric definitions for the initial and scattered x-ray polarizations as defined by Blume and Gibbs. The figure is reprinted from reference [44] with permission from the American Physical Society and was modified to include the conventions used in this thesis as well as the angle $\phi$ that rotates around the positive direction of $\hat{u}_1$.

as well as $\lambda' = \lambda$ and the elastic cross section simplifies to

$$
\frac{d\sigma}{d\Omega'}_{el} = \left( \frac{e^2}{mc^2} \right) \left[ \langle M_c \rangle + \frac{i\hbar \omega}{mc^2} \langle M_m \rangle \right]^2 
$$

While the modulus of the term $\langle M_c \rangle$ corresponds to Thomson scattering and is related to the Fourier transform of the charge density, the modulus of the second term $\langle M_m \rangle$ represents the pure magnetic scattering contribution and depends on the Fourier transforms of the orbital and spin magnetization densities. This contribution is reduced by a factor of $(\hbar\omega/(mc^2))^2$ as compared to Thomson scattering which is for relevant photon energies on the order of $10^{-4}$. In addition an interference term arises that scales with $i\hbar\omega/(mc^2)$.

We can further simplify expression 2.2 by defining the Fourier transform of the spin density

$$
S(Q) = \langle a | \sum_j e^{iQ \cdot r_j} s_j | a \rangle,
$$

and the Fourier transform of the orbital magnetization density [48, 49]

$$
L(Q) = \langle a | \sum_j f(Q \cdot r_j) l_j | a \rangle,
$$

(2.3)
with $l_j$ being the electron’s orbital momentum and

$$f(x) = \sum_{n=0}^{\infty} \frac{(ix)^n}{(n + 2)n!}. \tag{2.5}$$

We can then write the magnetization dependent scattering amplitude as \cite{44}

$$\langle M_m \rangle = \frac{1}{2} L(Q) \cdot A^{(1)} + S(Q) \cdot B. \tag{2.6}$$

with $A^{(1)} = -4 \sin^2(\theta) A - (A \cdot \hat{Q}) \hat{Q}$. Considering the polarization dependencies of $A^{(1)}$ and $B$ it becomes apparent that the orbital and spin contributions to the photon cross section can be distinguished by analyzing the polarization dependence of the scattered light \cite{44}. This specificity cannot be provided by neutron scattering as it is purely magnetic in origin.

Vectors $A^{(1)}$ and $B$ are given by the polarization and propagation of the incident and exit beams and can hence be controlled by the geometry of a scattering experiment. It was shown that these quantities can be represented by $2 \times 2$ matrices in a basis of in- and out-going beams whose components are parallel or perpendicular to the scattering plane normal vector given by $\hat{k} \times \hat{k}'$ \cite{50, 51, 44}, as shown in figure 2.1. These expressions are given by

$$A^{(1)} = \begin{pmatrix} A^{(1)}_{\sigma\sigma} & A^{(1)}_{\sigma\pi} \\ A^{(1)}_{\pi\sigma} & A^{(1)}_{\pi\pi} \end{pmatrix} = \frac{Q^2}{2k^2} \begin{pmatrix} 0 & -(\hat{k} + \hat{k}') \\ \hat{k} + \hat{k}' & 2\hat{k} + \hat{k}' \end{pmatrix}, \tag{2.7}$$

$$B = \begin{pmatrix} B_{\sigma\sigma} & B_{\sigma\pi} \\ B_{\pi\sigma} & B_{\pi\pi} \end{pmatrix} = \begin{pmatrix} \hat{k} \times \hat{k}' & -\hat{k}'(1 - \hat{k} \cdot \hat{k}') \\ \hat{k}(1 - \hat{k} \cdot \hat{k}') & \hat{k} \times \hat{k}' \end{pmatrix}. \tag{2.8}$$

For the magnetic scattering amplitude in equation 2.6 this results in\footnote{Here, the $\langle M_m \rangle_{\pi\sigma}$-component is corrected for the typo in the original publication.} \cite{44}

$$\langle M_m \rangle = \begin{pmatrix} \langle M_m \rangle_{\sigma\sigma} & \langle M_m \rangle_{\sigma\pi} \\ \langle M_m \rangle_{\pi\sigma} & \langle M_m \rangle_{\pi\pi} \end{pmatrix}$$

$$= \begin{pmatrix} S(Q) \cdot (\hat{k} \times \hat{k}') & -\frac{Q^2}{2k^2} \left( \frac{L(Q)}{2} + S(Q) \right) \cdot \hat{k}' + \frac{L(Q)}{2} \cdot \hat{k} \\ \frac{Q^2}{2k^2} \left( \frac{1}{2} L(Q) + S(Q) \right) \cdot \hat{k} + \frac{L(Q)}{2} \cdot \hat{k}' & \left( \frac{Q^2}{2k^2} L(Q) + S(Q) \right) \cdot (\hat{k} \times \hat{k}') \end{pmatrix}. \tag{2.9}$$

It is worth noting that in this representation the in-plane magnetization (in the sense of in-scattering-plane) contributes only to the off-diagonal terms of $\langle M_m \rangle$, while the out-of-plane magnetization components contribute only to the diagonal terms. Furthermore, the component $\langle M_m \rangle_{\sigma\sigma}$ is independent of $L(Q)$ and is hence only sensitive to the electronic spin $S(Q)$. The real beauty of this description is that the single components of $\langle M_m \rangle$ are directly accessible via polarization sensitive x-ray diffraction experiments, where the incoming and detected x-ray.
polarization can be controlled.

Using the definition of the scattering angle $\theta$ and the components of $S(Q)$ and $L(Q)$ in the basis defined in figure 2.1 we can write equation 2.9 in the simpler form

$$\langle M_m \rangle = \begin{pmatrix} \sin(2\theta)S_2 & -2\sin^2 \theta [\cos \theta (L_1 + S_1) - \sin \theta S_3] \\ 2\sin^2 \theta [\cos \theta (L_1 + S_1) + \sin \theta S_3] & \sin(2\theta) [2\sin^2 \theta L_2 + S_2] \end{pmatrix}. \quad (2.10)$$

For general polarizations, the scattered intensities can be calculated based on equation 2.10 by using the Poincaré representation for the polarization [44].

### 2.1.2 Fundamentals of x-ray diffraction

As we have seen in the previous section, electromagnetic radiation is scattered by electric charges and, to a much smaller extent, also by magnetic moments. By bringing several scattering centers, such as atoms, into close vicinity (close as compared to the so called coherence length$^2$ of the incoming light), interference between them may be observed. In an ordered material this is most striking, as scattered light can coherently add up along certain directions while scattering along other directions may be suppressed. In x-ray diffraction, light of a wavelength that is comparable to interatomic distances in materials is used. Hence, there is a considerable phase difference between neighboring scattering centers, and the interference pattern in such an experiment will contain structural information on the atomic scale. As interatomic distances are typically around $1 \, \text{Å} = 10^{-10} \, \text{m}$, x-ray energies on the order of $10^4 \, \text{eV}$ are required.

The method can be formalized by considering an idealized diffraction experiment where the incoming light with wave-vector $k$ is approximated by a plane wave with electric field $E(r, t) = E_0 e^{i(\omega t - k \cdot r)}$ and where the material is represented by a distribution of identical scattering sources as depicted in figure 2.2. In the so called kinematic approximation, we consider only elastic scattering events up to first order. This approximation is clearly violated in crystals of high quality where multiple scattering can occur, but is sufficient to describe diffraction by small, disordered or mosaic crystals, or when considering the weak magnetic contribution to diffraction.

In this approximation, the overall scattered intensity of a diffraction peak for a polarization combination $\epsilon$ scales in the same way as the cross section hence it is proportional to the square of the scattering factor

$$I_\epsilon(Q) \propto |F_\epsilon(Q)|^2. \quad (2.11)$$

Following reference [53] we can group the sum over all scattering contributions into three summations. The scattering factor $F_\epsilon(Q)$ for a given combination of in- and outgoing polarization

$^2$For a definition, please be referred to e.g. reference [52].
Chapter 2: Methods for detecting antiferromagnetic order

Figure 2.2: Momentum transfer $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$ from lattice to x-rays.

$\epsilon \in [\pi\pi, \pi\sigma, \sigma\pi, \sigma\sigma]$ (see section 2.1.1 for definition) can then be written as

$$F_\epsilon(\mathbf{Q}) \propto \sum_k^{[2]} \langle M(\mathbf{Q}) \rangle_k e^{i\mathbf{Q} \cdot \mathbf{r}_k} \cdot \sum_n^{[3]} e^{i\mathbf{Q} \cdot \mathbf{R}_n}$$  \hspace{1cm} (2.12)

• [1] Atomic scattering factor $\langle M(\mathbf{Q}) \rangle_k$
As defined in equation 2.2, the atomic scattering amplitude incorporates charge as well as magnetic scattering contributions of all $Z$ electrons of atom $k$ for the polarization combination $\epsilon$. For relevant photon energies, scattering from the nucleus can be neglected.

• [2] Unit cell structure factor
The unit cell structure factor is simply the scattering sum over all $k$ atoms at position $\mathbf{r}_k$ in the unit cell of a crystal. Here, the unit cell is the smallest group of atoms from which the whole crystal lattice can be built up by translational operations.

• [3] Lattice sum
The crystal symmetry is taken into account by the sum over all $n$ unit cells at positions $\mathbf{R}_n$. For an exemplary crystal grain diameter of 10 $\mu$m and a unit cell diameter of 4 Å, this considerably large sum has to account for about $10^{13}$ unit cells. In effect, only scattering vectors $\mathbf{Q}$ in close proximity of ideal constructive interference

$$\mathbf{Q} \cdot \mathbf{R}_n = 2\pi m,$$  \hspace{1cm} (2.13)
2.1.3 Diffraction from antiferromagnetic compounds

Antiferromagnets like NiO are ideal systems to be studied with magnetic diffraction since below the antiferromagnetic phase transition the Ni\(^{2+}\)-ions’ magnetic moments alternate along the modulation vector \((1\ 2\ 1\ 2\ 1\ 2)\) as introduced in section 1.1.

This can be incorporated in equation 2.12 by increasing the size of the unit cell along \((1\ 1\ 1)\) (while reducing the number of unit cells \(n\) in the integration volume) and by modulating the electronic spin \(s_j\) of contributing magnetic ions with the modulation period given by the reciprocal space vector \((1\ 2\ 1\ 2\ 1\ 2)\) as shown in figure 2.3. Although the lattice sum now allows for peaks at this reciprocal space coordinate, the electronic structure factor of the increased unit cell has a node at these positions in reciprocal space. However, due to the spin modulation the magnetic structure does not. Thus, for NiO it forms a super-lattice with half the periodicity of the structural lattice, that gives rise to solitary magnetic reflections in reciprocal space [19].

The reciprocal lattice vectors given here are still derived from the cubic paramagnetic phase. In reality, the antiferromagnetic phase transition is connected to a magnetostrictive distortion from cubic to rhombohedral structure with a slight rhombohedral angle \(\alpha\) of 90.07° at room temperature [20]. Since the magnetic moments point along \([1\ 1\ 2]\) instead of along the symmetry axis of the rhombohedral lattice, the point group further reduces to the monoclinic 2/m point symmetry which even allows for further structural distortion of the rhombohedron [54, 55]. This distortion leads to small shifts of the Bragg peaks and the twinning discussed in section 1.1, but does not allow for structural peaks along coordinates close to the magnetic reflections of the \((1\ 1\ 1\ 1\ 1\ 1)\)-family [54].

As the electronic contributions along these momentum transfers \(Q\) vanish, their diffraction
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Figure 2.3: The sublattices of antiferromagnetic NiO. Below $T_N$, the cubic unit cell doubles along the three spatial coordinates. The two different spin orientations at the Ni$^{2+}$ sites are depicted in black and white. The dotted plane indicates one of the magnetic sublattices that is periodic along $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$. Reproduced from Cracknell et al. [54] with permission from Cambridge University Press.

Figure 2.4: a) The integrated diffraction intensity of the magnetic $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$-peak at a photon energy of 7.84 keV as function of temperature. Reprinted from Neubeck et al. [56] with permission from the American Institute of Physics. The intensity disappears around the Néel temperature of NiO at 523 K. b) Energy dependence of the $(\sigma\sigma)$-component of the magnetic x-ray diffraction intensity in NiO shown for the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$-reflection. The resonance at 8.33 keV is due to E2 transitions ($1s - 3d$). Adapted from Neubeck et al. [57] with permission from the American Physical Society.
intensity is proportional to the square of the magnetic structure factor $\langle F_m(Q) \rangle$ (see equation 2.11). In absolute terms, this reads [58]

$$\langle F_m(Q) \rangle = -r_0 \frac{i\hbar \nu}{m_e c^2} \langle M_m(Q) \rangle,$$  \hspace{1cm} (2.16)

where $m_e$ and $r_0$ are the mass and classical radius of the electron, $c$ is the speed of light, $\hbar \nu$ gives the photon energy and the magnetic scattering amplitude $\langle M_m \rangle$ is given by equation 2.10. Figure 2.4 a) shows that the diffraction signal at these positions in reciprocal space completely disappears above the antiferromagnetic phase transition.

Due to the low magnetic scattering factor, measurements of these magnetic peaks are experimentally challenging and the first observation was not made before 1972, when Brunel and Bergevin used a Cu-anode source for the first observation of magnetic diffraction peaks in the very same material as studied here. Since then, the brightness of light sources increased tremendously and today cosmic radiation is no longer the main source of background as it was back then. Yet, for magnetic diffraction it is common practice to make use of electronic resonances to considerably amplify the cross section as was briefly mentioned before in the discussion of equation 2.1. However, in NiO the L-edge is not accessible by diffraction and in the hard x-ray regime the material provides, similar to other 3d-transition metal antiferromagnets, only a rather weak and narrow K-edge resonance at 8.33 keV which is shown in figure 2.4 b). Resonant measurements were carried out in references [59, 57], though in practice it is often more efficient to study the non-resonant case below the K-edge as was done for example in references [60, 58, 61].

For time-resolved magnetic x-ray diffraction the low scattering efficiency still imposes a serious experimental difficulty as will be further discussed in section 4.3.
2.2 Second-Harmonic Generation (SHG)

In this section second-harmonic generation (SHG) of optical laser beams as the degenerate case of sum frequency generation will be presented as a technique to study magnetic order in antiferromagnetic materials that do not possess a macroscopic magnetization. For this, we are going to have a closer look at the light field induced nonlinear polarization and its multipole expansion that can reveal insight into the coupling mechanisms to microscopic magnetic moments in the material in section 2.2.1. Furthermore, the symmetry of these systems will refine our interpretation of second-harmonic polarization in section 2.2.2 and it will be shown how resonance enhancement can make such weak induced polarizations accessible in an experiment in section 2.2.3. The last part of this section 2.2.4 is dedicated to the dispersion dependence of SHG, which turns out to be the basis of a wealth of dynamics observed in pump-probe experiments on NiO as will be discussed in chapter 5.

2.2.1 Nonlinear polarization

Following Fiebig et al. [62], electromagnetic waves that travel through a medium induce electric polarization $\mathbf{P}$, magnetization $\mathbf{M}$ or quadrupole polarization $\hat{\mathbf{Q}}$ at any frequencies that are linear combinations of the frequencies of the incident waves. The induced multipole moments can be expanded in the driving fields $\mathbf{E}$ and $\mathbf{H}$ and represented by

$$
\mathbf{P} = \epsilon_0 \left( \hat{\chi}^{ee} \mathbf{E} + \hat{\chi}^{em} \mathbf{H} + \hat{\chi}^{eem} \mathbf{EE} + \hat{\chi}^{eme} \mathbf{HE} + \hat{\chi}^{emm} \mathbf{HH} + \mathcal{O} \left[ (\mathbf{E}, \mathbf{H})^3 \right] \right), 
$$

or using the sum convention

$$
P_i = \epsilon_0 \left( \hat{\chi}^{ee}_{ij} E_j + \hat{\chi}^{em}_{ij} H_j + \hat{\chi}^{eem}_{ijk} E_j E_k + \hat{\chi}^{eme}_{ijk} E_j H_k + \hat{\chi}^{emm}_{ijk} H_j E_k + \mathcal{O} \left[ (\mathbf{E}, \mathbf{H})^3 \right] \right). 
$$

Note that the various $\hat{\chi}$ are tensors of different rank. Similar expressions can be found for the magnetic polarization $\mathbf{M}$ and the quadrupole moment $\hat{\mathbf{Q}}$ [62, 63]. The term $\mathcal{O} \left[ (\mathbf{E}, \mathbf{H})^3 \right]$ in reality still contains a large amount of interesting and relevant physics, but for now we intend to focus our interest on the terms involving three light quanta, i.e. three-wave-mixing. Then we may use the matrix representation and write for the second order moments, i.e. the multipoles induced by two waves [64]

$$
\begin{pmatrix}
P^{(2)} \\ M^{(2)} \\ Q^{(2)}
\end{pmatrix}
\propto
\begin{pmatrix}
\hat{\chi}^{ee} & \hat{\chi}^{eem} & \hat{\chi}^{eme} & \hat{\chi}^{emm} \\
\hat{\chi}^{eem} & \hat{\chi}^{mme} & \hat{\chi}^{mem} & \hat{\chi}^{mmm} \\
\hat{\chi}^{eme} & \hat{\chi}^{mem} & \hat{\chi}^{emm} & \hat{\chi}^{mmm} \\
\hat{\chi}^{emm} & \hat{\chi}^{mm} & \hat{\chi}^{mme} & \hat{\chi}^{mmm}
\end{pmatrix}
\begin{pmatrix}
\mathbf{EE} \\
\mathbf{EH} \\
\mathbf{HE} \\
\mathbf{HH}
\end{pmatrix}
\right). 
$$
The fields emitted by the medium are given by the source term which is defined as [52]

$$S = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} - \nabla^2 E,$$  \hspace{1cm} (2.20)

while the multipole fields are connected to the source via [62, 63]

$$S = -\mu_0 \left( \frac{\partial^2 P}{\partial t^2} + \nabla \times \frac{\partial M}{\partial t} - \nabla \frac{\partial^2 \hat{Q}}{\partial t^2} + \ldots \right).$$  \hspace{1cm} (2.21)

Thus, equation 2.19 allows for a vast number of terms contributing as nonlinear sources. However, in the following section 2.2.2 we will see that this number can be greatly reduced for media that possess symmetries.

### 2.2.2 Symmetry considerations for nonlinear processes

Symmetry is one of the main driving concepts in modern physics. Whenever we can formulate a transformation that leaves a physical property unchanged, a symmetry is found and we can reduce and simplify the description of the physical system at hand. In the case of continuous transformations Emmy Noether showed that we even obtain an associated conserved quantity [65]. In crystals, however, we deal with discrete symmetry operations such as translations of a unit cell onto its identical neighbors. Nonetheless, this type of symmetry can help reduce the complexity of calculating and measuring material properties, as these symmetries are reflected in the symmetries of the tensors describing their spatial and temporal physical properties. This is also coined Neumann’s principle

“Any type of symmetry which is exhibited by the crystal is possessed by every physical property of the crystal.”

as he was quoted in reference [66]. Luckily, the number of possible symmetries that can be found for three dimensional repetitive patterns is limited and all crystals can be sorted according to their allowed symmetry operations into 32 point groups, though the additional degree of freedom introduced by magnetism increases this number to 122 [66].

A selection of antiferromagnets and their point groups is shown in table 2.1. Interestingly, the majority of these materials shows the monoclinic crystal structure 2/m in the antiferromagnetic phase. This point group possesses a two-fold rotational symmetry and a mirror plane whose plane vector points along the rotational axis and is thus centrosymmetric.

### Tensor symmetry

Tensors are the geometric representations of physical quantities and the linear relations between them. Tensors of crystal properties have to show the same symmetry as the respective crystal structure which allows us to classify crystal tensors according to the corresponding symmetry
Chapter 2: Methods for detecting antiferromagnetic order

<table>
<thead>
<tr>
<th>AFM</th>
<th>$T_N$ [K]</th>
<th>PG $T \geq T_N$</th>
<th>PG $T \leq T_N$</th>
<th>Centrosymmetric</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO$^{[40]}$</td>
<td>523</td>
<td>$m3m$</td>
<td>$2/m$</td>
<td>yes</td>
</tr>
<tr>
<td>Cr$_2$O$_3$$^{[66],[67]}$</td>
<td>308</td>
<td>$3m$</td>
<td>$3m$</td>
<td>no</td>
</tr>
<tr>
<td>CoO$^{[68],[55]}$</td>
<td>292</td>
<td>$m3m$</td>
<td>$2/m$</td>
<td>yes</td>
</tr>
<tr>
<td>KNiF$_3$$^{[68]}$</td>
<td>246</td>
<td>$m3m$</td>
<td>$4/mmm$</td>
<td>yes</td>
</tr>
<tr>
<td>Cu$_2$O$^{[69],[70]}$</td>
<td>213 (230)</td>
<td>$2/m$</td>
<td>$2/m$ (2)</td>
<td>yes (no)</td>
</tr>
<tr>
<td>FeO$^{[71]}$</td>
<td>198</td>
<td>$m3m$</td>
<td>$2/m$</td>
<td>yes</td>
</tr>
<tr>
<td>MnO$^{[55]}$</td>
<td>120</td>
<td>$m3m$</td>
<td>$2/m$</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 2.1: Point groups (PG) of selected antiferromagnets below and above the Néel temperature $T_N$. Point group $m3m$ is cubic, $4/mmm$ is tetragonal, $3m$ is trigonal and $2/m$ is monoclinic. The values in brackets indicate the spin spiral phase of CuO that shows ferroelectric polarization$^{[69]}$.

A comprehensive classification is given by Robert Birss in his book Symmetry and Magnetism$^{[66]}$. He sorts the tensors in two groups according to their transformation properties to spatial inversion, here defined by $\hat{I} = l_{i'j'} \cdots l_{n'n} = (-\delta_{i'j'}) \cdots (-\delta_{n'n})$ which transforms spatial coordinates as $\hat{\mathbf{r}} = -\mathbf{r}$. The two groups are coined polar and axial, corresponding to true tensors and pseudotensors, and transform under spatial inversion according to

$$
\hat{d}_{i' \cdots n'} = \hat{I} \hat{d}_{i \cdots n},
$$

polar: $\hat{d}_{i' \cdots n'} = l_{i'j'} \cdots l_{n'n} \hat{d}_{i \cdots n}$, axial: $\hat{d}_{i' \cdots n'} = -l_{i'j'} \cdots l_{n'n} \hat{d}_{i \cdots n}$. (2.22)

It follows that the product of a polar and an axial tensor is itself axial, while two axial tensors give a polar tensor. This puts constraints on the symmetry of an arbitrary tensor $\hat{d}$ that relates other tensors such as the susceptibilities defined in equation 2.18.

At the same time, the crystal symmetry dictates the symmetry and in fact the very existence of such polar or axial tensors. Results of these symmetry considerations in the static limit are tabulated in reference$^{[66]}$ and shown in table 2.2 and 2.3 for the particularly interesting case of crystals with point symmetry $2/m$. For this symmetry group, only even-rank polar and odd-rank axial tensors exist.

In part II of this work we will also consider crystals of the non-inversion symmetric cubic point group $\overline{4}3m$ which is found in zincblende and the III-V semiconductors. Its tensor symmetries up to rank 4 are given in table 2.4.
2.2 Second-Harmonic Generation (SHG)

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Tensor</th>
<th>Rank</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fields and moments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electric field</td>
<td>E</td>
<td>1</td>
<td>polar</td>
</tr>
<tr>
<td>Magnetic field</td>
<td>H</td>
<td>1</td>
<td>axial</td>
</tr>
<tr>
<td>Electric polarization</td>
<td>P</td>
<td>1</td>
<td>polar</td>
</tr>
<tr>
<td>Magnetic moment</td>
<td>M</td>
<td>1</td>
<td>axial</td>
</tr>
<tr>
<td>Quadrupole moment</td>
<td>Q</td>
<td>2</td>
<td>axial</td>
</tr>
<tr>
<td>Two field tensors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>EE</td>
<td>2</td>
<td>polar</td>
</tr>
<tr>
<td></td>
<td>EH</td>
<td>2</td>
<td>axial</td>
</tr>
<tr>
<td></td>
<td>HE</td>
<td>2</td>
<td>axial</td>
</tr>
<tr>
<td></td>
<td>HH</td>
<td>2</td>
<td>polar</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Linear susceptibilities</th>
<th>Allowed in: 2/m</th>
<th>3/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \hat{\chi}_{ ee} )</td>
<td>2 polar</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ em} )</td>
<td>2 axial</td>
<td>-</td>
</tr>
<tr>
<td>( \hat{\chi}_{ me} )</td>
<td>2 axial</td>
<td>-</td>
</tr>
<tr>
<td>( \hat{\chi}_{ mm} )</td>
<td>2 polar</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ eq} )</td>
<td>2 axial</td>
<td>-</td>
</tr>
<tr>
<td>( \hat{\chi}_{ eq} )</td>
<td>2 axial</td>
<td>-</td>
</tr>
<tr>
<td>( \hat{\chi}_{ qm} )</td>
<td>2 polar</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ qm} )</td>
<td>2 polar</td>
<td>yes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2nd order susceptibilities</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ED-type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \hat{\chi}_{ eee} )</td>
<td>3 polar</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ mee} )</td>
<td>3 axial</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ qee} )</td>
<td>3 axial</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>MD-type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \hat{\chi}_{ eem} )</td>
<td>3 axial</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ eme} )</td>
<td>3 axial</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ emm} )</td>
<td>3 polar</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ mem} )</td>
<td>3 polar</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ mme} )</td>
<td>3 polar</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ qee} )</td>
<td>3 axial</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ qme} )</td>
<td>3 polar</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td>( \hat{\chi}_{ qmm} )</td>
<td>3 axial</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

| Table 2.2: The tensor classification of relevant fields, momenta and susceptibilities up to rank three. |
Chapter 2: Methods for detecting antiferromagnetic order

Table 2.3: Symmetry-allowed components of 2nd and 3rd rank tensors for the monoclinic point group 2/m.

<table>
<thead>
<tr>
<th>Tensor rank</th>
<th>Symmetry</th>
<th>Nonvanishing elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>polar</td>
<td>$d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{yz}$</td>
</tr>
<tr>
<td>3</td>
<td>axial</td>
<td>$d_{zz}, d_{xxz}, d_{xzz}, d_{yyz}, d_{yzx}, d_{xyz}, d_{xzy}, d_{zxy}$</td>
</tr>
</tbody>
</table>

Table 2.4: Symmetry-allowed components of 2nd, 3rd and 4th rank tensors for the cubic point group 43m.

<table>
<thead>
<tr>
<th>Tensor rank</th>
<th>Symmetry</th>
<th>Nonvanishing elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>polar</td>
<td>$d_{xx} = d_{yy} = d_{zz}$</td>
</tr>
<tr>
<td>3</td>
<td>polar</td>
<td>$d_{xyz} = d_{zyx} = d_{yxz} = d_{zxy}$</td>
</tr>
<tr>
<td>4</td>
<td>polar</td>
<td>$d_{xxxy} = d_{yyyy} = d_{zzzz}$, $d_{xyyg} = d_{yyxx} = d_{zzxz}$, $d_{xyyx} = d_{xxyy} = d_{zxxx}$, $d_{xyzx} = d_{yxzx} = d_{zyzy}$, $d_{xyyz} = d_{yxyx} = d_{zyxz}$, $d_{xyzy} = d_{yxzy} = d_{zyyz}$</td>
</tr>
<tr>
<td>3</td>
<td>axial</td>
<td>$d_{xx} = d_{yy} = d_{zz}$, $d_{xyz} = d_{zyx} = d_{yxz} = d_{zxy}$, $d_{xy} = d_{yz} = d_{zy} = d_{xz}$</td>
</tr>
<tr>
<td>4</td>
<td>axial</td>
<td>$d_{xx} = d_{yy} = d_{zz}$, $d_{xyz} = d_{zyx} = d_{yxz} = d_{zxy}$, $d_{xy} = d_{yz} = d_{zy} = d_{xz}$</td>
</tr>
</tbody>
</table>

Although the tensor symmetries affect every physical aspect of a material, from its mechanical and optical to its transport properties, here we want to focus our attention on its impact on second order optical effects.

Optical sum frequency generation is particularly dependent on the crystal symmetry, as the usually dominant electric-dipole-type (ED) susceptibility $\hat{\chi}^{eee}$ is described by a polar tensor and is thus only allowed in materials that do not possess spatial inversion symmetry. Sum frequency generation, and in particular SHG, is hence a very sensitive tool to study the breaking of inversion symmetry. However, it has to be noted that ED type SHG is symmetry allowed in materials showing crystallographic centrosymmetry but non-centrosymmetric magnetic order, such as Cr$_2$O$_3$ [62]. As can be seen in table 2.1, most fully compensated antiferromagnets such as NiO, CoO or KNiF$_3$, however, possess 2/m symmetry in which the magnetic as well as the crystallographic order is centrosymmetric and which makes the previous argument applicable. In these systems magnetic dipolar and quadrupolar contributions have to be considered as the leading terms in SHG, see table 2.2.
2.2 Second-Harmonic Generation (SHG)

2.2.3 Resonant sum frequency generation in centrosymmetric AFM compounds

Most common sum frequency generation phenomena are based on the ED nonlinear polarization. However, already in the early days of ruby lasers [72, 73, 74] it was shown that other coefficients of the multipole expansion in equation 2.18 and 2.19 can lead to non-vanishing contributions. But the induced polarization, based for example on magnetic dipole coupling (∝ $\hat{\chi}^{eme}$ or $\hat{\chi}^{eme}$), is typically several orders of magnitude ($\approx 6$) lower than for $\hat{\chi}^{eee}$-type SHG [75]. Making use of resonant enhancement is therefore an experimental necessity in these materials. The nonlinear susceptibility then becomes a strong function of frequency and the so called Kleinman symmetry, that is often used to simplify the susceptibility tensors, cannot be applied. Effects of resonance enhancement have already been treated in early papers on SHG by Armstrong and Bloembergen [76] but have more recently been discussed in an experimental context [64].

In the following we will discuss the particularly interesting case of antiferromagnetic NiO where one can make use of experimental observations to simplify the treatment of resonance enhanced sum frequency generation. A pioneering work by Fiebig et al. [40, 64] dissected the various contributions to the second-harmonic and sum frequency emission in this material. They started by applying the symmetry arguments shown in table 2.2 for the $2/m$ point group and were left with 6 axial susceptibility tensors that may contribute to the signal: $\hat{\chi}^{mee}$, $\hat{\chi}^{eem}$, $\hat{\chi}^{eme}$, $\hat{\chi}^{mmm}$, $\hat{\chi}^{qee}$ and $\hat{\chi}^{qmm}$. The latter two are also allowed in the paramagnetic phase of NiO that possesses the $m3m$ point group [40]. As no SHG was observed in this phase, these can be neglected. The same argument ruled out surface contribution of NiO, although small contributions could be observed on the (001) surface [77]. From the residual 4 tensors, $\hat{\chi}^{eem}$ was identified as the main contribution by a careful study of the spectral dependence of the SHG signal and applying group theory for octahedral crystal fields [64].

Thus they could identify a single tensor giving rise to SFG in NiO with the possible non-zero components shown in table 2.3 for a rank 3 tensor. For SHG we can further make use of the fact that the two incoming photons are indistinguishable $\hat{\chi}_{ijk} = \hat{\chi}_{ikj}$.

For sum frequency generation the frequency dependence of the tensor $\hat{\chi}^{eem}$ can be expressed as [78, 63, 40, 68, 64, 62]

$$\hat{\chi}^{eem}_{ijk}(\omega' = \omega_a + \omega_b) \propto \sum_{g,m,n} \left[ \langle g | P_i | n \rangle \langle n | P_j | m \rangle \langle m | M_k | g \rangle \right] \rho_g(T) + \ldots,$$

where $g$, $m$ and $n$ refer to the ground, intermediate and highest state and $\langle g | P_i | n \rangle$, $\langle n | P_j | m \rangle$ and $\langle m | M_k | g \rangle$ give the respective polarization dependent transition matrix elements. $\rho_g$ represents the thermal distribution of the ground state. Here, the first transition to the intermediate state is of magnetic dipole character, while the other two are represented as electric dipole transitions. Since in solids the electronic properties are described by the band structure and
its states essentially form a continuum [63], the width of the resonance in equation 2.23 can be taken into account by summation over a large set of neighboring states $g, m, n$.

In the degenerate case of SHG we have $\omega_a = \omega_b = \omega$ and equation 2.23 is often reduced to

$$\chi_{ijk}^{\text{em}} (2\omega) \propto \sum_{g,m,n} \left[ \frac{\langle g | P_i | n \rangle \langle n | P_j | m \rangle \langle m | M_k | g \rangle}{(2\omega - \omega_{mg})(\omega - \omega_{mg})} + \ldots \right] \rho_g(T). \tag{2.24}$$

However, it must be stressed that for femtosecond beams, the laser pulse can span enough bandwidth to couple several different electronic states and the description using equation 2.23 is quantitatively as well as qualitatively more appropriate. Resonantly enhanced SHG using e.g. 70 fs optical parametric amplifier pulses might be considered to be rather (non-degenerate) intra-pulse sum frequency generation than proper SHG. As this technique is strongly wavelength dependent, nonlinear spectra acquired with different bandwidths may show different results as can be seen by the comparison of SHG and SFG in NiO in figure 2.6 a). At room temperature, this discrimination is less relevant as thermal broadening has a strong influence on the spectra which can be seen from comparison between figure 2.6 a) and b).

In contrast to SFG that can be applied to most $3d$ transition metal compounds [64], SHG restricts the resonant enhancement method to systems, like NiO, CoO or KNiF$_3$, where an intermediate state at $\hbar\omega$, in between the ground state and $2\hbar\omega$, exists [68], see figure 2.5.

---

**Figure 2.5:** Electronic diagram of the Ni$^{2+}$ $(3d)^8$ states taking part in the resonance enhancement of the $\chi_{\text{em}}^{(2)}$-type SHG in NiO. Reprinted from Fiebig et al. [40] with permission from the American Physical Society.
2.2 Second-Harmonic Generation (SHG)

Figure 2.6: The spectral dependence of SHG compared to SFG in NiO measured at different temperatures. a) Comparison between SHG and SFG with fixed $\hbar \omega_1 = 0.972$ eV at a temperature of 6 K. Reprinted from Satoh et al. [64] with permission from Springer Science and Business Media. b) The SHG spectrum at room temperature measured using a 3 ns laser in transmission and in reflection using a 100 fs system. Reprinted from Duong et al. [38] with permission from the American Physical Society.

2.2.4 Phase matching and analytic solutions of instructive special cases

Three-wave mixing in absorptive media

The induced nonlinear polarization that was discussed so far gives rise to locally oscillating fields at various frequencies. However, light will only be radiated off from an extended volume if the polarizations induced at different locations add up coherently. This depends on the different propagation properties of the fundamental and second-harmonic beams inside the medium. A general description of this process is given by the coupled wave equations [79, 52, 80]. For homogeneous media without free charges $\nabla \cdot \mathbf{E} = 0$, but allowing for absorption, the general form of the nonlinear wave equation can be found in references [79, 63, 52]. A derivation using the terminology used throughout this thesis is given in appendix B. For SHG these coupled differential equations simplify to (equations B.6 and B.7)

$$\left(\nabla^2 + k_{2\omega}^2\right) \mathbf{E}_\omega = i \frac{\omega^2}{c^2} \epsilon' \mathbf{E}_\omega - 2 \frac{\omega^2}{c^2} \chi \mathbf{E}_{2\omega} \mathbf{E}^*_{\omega}, \quad (2.25)$$

$$\left(\nabla^2 + k_{2\omega}^2\right) \mathbf{E}_{2\omega} = 4i \frac{\omega^2}{c^2} \epsilon' \mathbf{E}_{2\omega} - 4 \frac{\omega^2}{c^2} \chi \mathbf{E}_\omega^2. \quad (2.26)$$

In part II, we will discuss a technique that treats nonlinearities with even more generality than the coupled wave equation ansatz, but they already provide sufficient insight and may be more instructive for the case of SHG in centrosymmetric antiferromagnets.
Chapter 2: Methods for detecting antiferromagnetic order

Weak nonlinear coupling approximation

In the scope of this thesis, it is sufficient to consider SHG with inefficient coupling in which the pump beam is not being depleted by the second-harmonic. The latter is the case when either the nonlinear susceptibility is weak, for example due to a magnetic or quadrupole type coupling, or if there is considerable phase mismatch. Both is the case in the material studied in section 5. Using this approximation, we will present in section 5.5.1 a full solution for SHG from slab crystals allowing for depth inhomogeneities. However, in order to get some insight into the phenomena arising in non-phase-matched SHG in absorbing media, we can first investigate analytic solutions to a simplified problem. We start by considering collinear generation of second-harmonic light in a semi-infinite homogeneous medium.

Collinear generation of second-harmonic light

To solve equations 2.25 and 2.26 analytically, we restrict the problem to collinearly propagating beams in the \( z \)-direction that couple along polarizations orthogonal to \( z \). We may then use the plain wave ansatz from appendix B.2, which separates the envelope function \( \tilde{E}_a(z) \) from the spatially oscillatory component. If the absorption lengths of the beams is longer than their wavelengths, we can make use of

\[
\left| k'_a \frac{d\tilde{E}_a(z)}{dz} \right| \gg \left| \frac{d^2\tilde{E}_a(z)}{dz^2} \right|, \tag{2.27}
\]

and approximate the left hand side of equation 2.25 and 2.26 to get

\[
(\nabla^2 + k'^2_a) \left[ \tilde{E}_a e^{-ik'_a z} \right] \approx -i2k'_a \frac{d\tilde{E}_a}{dz} e^{-ik'_a z}. \tag{2.28}
\]

Using equation 2.28 to simplify equations 2.25 and 2.26 and canceling the oscillatory terms that appear on both sides we get the coupled differential equations for the field envelope functions

\[
\frac{d\tilde{E}_\omega}{dz} = -\alpha \omega \tilde{E}_\omega - i\frac{\omega}{n'_c} \tilde{\chi} \tilde{E}_{2\omega} \tilde{E}_\omega e^{-i\Delta k z}, \tag{2.29}
\]

\[
\frac{d\tilde{E}_{2\omega}}{dz} = -\alpha_{2\omega} \tilde{E}_{2\omega} - i\frac{\omega}{n_{2\omega} c} \tilde{\chi} \tilde{E}_\omega \tilde{E}_{2\omega} e^{i\Delta k z}, \tag{2.30}
\]

where now \( \Delta k = k'_{2\omega} - 2k'_\omega \) and \( \alpha = k'' = \omega \epsilon''/(2n'c) \).

By assuming weak nonlinear coupling, so that \( E_\omega \gg E_{2\omega} \) at all times, which holds true for SHG in NiO, as the leading coupling constant \( \tilde{\chi}_{em} \) is very small and \( \alpha_{2\omega} \neq 0 \), the differential equation for the fundamental beam becomes decoupled. Assuming a semi-infinite medium starting at \( z = 0 \), equation 2.29 reduces to

\[
\frac{d\tilde{E}_\omega}{dz} = -\omega \alpha \tilde{E}_\omega, \text{ so that } \tilde{E}_\omega(z) = \tilde{E}_{\omega,0} e^{-\alpha \omega z}, \tag{2.31}
\]
2.2 Second-Harmonic Generation (SHG)

Figure 2.7: The red line shows the normalized envelope field of the collinearly generated SHG following equation 2.32 until a distance \(d = 50 \mu m\) inside the crystal, \(\alpha = 1/d\), \(\alpha_2 = 1/2\alpha_1\), \(n = 2.4\) and \(n_2 = 2.35\). The blue and orange lines depict the attenuation of incoming waves at the fundamental frequency and its second-harmonic, respectively.

where \(\tilde{E}_{\omega,0}\) denotes the fundamental field amplitude transmitted into the medium. We can then solve the differential equation 2.30 to obtain

\[
\tilde{E}_{2\omega} = -\frac{i\omega}{n_{2\omega}c} \chi_{eeem} E_{\omega,0}^2 e^{(i\Delta k - 2\alpha_\omega)z} e^{-\alpha_{2\omega}z} \alpha_{2\omega} - 2\alpha_{\omega} + i\Delta k.
\]  

(2.32)

Results of equation 2.32 are shown in figure 2.7. One remarkable consequence is that it leads to spatial oscillations of the amplitude field inside the medium in the direction of propagation at spatial frequency

\[
\Delta k = 2\omega \Delta n/c,
\]

(2.33)

which are directly related to the so called Maker-fringes [81]. Furthermore, unlike for SHG in transparent media, absorption, both of fundamental and second-harmonic beams, leads to the emergence of an increasing pedestal value of the SHG field that exists even in the condition of maximum deconstructive interference.

**Anti-collinear generation of second-harmonic light**

Anti-collinearly generated second-harmonic light is intrinsically inefficient as the phase mismatch between the induced polarization due to the fundamental beam and counter-propagating second-harmonic typically correspond to a coherence length of about \(\lambda/4\). Hence, in insulators it can only be observed emitted from the bulk polarization right below surfaces or from strongly absorbing media. The slowly varying amplitude approximation is not applicable in this treatment as the second order derivative \(\partial^2 E_{2\omega}(z)/\partial z^2\) is of similar magnitude as \(k_{2\omega}E_{2\omega}(z)/\partial z\) (in fact even
larger). Mizrahi and Sipe give an analytic derivation for the SHG contributions arising from the bulk in anti-collinear direction [82, 83]. Without the interface contributions, their result can be formulated for anti-collinear fields just below the surface as

$$\tilde{E}_{2\omega}(0) = \frac{i\omega}{cn_{2\omega}} \tilde{\chi} \tilde{E}_{\omega}^2 \omega \int_{-\infty}^{0} e^{-i\Delta k + \alpha_{2\omega} - 2\alpha_{\omega} + i\Delta k} \, dz.$$  

(2.34)

Note that the phase mismatch is now given by the sum $\Delta k = k_{2\omega} + 2k_{\omega}$. 

Chapter 3

Creation and detection of coherent acoustic phonons

So far, we were merely considering the light fields to be dynamic, while treating the media under study as passive and essentially represented by a homogeneous susceptibility $\chi$. Neglecting effects from surface reconstruction, which may vary $\chi$ in the vicinity of the surface, the latter is a reasonable assumption for experiments on bulk crystals using small electromagnetic fields such that the thermal equilibrium state is unperturbed by the measurement. However, in the regime of ultrafast lasers, we go intentionally beyond this limit to observe non-equilibrium states of matter. One of these non-equilibrium states, that can, without exception, be induced in any kind of matter, liquid or solid, is the coherent acoustic phonon.

In condensed matter physics, displacement of atoms is described by quantized lattice excitations called phonons. The name was chosen to stress their similarity to photons, the bosonic quanta of the electromagnetic field. And similar to photons, these vibrational modes of the lattice, are derived as non-interacting with other quanta of their kind. In the derivation of phonons, this is due to the harmonic approximation of all interatomic forces [84].

Yet, thermal expansion is one obvious example for anharmonic behavior of crystals. The lattice potential, and hence the lattice parameters, depends on the acoustic phonon population. As their dispersion conversely depends on the lattice potential, this gives rise to phonon-phonon interaction. In thermal equilibrium, remote parts of the crystal observe the same phonon bath population and hence share common lattice parameters. Fluctuations in phonon population form wave-packets that travel at the group velocity of the acoustic branches, i.e. the speed of sound, through the crystal and will eventually equilibrate, most commonly via phonon-phonon scattering, another example of anharmonic behavior.

Such spontaneously created wave-packets locally alter the density of the crystal which can in various ways be experimentally observed, e.g. via spontaneous Brillouin scattering which may be understood as the solid-state equivalent of Rayleigh scattering.
We can also induce such acoustic wave-packets intentionally by using ultrashort electromagnetic pulses that interact with the crystal on timescales short compared to the scattering time and inverse frequency of the phonon. Such an ultrafast pulse locally applies stress to the crystal generating phonons that move in-phase to form a macroscopic non-equilibrium phonon population. This type of coherent state of the crystal lattice is in stark contrast to the fully randomized phase relations between phonons obeying the equilibrium Bose-Einstein distribution and is frequently referred to as \textit{coherent phonon}.

A common way to realize such a state is by absorption of mode-locked laser pulses, though there is a variety of mechanisms allowing for stimulated acoustic phonon generation which will be shown in the next section 3.1. We will then continue to have a closer look at thermoelastic coupling as a means to generate acoustic phonons and discuss the phenomenon using macroscopic physical quantities. Finally, section 3.3 will discuss the implications of the presence of coherent acoustic phonons on optical probes.

### 3.1 Coupling photons to acoustic phonons

In contrast to polar optical phonons, there is no direct way to excite acoustic phonons in bulk material by electromagnetic waves, as photon interaction is to first-order limited to the vicinity of the \( \Gamma \)-point, where acoustic modes tend towards zero frequency. There is, however, a large number of indirect ways of generating acoustic phonons, since literally any excitation will eventually release part of its energy to populate the lower lying acoustic bath. An attempt to classify acoustic coupling mechanisms was given by Ruello and Gusev \cite{85}, who proposed 4 classes of mechanisms. From rather exotic to more common, these are: electrostriction, the inverse piezoelectric effect, deformation potential coupling and thermoelasticity. While they surely cover the majority of observations, optical phonon decay and magnetic phenomena are omitted in this list. It is nonetheless interesting to consider these as instructive examples showing different dependencies on excitation polarization and order of electric field strength. The piezoelectric effect e.g. scales with field strength \( E \), while electrostriction may depend on the tensor \( E_iE_j \) and the other 2 simply scale according to intensity \( \propto |E|^2 \). This implies that the piezoelectric effect and electrostriction show polarization dependence, while deformation potential and thermoelasticity follow the absorbed intensity \cite{85}. The latter two can be modeled by considering the optically induced increase in electronic and lattice temperature.

In the scope of this thesis, we may also mention the case of magnetostrictively distorted crystals, such as the binary antiferromagnets. In these systems an optically induced quenching of the magnetic order can lead to a reduction of lattice striction releasing acoustic phonons to the lattice.
3.2 Optically induced strain via thermoelastic coupling

So far, we were mainly concerned with the microscopic quantities, but coherent motion has a macroscopic, or rather mesoscopic, counterpart in the continuum description of elastodynamics which is the structural distortion of the lattice that can be expressed by the strain tensor $\eta$.

In this picture, the different coupling mechanisms ultimately end up in applying a stress profile $\sigma(z, t)$ to the crystal which leads to a propagating deformation profile $\eta(z, t)$. Keeping this in mind, it may be instructive to discuss the most common coupling mechanism in more detail, which is the thermoelastic effect.

Following Thomsen et al. [86], optically induced strain can be expressed based on the crystal stress that is caused by a sudden local increase in temperature after optical excitation. Due to the absorption in the crystal and the boundary conditions introduced by the surfaces, where applied stress is compensated, the induced stress is not isotropic in the direction normal to the surface. In isotropic media with density $\rho$, stress $\sigma_{33}$ and the displacement in $z$ direction $u_3$, the equations of elasticity can be expressed as [86]

$$\rho \frac{\partial^2 u_3}{\partial t^2} = \frac{\partial \sigma_{33}}{\partial z}, \quad \eta_{33} = \frac{\partial u_3}{\partial z}. \quad (3.1)$$

With the boundary conditions given by the crystal surfaces and the initial condition of 0 strain before excitation, we obtain solutions that consist of strain waves propagating at the speed of sound in $z$ direction. This picture is equivalent to the description as propagating longitudinal acoustic phonon wave-packets. The solution to equation 3.1 reads

$$\eta_{33}(z, t) = (1 - R)^2 \alpha Q A b C 1 + \nu F(z - v_s t) e^{-\alpha t}, \quad (3.2)$$

where $(1 - R)$ accounts for the reflection loss of the optical beam, $2\alpha Q/A$ gives the excitation energy density, $b/C \frac{1 + \nu}{1 - \nu}$ is the material specific geometric response to laser induced heat with $b$ being the expansion coefficient, heat capacity $C$ and Poisson’s ratio $\nu$. Limited crystal dimensions require to consider acoustic reflections, which is here taken into account by the dimensionless wave solution to the equation of elasticity $F(z - v_s t)$ that solves the boundary conditions. An explicit solution of $F(z, t)$ is given for a slab crystal in section D.

For simplicity, here an exponential decay term $e^{-\alpha t}$ is added to account for acoustic diffusive loss. Although actual diffusion can be taken into account as was done in reference [86]. In optically semi-transparent crystals, such as the binary antiferromagnetic insulators, the maximum generated strain is usually much smaller than for metals as is shown in figure 3.1. Due to the large penetration depth it is often necessary to consider the whole volume of the samples, as one can expect strain waves also arising from the sample’s backside.

The solution given above solves the equation of elasticity for instantaneous excitation, i.e. an immediate application of a finite stress profile. This results in arbitrarily high frequency
Chapter 3: Creation and detection of coherent acoustic phonons

Figure 3.1: Calculated strain profiles $\eta_{33}(z,t)$ following equation 3.2 at different times $t$ in a 36 $\mu$m thick slab crystal. Traces were offset for clarity. Here, diffusion was neglected leading to a permanent strain profile at the surface as the thermal stress is still present. a) The case for strong absorption $\alpha = 100 \times \alpha_{\text{NiO}}$. Here, $\alpha_{\text{NiO}} = 355$ cm$^{-1}$ gives a typical 800 nm absorption coefficient of NiO, see figure 1.3. b) Strain in weakly absorbing semi-transparent NiO with $\alpha_{\text{NiO}}$ showing an additional strain wave arising from the backside. Notice the different scales in a) and b).

The presence of crystal strain implies local variations of interatomic distances, therefore it does not only affect mechanical but also optical properties of the crystal. The absolute deformation typically corresponds to a relative change in length of $10^{-4}$, which allows to treat the influence on optical parameters as perturbation. To first order the change of the linear susceptibility is then given by

$$\Delta \chi^{(1)}(z,t) = 2(n + ik) \left[ \frac{\partial n}{\partial \eta_{33}} + i \frac{\partial \kappa}{\partial \eta_{33}} \right] \eta_{33}(z,t).$$

(3.3)

Here, we will further limit this dependence by not treating changes of the imaginary part of components contained in the created acoustic wave-packet. Corrections to this approximation can be made by considering the time it takes to transfer the absorbed energy from the electrons to the lattice, which is typically on the order of 1 ps, and furthermore by accounting for the optical pulse-length, which for our purposes is around 100 fs. The acoustic phonon wave-packet can further be dispersed by low surface quality.

3.3 Effect of strain on the linear and nonlinear susceptibilities

The presence of crystal strain implies local variations of interatomic distances, therefore it does not only affect mechanical but also optical properties of the crystal. The absolute deformation typically corresponds to a relative change in length of $10^{-4}$, which allows to treat the influence on optical parameters as perturbation. To first order the change of the linear susceptibility is then given by

$$\Delta \chi^{(1)}(z,t) = 2(n + ik) \left[ \frac{\partial n}{\partial \eta_{33}} + i \frac{\partial \kappa}{\partial \eta_{33}} \right] \eta_{33}(z,t).$$

(3.3)

Here, we will further limit this dependence by not treating changes of the imaginary part of
3.3 Effect of strain on the linear and nonlinear susceptibilities

the refractive index \( \partial \kappa / \partial \eta_{33} = 0 \)

\[
\Delta \chi^{(1)}(z, t) = 2(n - i\kappa) \frac{\partial n}{\partial \eta_{33}} \eta_{33}(z, t).
\]  

(3.4)

The local change of the susceptibility will surely have an impact on the transmission and reflection coefficients, which for a semi-infinite sample in the linear case then reads [86]

\[
r(z, t) = r + \Delta r(z, t) = r + \frac{ik_0^2}{2k} t_0 \int_0^\infty dz' e^{2ikz'} \left[ 1 + \Delta \chi^{(1)}(z', t) \right].
\]  

(3.5)

We can immediately see that equation 3.5 allows for interference between the surface reflection \( r \) and reflections arising from variations of the dielectric function below the surface that depend on time \( t \). Given that the reflected intensity is \( |r|^2 \) we can expect to observe this interference as intensity oscillation in time leading to oscillations at frequency

\[
\nu = \frac{2nv_s}{\lambda},
\]  

(3.6)

with the refractive index \( n \), speed of sound in the material \( v_s \) and probe wavelength \( \lambda \).

We may briefly take the opportunity to put this effect in a somewhat wider context. The modulation of the susceptibility is proportional to the strain, thus travels at the speed of sound into the material and is reflecting a fraction of the transmitted light back to the source. This is equivalent to the optical Doppler shift from a moving reflector and leads to a spectral sideband that could be observed using a grating spectrometer [87]. Since we use ultrashort-pulse sources, we may as well study the effect in the time domain, where we can observe the frequency shift in a pump-probe measurement via the interference in equation 3.5.

In an early experiment by Bosco et al. it was shown using time-resolved reflectivity measurements that coherent acoustic phonons can be detected in NiO films via the process described in equation 3.5. For their experiment they employed a thin NiFe transducer layer to generate high amplitude acoustic phonons that were coupled into the NiO film. Later, Takahara et al. showed birefringence measurements that were used to additionally observe the generation of coherent acoustic phonons in pure (001)-cut bulk NiO samples by 800 nm absorption [28]. At a probe wavelength of 700 nm, they were able to induce relative reflectivity changes on the order of \( 5 \times 10^{-4} \), which is considerable given that NiO is an insulator with a band gap in the range of 3.4-4.0 eV [88, 30] that shows weak absorption in this wavelength range. As Bosco et al. showed, the coefficient \( \partial n / \partial \eta_{33} \) is a strong function of wavelength and they observed a strongly enhanced amplitude for probe wavelength in the vicinity of the band gap as can be seen in figure 3.2.

Not only the linear response will be sensitive to the presence of strain. As we saw in section 2.2.4 and in particular in equation 2.32, already the modulation of the refractive index alone implies consequences for the SHG response as alterations of \( n(z, t) \) directly affect the phase matching integral. Equations 2.29, 2.30 and the integral in 2.34 directly depend on the refractive
Figure 3.2: First observation of coherent acoustic phonons in NiO by Bosco et al. using transient reflectivity from a 274 nm thick NiO sample on a Si (001) substrate that was covered with a 10 nm NiFe transducer [88]. Copyright (2002) by the American Physical Society. After 45 ps the strain pulse generated in the transducer reaches the Si substrate. The pump wavelength was 800 nm.

index, and the phase matching condition is a sensitive function of the small difference between $n_\omega$ and $n_{2\omega}$. Additionally, the fundamental light field will be modified by the Brillouin scattering, which also modulates the SHG as observed in reference [89]. Furthermore, when observing resonantly enhanced SHG following equation 2.24 it seems highly plausible that strain could also influence $\chi^{(2)}$ via small shifts of electronic states or spin population.

In chapter 5.5.1 we will present a simulation technique that addresses all of these influences using a propagation matrix approach [90] that is applied to the time-dependent SHG problem.
Chapter 4

Time-resolved magnetic x-ray diffraction in NiO

4.1 Introduction

In this chapter we investigate the validity of the previously proposed spin dynamics model (section 1.4) by applying the technique of magnetic x-ray diffraction as a time-resolved probe to measure the dynamics of the absolute AFM ordering with ps resolution. Bergevin and his coworkers demonstrated the suitability of magnetic x-ray diffraction as a means to quantify antiferromagnetic order in NiO in static measurements [60, 58, 56]. However, conventional third generation light sources such as the ones used in their work are not able to provide sufficient temporal resolution to study dynamics on the 50 GHz scale. For this reason our time-resolved experiments in section 4.3 were carried out at beamline 3 of the hard x-ray free electron laser (XFEL) SACLA\textsuperscript{1}, Japan [91]. In order to assess the crystalline quality of our samples, in section 4.2.1 we first went to a third generation light source that has a higher total photon count rate, the Petra III storage-ring on the DESY campus in Hamburg.

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

Coherent acoustic perturbation of second-harmonic generation in NiO.

\textsuperscript{1}SPring-8 Angstrom Compact free electron Laser
Figure 4.1: Diffractometer at the experimental hutch EH01 of beamline P09 at Petra III. The beam enters the experimental area from the right and after passing the vacuum window propagates about 50 cm in air to the sample. The latter is mounted on a pin sitting in the exact center of the diffractometer’s rotational axes. The scattered x-rays are then detected using the 2θ-detection arm that includes the analyzer crystal, here shown to the left with its He-filled flytube pointing towards the sample. The schematic diffraction geometry is depicted in figure 4.2.

4.2 Static x-ray characterization

4.2.1 Magnetic x-ray diffraction at a synchrotron

In order to characterize the magnetic ordering and exact orientation of our NiO samples that are nominally (111)-cut, we carry out a static non-resonant magnetic diffraction experiment using a high precision diffractometer in experimental hutch EH1 of the P09 Resonant Scattering and Diffraction beamline at Petra III, which is shown in figure 4.1. Experimental details on the beamline and diffractometer can be found in reference [93]. The setup, schematically shown in 4.2, is similar to the one used by Fernandez et al. [58] and is able to measure the four polarization components of magnetic scattering as defined in equations 2.9 and 2.10.

The 7.84 keV x-ray photons are monochromatized using a Si (111) double crystal monochromator and linearly polarized in horizontal direction. After alignment of the 36 µm thick NiO sample, we observe the symmetric magnetic \((\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2})\) and \((\frac{3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2})\)-diffraction peaks at room temperature. The beamline is equipped with a pyrolytic graphite analyzer that allows us to detect the \(\langle M_m \rangle_{\sigma\sigma}\) component which is purely spin dependent. The \((\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2})\)-peak can be observed but suffers from strong background caused by a diffraction ring from the Teflon mount. The result for the \((\frac{3}{2}\frac{3}{2}\frac{3}{2}\frac{3}{2})\)-peak is shown in figure 4.3.
4.2 Static x-ray characterization

Figure 4.2: a) Diffraction geometry of the NiO characterization experiment at Petra III. The incoming vertically polarized beam is magnetically diffracted from the sample, thus the polarization is slightly rotated according to equation 2.10. Afterwards the pyrolitic graphite analyzer (PG) diffracts only the $(\sigma\sigma)$-polarization component into the detector. b) The diffraction geometry with respect to the sublattice spin direction as defined in figure 2.1. The picture shows the crystal rotation $\phi$ such that [112] is pointing along $e_2$, i.e. is maximized for $(\sigma\sigma)$-scattering intensity.

The signal to background ratio is about 1.1 which can partly be attributed to the background from the Teflon mount. Closing the detector slits helps to improve this ratio considerably on the cost of dropping overall peak countrate. The configuration allowing to measure the $\langle M_m \rangle_{\sigma\sigma}$ component of the diffraction, does not suppress charge scattering. This can be expected to be reduced for the $\langle M_m \rangle_{\sigma\pi}$ and $\langle M_m \rangle_{\pi\sigma}$ components as only magnetic diffraction is able to rotate the polarization, see equation 2.10. The detected photon countrate of the magnetic $(3/2 3/2 3/2)$-peak is 12000 photons/s. With a measured direct beam rate of $3 \times 10^{12}$ monochromatized photons/s, this corresponds to a diffraction efficiency of $0.4 \times 10^{-8}$. In comparison, Fernandez et al. measured at the same energy and for the same geometry a ratio of $1.1 \times 10^{-8}$ between the photon rate at the sample position and the detected $(3 3 3)$-peak intensity [58]. However, they report to have measured a single T-domain crystal that also shows better lateral coherence, with peak widths of about half of the ones observed in this study. In particular, since we know from optical measurements, that the 36 $\mu$m NiO sample has structural domains below 10 $\mu$m and the x-ray full width at half maximum (FWHM) beamsize was 70 $\mu$m, we most likely measure a fully randomized domain sample reducing the scattering efficiency by at least a factor of 4 [60]. The influence of domains will be discussed in more detail in section 4.4.1.

The experimental time also allowed for testing of a 0.5 mm thick bulk NiO sample which also shows magnetic peaks of same width as the 36 $\mu$m sample. The 45 $\mu$m thick crystal was not characterized at this source.
Figure 4.3: a) A coordinated ‘Theta2Theta’ scan following the Bragg condition of the magnetic \((\frac{3}{2} \frac{3}{2} \frac{3}{2})\)-peak’s \(\langle M_m \rangle_{3\sigma}\)-component measured without attenuation. b) The corresponding rocking curve of the same peak. A Pseudo-Voigt-function is fitted to the data resulting in a peak position at \((29.50 \pm 0.01)\)° and a peak width of \((0.120 \pm 0.005)\)° (FWHM).
4.2 Static x-ray characterization

**Figure 4.4:** Diffractometer at the experimental hutch EH2 at beamline 3 of SACLA on the Spring-8 campus, Hyogo, Japan. The horizontally polarized x-rays enter the experimental hutch coming from the vacuum pipe in the back, are then diffracted off the NiO sample that is mounted on the tip of the brass pin to the right and enter the He-flytube that leads them to the MgO analyzer in the lower left of the picture. The latter then diffracts the $\sigma$-polarized x-rays vertically into the detector.

4.2.2 Magnetic x-ray diffraction at an XFEL

In order to support time-resolved x-ray diffraction measurements with a time resolution on the order of picoseconds as well as sufficient photon flux, the final experiment needed to be carried out at a hard x-ray free electron laser. While for example synchrotron sources as Petra III or the Swiss Light Source typically deliver $10^6$-$10^7$ photons per electron bunch of 30-100 ps pulse-length [94, 53], an x-ray free electron laser can provide in excess of $10^{11}$ photons per bunch at pulse-lengths on the order of 50 fs [91, 95].

Our collaboration for this experiment was granted experimental time at the XFEL SACLA in Japan. The total photon countrate of this new type of light-source was, however, still considerably lower than at a synchrotron. In spring 2013 SACLA was running at 10 Hz repetition rate with 180 $\mu$J per pulse at a photon energy of 7.2 keV. This sums up to $1.5 \times 10^{12}$ photons per second to start with at a relative bandwidth of about 0.6% [96].

Although the 36 $\mu$m NiO sample was characterized in the previous experiment in section 4.2.1 and was found to be well suited, measurements of the same crystal at SACLA found a much smaller lateral coherence length leading to a considerable decrease in peak diffraction efficiency.
Chapter 4: Time-resolved magnetic x-ray diffraction in NiO

Figure 4.5: a) The experimental diffraction setup in horizontal scattering geometry at beamline 3 of the XFEL SACLA. An MgO crystal at a Bragg angle of 45° is used to select outgoing $\sigma$ radiation that is detected using an yttrium aluminium perovskite detector (YAP). b) The spin orientation in the antiferromagnetic phase of NiO for a single spin domain of a (111)-cut crystal, where the spin points along [112].

Figure 4.6: The rocking curve of the ($\frac{3}{2}\frac{3}{2}\frac{3}{2}$)-peak’s $\langle M_m \rangle_{\pi\sigma}$-component at the XFEL SACLA, as published in reference [61]. A Pseudo-Voigt-function is fitted to the data resulting in a peak position at $(32.41 \pm 0.01)^\circ$ and a peak width of $(0.10 \pm 0.01)^\circ$ (FWHM). Errorbars are calculated from the shot-noise.
We tentatively attribute this to excessive application of strain when de- and remounting the thin NiO sample on the two sample holders. Instead, the 45 µm thick (111)-oriented NiO crystal, see section 1.3, has been mounted on a multi-axis diffractometer in horizontal scattering geometry as depicted in figure 4.4 and 4.5 a) (π incident x-ray geometry). The peak intensity of the magnetic diffraction from the (323)-planes is found at a Bragg angle of 32.41° for the 7.2 keV photon energy, see figure 4.6.

Polarization analysis using a magnesium oxide (MgO) analyzer crystal in (πσ)-configuration efficiently suppresses the charge-scattered background, allowing an improved measurement of the weak magnetic signal. Here, MgO is chosen over pyrolytic graphite, used in section 4.2.1 and reference [58], to allow for a higher analyzer reflectivity while still matching the bandwidth of the NiO (323)-plane diffraction. The choice of MgO is also the reason for setting the photon energy to 7.2 keV, as the efficient MgO (222)-reflection then fulfills the analyzer condition of a Bragg angle of 90°. In this configuration the NiO (323)-reflection gives the strongest signal relative to other magnetic reflections in the ⟨Mm⟩πσ-channel, yielding 0.8 photons per XFEL-pulse, as shown in figure 4.6.

Comparing figure 4.6 to figure 4.3 shows a striking difference in detected countrate of 3 orders of magnitude, two of which are due to the overall lower incoming photon rate and larger x-ray bandwidth. Another order of magnitude is due to the fact that the rotated (πσ)-component is measured rather than (σσ), which is in agreement with the observations by Fernandez et al. [58]. Nonetheless, the (πσ)-component improves the signal to background ratio considerably and warrants the magnetic origin of the detected x-rays.

To additionally test for possible contributions from the XFEL second-harmonic diffracting off the NiO (333) structural planes, we insert a Si filter with a nominal thickness of 100 µm into the beam path. This thickness of Si transmits 14% of x-ray radiation at 7.2 keV, but for any potential second-harmonic contributions at 14.4 keV the transmission is 77% [97]. We observe a transmission of the diffracted signal of (12.2 ± 0.6)%, indicating that second-harmonic contributions from the (333) structurally allowed reflection are not significant in this experiment. We can conclude this section by stating that, although the observed signal is not strong, it is to a high degree of certainty of magnetic origin.

### 4.3 Time-resolved experimental results

To excite the sample, an amplified Ti:sapphire laser system that is synchronized to the XFEL provides pump pulses centered at 800 nm wavelength with 50 fs FWHM duration. The timing jitter of less than 1 ps exceeds our requirements in order to resolve a potential 20 ps oscillation period, corresponding to a 50 GHz response [98]. These specifications are defined by the proposed model for magnetization dynamics described in section 1.4. The pump pulses are focused onto a (0.7×1.7) mm² (FWHM) spot on the sample at an incidence angle of 24.4° in p-geometry, which is close to the Brewster angle of NiO and is 8° degrees from the incoming x-ray beam. The latter
Chapter 4: Time-resolved magnetic x-ray diffraction in NiO

has a footprint on the crystal of (0.40×0.75) mm$^2$. The large excitation area warrants spatial overlap. The intensity attenuation depth is 24 µm and 26 µm for the x-rays and the laser beam, respectively. The incident excitation fluence is 37 mJ/cm$^2$, leading to an excitation density of 0.5 × 10$^{20}$ cm$^{-3}$ near the sample surface. As can be seen in figure 5.3, these pump conditions lead to large magnitude SHG dynamics, which were previously interpreted as a reorientation of spins in the [111] direction [38]. Spatial and temporal overlap of the pump and probe pulses is verified by measuring the x-ray induced optical transmission changes of a GaAs wafer temporarily inserted into the sample position [99]. We measure the intensity of the (3 2 3 2 3 2)-peak at room temperature as a function of relative pump-probe delay time over a range of −30 to 30 ps at 3 different positions on the sample. As shown in figure 4.7, the measured relative changes in the diffraction intensity do not exceed a value of two times the mean error of photon counting statistics of 2% over the first 30 ps after excitation.

![Figure 4.7:](image)

**Figure 4.7:** The time-resolved diffraction measurements on NiO are shown as blue dots. Broken blue lines indicate two times the mean standard error of photon counting statistics, approximately 2%. We do not observe a relative change in diffraction intensity exceeding this value. Temporal and spatial overlap are verified using an x-ray pump–optical-transmission probe experiment on GaAs depicted as orange triangles. The time scan is carried out at the (3 2 3 2 3 2)-peak position of the diffraction peak shown in figure 4.6 at θ = 32.4°. The figure has been modified from reference [61].

4.4 Discussion

4.4.1 The effect of spin rotation on magnetic diffraction in a twinned crystal

Before we come to final conclusions about this negative result a few considerations may be made first. We start with stating that according to equation 2.10 and 2.11 the observed intensity is proportional to the square of the sublattice magnetization, thus to the order parameter $l$ of the
antiferromagnet. We may raise the question what exactly is observed by the experiment, knowing that the NiO crystals measured here consist of spin as well as structural domains of around 10 µm size as shown in section 1.3. We will briefly discuss what the implications of a distribution of domains on the signal are and what the effect of a potentially induced reorientation and decrease of the magnetic moment would look like.

Given that the footprint is particularly large in this experiment, we can assume that we sample a random distribution of the 12 different domain structures. Only one of the 4 different lattice contractions along the sublattice stacking directions can be observed in the experiment, which simply reduces the measured intensity by a factor of 4 in the case of random domains as compared to a single domain sample [60]. Furthermore, from equation 2.6 we see that the magnetic scattering factor is related to a sum of projections of $S(Q)$ and $L(Q)$. For our measurement geometry and x-ray polarizations the scattering factor is given by

$$M_{\pi\sigma} = 2 \sin^2 \theta \left[ \cos \theta (L_1 + S_1) + \sin \theta S_3 \right]. \quad (4.1)$$

Here, $L_1$ and $S_1$ are the components of $L(Q)$ and $S(Q)$ along the (112) direction as depicted in figure 2.1 and figure 4.5 b). $S_3$ is the component of $S(Q)$ in the (111) direction. We will neglect contributions from $L_1$, although it was found to lead to small contributions to the equilibrium magnetic moment in NiO [58]. The diffracted intensity is then

$$I(\theta)_{\pi\sigma} \propto \sin^2 \theta \tan \theta \left( S_1 \cos \theta + S_3 \sin \theta \right)^2. \quad (4.2)$$

As discussed in the previous section, the equilibrium sublattice spins can point along any of three equivalent \{11\} directions, resulting in three possible spin domains: (11\overline{2}) (domain “A”), (1\overline{2}1) (domain “B”), and (\overline{2}1\overline{1}) (domain “C”). Using superscripts to denote the different spin domains with their respective ratios $a$ of the total population, satisfying $a^A + a^B + a^C = 1$, we have in equilibrium $S_1^A = a^A S$, $S_1^{B,C} = -a^B^C S/2$, and $S_3^{A,B,C} = 0$. Assuming a completely random domain distribution incoherently contributing to the signal, and furthermore assuming that the diffraction signal has been maximized by optimizing $\phi$, then the measured static intensity would consist of 50% photons scattered by domains of type A, and 50% by B and C combined.

The dynamics inferred from previous interpretations of the excited state imply both a reduction of the average spin moment and a reorientation of the spin sublattice vector along (111) as discussed in section 1.4. In our treatment this would lead to a decrease in the $S_1$ component and an increase in the $S_3$ component. We can parameterize this change through new time-dependent variables $\xi$ and $\gamma$, with $\xi$ representing the dimensionless magnitude of the average sublattice spin and $\gamma$ the reorientation toward the (111) direction as depicted schematically in figure 4.8. We then have $S_1^A = \xi a^A S \cos \zeta$, $S_1^{B,C} = -\xi a^{B,C} S \cos \gamma/2$ and $S_3^{A,B,C} = \xi a^{A,B,C} S \sin \gamma$. This
Figure 4.8: Geometric definitions of $\xi$ and $\gamma$ and the effect of a potential excitation induced reorientation on the spin domains A, B and C.

leads to relative changes in the diffraction intensity for each domain type

$$\frac{I(\theta)_{\pi\sigma}}{I(\theta)_{\pi\sigma}^{(0)}} = \xi^2 (\cos \gamma + \tan \theta \sin \gamma)^2$$

(4.3)

$$\frac{I(\theta)_{\pi\sigma}}{I(\theta)_{\pi\sigma}^{(0)}} = \xi^2 \left( \frac{1}{2} \cos \gamma - \tan \theta \sin \gamma \right)^2$$

(4.4)

In equilibrium, $\xi = 1$ and $\gamma = 0$. In case of spin reorientation $\gamma$ should assume some non-zero value. If the relative spin population is unknown, the contributions from different domains given by equation 4.3 and 4.4 could counteract each other for specific configurations.

In our data we observe no changes at any time within our estimated 2% uncertainty. However, since the spin domain population for the probed volume is a priori unknown, it is difficult to place a definite upper bound for changes in $\xi$ and $\gamma$. We can, however, point out that the x-ray data show no evidence of strong oscillatory behavior, suggesting that a re-examination of the proposed dynamics is warranted.

4.4.2 Discussion of the diffraction results

The absence of a change in magnetic diffraction intensity exceeding 2% stands in contrast to the interpretation of the previously reported anti-collinear SHG response where a drop of more than 20% is seen with similar excitation conditions. We were able to reproduce these experimental observations in figure 5.5. The SHG intensity $I_{2\omega}$ should in principle obey the relationship $I_{2\omega} \propto S^4$, where $S$ is the magnitude of the sublattice magnetization [40]. Based on this one could infer that the magnetic order in the excited state drops on the order of several percent. As described in section 4.4.1, the intensity of the magnetic diffraction depends on both the magnitude of the sublattice magnetization and on the orientation of the spin order. In addition, there are three different spin domains that can all contribute to the diffraction signal. Due to the lack of information on the probed spin domain distribution, it is not generally possible to extract a definite upper bound for the changes in either the sublattice magnetization or the
reorientation of the domains since these effects could potentially cancel out. While the x-ray results do not necessarily exclude the possibility of particular combinations of demagnetization and reorientation, they themselves show no direct evidence of large amplitude magnetic sublattice changes. This serves as a motivation to re-examine the interpretation of the previous SHG results by extending these optical studies to explore additional parameter spaces.

As an outlook, we may comment on how similar experiments could be carried out in the future. In 2017, the XFEL SACLA runs at an increased repetition rate and pulse energy, increasing the photon countrate by a factor of 5, while the Linac Coherent Light Source in Stanford (LCLS) can easily achieve a factor of 20 higher countrate as in the current study [100]. In addition, measurement of the magnetic ($\sigma\sigma$)-channel rather than the ($\pi\sigma$)-channel studied here yields an order of magnitude higher countrate [58]. Unfortunately, in this study we were restricted to a horizontal diffraction geometry by the four-circle diffractometer available on-site. Furthermore, the mediocre quality of the crystals measured here is not an intrinsic limitation of the material - higher quality can be achieved by achieving higher stoichiometry in the annealing process, additional straining and magnetically biasing the sample [19]. This may allow for an intensity increase of another order magnitude. Furthermore, single spin domain samples would enable to make more definitive statements about the spin orientation after ultrafast excitation.
Chapter 5

Time-resolved SHG in NiO

5.1 Introduction

The results gained from the experiments discussed in the previous chapter stand in contrast to expectations one could infer based on the previously proposed model of antiferromagnetic ordering dynamics in NiO, see section 1.4.

For this reason, we went back to the ultrafast laser laboratory to further investigate the method that led to the dynamical observations in the first place, time-resolved SHG. Over the last two decades, extensive work on NiO has already been published using this technique [37, 38, 39]. A major limitation to time-resolved SHG studies of this material is the restriction imposed by the experimental necessity of fulfilling the resonance enhancement condition for SHG as discussed in section 2.2.3. In NiO this means that SHG is only efficient when using probe light of a narrow spectral band around 1200 nm. Even then, the generated second-harmonic intensity is very weak, requiring intense probe light pulses and long acquisition times. Due to the limited available laser power at the time, prior studies were only carried out at the resonance condition. Furthermore, all of these studies limited their observation to the anti-collinear geometry.

We see that the existing studies on this material were by no means exhaustive and in this chapter we present and discuss results that extend the time-resolved SHG investigations using the experimental setup described in section 5.2 in three major respects in an effort to understand these dynamics more completely. First, we carry out measurements in both reflection (section 5.3) and transmission geometries (section 5.4) to test the sensitivity of the dynamics to the phase-matching conditions of the SHG process as discussed in 2.2.4. Second, for both geometries we perform measurements at multiple probe wavelengths to determine whether the observed oscillations change with probe frequency which would be expected if acoustic phonons play a role in the dynamics, see section 3.3. Third, we measure the dynamics with different sample thicknesses to determine any possible role of the distance between the interfaces in section 5.4.1. In section 5.3.1, we investigate the pump intensity and pulse-length dependence of the dynamics which was a critical experimental foundation of the previously proposed dynamics model.
5.2 Experimental setup

For our experiments, we employ an amplified 800 nm Ti-sapphire laser system providing \((93 \pm 5)\) fs pulses at 1 kHz repetition rate. A fraction of the output beam is fed into an optical-parametric-amplifier (OPA) that can generate probe pulses tunable between 1140 and 2600 nm wavelength \[101\]. To allow for the investigation of dynamics extending over several nanoseconds, the probe beam makes two round trips over a 1.3 m long double-pass delay as shown in figure 5.1. The latter consists of a polarizing beam-splitter cube (PBS) that reflects the beam onto a hollow-cube retro-reflector on a motorized stage, which reflects the beam onto a \(0^\circ\)-mirror behind a quarter-wave plate \((\lambda/4\ WP)\). This configuration applies a polarization rotation of \(\pi/2\), allowing the retro-reflected beam to eventually transmit through the PBS.

![Experimental setup diagram](image)

**Figure 5.1:** The experimental setup used for the time-resolved SHG experiments in reflection and transmission geometry. The fundamental vertically polarized probe beam enters the setup from the top and arrives at the double pass delay. The probe beam polarization is controlled using a half-wave plate \((\lambda/2\ WP)\) in front of the focusing lens. Residual SHG light is filtered out with a longpass filter and the probe beam is combined with the 800 nm beam at a small angle using a dichroic mirror (DC). The weak NiO SHG emission in reflection geometry \(R_{2\omega}\) is collimated with a lens, filtered for the fundamental with a short-pass filter (IR), polarization selected with a Glan-laser polarizer (GL) and filtered again with another short-pass and an interferometric band-pass filter \((\pm 40\ nm)\) fit to the applied fundamental frequency. The SHG is then detected with either a PMT or an APD.

Pump and probe beams originate from two independent grating compressors and can be optimized (or detuned, see section 5.3.1) independently. The 800 nm pump and the OPA probe beams are combined at a relative angle of \(2^\circ\) using a dichroic mirror. The two beams are then delivered to the sample with typical pulse energies of 120 \(\mu J\) and 20 \(\mu J\), respectively, and filtered for second-harmonic light generated by the optical components, in particular coming from the quartz wave-plates. The setup also allows for the measurement of SHG in transmission geometry.
by rerouting the forward emitted SHG $T_{2\omega}$ into the detection.

As previous publications suggested a strong dependence on the pump intensity, we choose an excited area approximately 30 times larger than that of the probe beam. With $(1/e^2)$-beam diameters on the sample of 770 $\mu$m for the pump beam and 145 $\mu$m for the probe beam this leads to considerable pump and probe peak fluences of 50 and 240 mJ/cm$^2$, respectively. Note that the pumped area is much larger than the thickness of the NiO crystal.

After the sample, a series of polarizers, color and interference filters filter out both the fundamental probe and scattered 800 nm light, as well as third harmonic light and multi-photon fluorescence. The detection is carried out with either an uncooled Hamamatsu R-636-10 GaAs photomultiplier tube (PMT) with a large effective area of $3 \times 12$ mm$^2$ or a Hamamatsu C12702-11 avalanche photo-diode (APD) with a sensor area of 1 mm$^2$.

### 5.3 Reflection geometry measurements

Using a probe beam wavelength of 1200 nm and detecting the SHG light in reflection geometry, we are able to reproduce the SHG response after optical excitation as previously reported [38, 37, 39] in the 36 $\mu$m thick sample that shows evenly distributed small domains, as well as in the 50 $\mu$m thick sample showing domain sizes of between 100 and 500 $\mu$m as described in section 1.1.

As shown in figure 5.2, the SHG response features a drop of 14% followed by a 55 GHz oscillation, showing an amplitude of about 10% and a decay time exceeding 250 ps. In addition, there is a weak indication for a feature slightly rising above the noise floor at 24 GHz, which may be related to the observation of a broad feature at 28 GHz in reference [38]. All measurements are carried out at the probe polarization that yields maximal detected signal. A study of the probe as well as pump polarization dependence of the time-resolved signal is shown in appendix C.

#### 5.3.1 Excitation density and pulse-length dependence

A careful study of the observed oscillation amplitude on excitation density is shown in figure 5.3. Here, the excitation density is defined as the density of absorbed 800 nm photons right below the NiO surface

$$n_{exc} = \frac{\alpha}{A} \frac{E_{pu}}{1.55 \text{eV}},$$

where $\alpha$ is the intensity absorption coefficient of the pump beam, $E_{pu}$ gives its pulse energy and $A$ is its FWHM area. The above equation is an approximation, in reality, the internal reflections in the slab crystal will contribute to this value. However, we assume this definition to be equivalent to the one used in references [38, 37, 28] which allows for comparison.

The different data points shown in figure 5.3 have been acquired under the same experimental conditions in a single run over 3 days, where the two lowest excitation density data points alone correspond to more than 24 hours of uninterrupted data acquisition. The amplitude of
Figure 5.2: The lower panel shows the time-resolved relative change in SHG in reflection geometry for a fundamental wavelength of 1200 nm in the 36 µm thick sample at room temperature. The upper panel shows the corresponding spectrum of the signal after $t = 0$ ps, subtraction of a fitted 3rd order polynomial and zero-padding. A prominent peak at 55 GHz can be observed.

the oscillations is extracted from the data by fitting a sinusoidal function to the period from 10 to 80 ps of all datasets. The phase is fit to the four measurements of largest excitation density and is then set as global phase for all measurements. Errors shown here correspond to the 95%-confidence interval of the fits. While the linear fit lies slightly outside these errorbars for half of the measurements, there is no indication of a threshold behavior. We assign the small discrepancies to a drift of the signal over the acquisition period in which the order of the measurements was randomized.

Another intriguing observation was made in reference [39] where measurements indicated an excitation pulse-length dependent threshold behavior of the 55 GHz oscillation (more details can be found in section 1.1). The threshold discussed in this publication was observed between 110 fs and 130 fs for the fluences applied. For a comparative study, we rely on a qualitative assessment of exciting dynamics of similar magnitude as in reference [39]. Here, an excitation density of $0.4 \times 10^{20}$ cm$^{-3}$ is used to achieve a relative modulation of oscillatory SHG amplitude of about 5%. To make up for the uncertainties we scan a wider range of pulse-lengths from 93 fs at optimal compression to 250 fs adding positive as well as negative dispersion. Our experimental setup offers to alter the pump compression independently from the OPA probe, see section 5.2.
5.3 Reflection geometry measurements

A fraction of the pump is sent to a commercial frequency-resolved optical gating measurement device (FROG) by MesaPhotonics\(^1\) in order to measure the pump pulse-length simultaneously to the NiO experiment \([102]\). The optical path of the pump beam only comprises of 3 transmissive components, a fused silica lens, an attenuation filter and a dichroic mirror made of fused silica, thus it adds negligible additional dispersion. Results of the pulse-length dependent measurements are shown in figure 5.4.

Despite measuring a much wider range than in reference \([39]\), the fast oscillations can be resolved for all applied pulse-lengths in figure 5.4 a). Although the fully compressed beam may present the strongest oscillatory modulation, we see no indication for any threshold behavior.

To further investigate the absence of the previously observed thresholds we measure the case of 180 fs excitation also for longer delays as shown in figure 5.4 b). In contrast to the previous findings in reference \([39]\), we observe the 55 GHz oscillation and a 1 GHz oscillation in the same measurement. Excitation gradient effects can only play a minor role as the pump diameter is 5 times larger than the probe beam, see section 5.2.

### 5.3.2 Probe wavelength dependence in reflection geometry

Takahara et al. previously noted the close resemblance between the frequencies observed in the SHG response to optical excitation and stimulated Brillouin scattering \([28]\). As discussed in section 3.3, a strong hint that the origin of the oscillations is connected to impulsive Brillouin

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\(^1\)MesaPhotonics / 1550 Pacheco Street / Santa Fe NM 87505 / USA
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Figure 5.4: a) Relative change of SHG in reflection geometry as a function of excitation pulse-length which is simultaneously measured using a FROG. Traces are displaced vertically for better visibility. The values are given in reconstructed FWHM pulse width. Pulse stretching was achieved by detuning the retro-reflector in the pump’s grating compressor adding linear chirp. The data shown here is compensated for the $t_0$-shifts due to this additional delay. Positive dispersion is indicated by (+). Around $t_0$ several outliers due to four-wave-mixing of reflections between fundamental and pump beam can be observed. b) Observation of two oscillation periods of 18 ps and 1 ns in the same measurement, corresponding to frequencies of 55 and 1 GHz, respectively. The measurement is acquired using 180 fs pulses.

scattering from coherent acoustic phonons is the observation of probe wavelength dependence. The necessity for resonance enhancement of SHG in NiO, as discussed in section 2.2.3, imposes some restrictions on the tunability of the fundamental frequency, nonetheless, figure 5.5 shows that over an accessible wavelength range between $\lambda = 1140$ and 1300 nm it is possible to acquire time-resolved data with sufficient signal-to-noise.

Our measurements show a remarkable dependence of the oscillatory frequency on the probe wavelength. Similar to stimulated Brillouin scattering, the observed frequencies in the pump-probe measurements increase with increasing probe frequency. This suggests that the frequencies of the oscillations are not an intrinsic property of the material, but arise instead from an interaction between material and the probe beam. These measurements are carried out at room temperature and repeated at 150 K using a cold nitrogen gas jet to test for temperature dependencies. The
5.3 Reflection geometry measurements

Figure 5.5: b) Relative change in SHG in reflection geometry for 3 different wavelengths in the 36 µm thick sample. A modified version of this figure has been published in reference [61]. Lines are shown to guide the eye and the measurement of \( \lambda = 1140 \) nm is scaled for better comparison. Its smaller modulation amplitude may be due to an increase in fluorescence background for shorter wavelengths. a) The Fourier transforms and their corresponding peaks are shown, together with the result for the simulated frequency \( \omega_+ \) given by equation 5.17 in section 5.5.1.

Data is shown in figure 5.6. The jet introduces some additional noise to the measurement due to fluctuations of air density and water vapor. Within the precision of our measurement, we do not, however, observe significant differences in the measured frequencies.

In addition to studying fluence, pulse-length and probe wavelength dependence, we investigate different NiO samples and observe considerable differences in the SHG yield. SHG from a 0.5 mm thick bulk crystal is undetectable, while 36 µm and 50 µm thick samples give observable yield in reflection geometry. As optical properties and the domain structure in NiO vary depending on their exact stoichiometry [30], this might be caused by differences in the annealing process, see section 1.1. It seems, however, probable that these differences reflect instead a thickness dependence, as the slab thicknesses are of the same order as the \( \omega \) and \( 2\omega \) absorption lengths of 23 µm and 35 µm (for 1200 nm and 600 nm), respectively. This would imply that the detected signal in reflection geometry consists largely of internally reflected SHG. For this reason, we also study collinearly generated SHG in a transmission geometry.
5.4 Transmission geometry measurements

The coherence length of anti- and collinear second-harmonic generation in NiO typically differ by two orders of magnitude around the resonant enhancement condition, thus anti-collinear SHG will in a slab crystal of thickness $d$ rarely dominate over the contributions from internal reflections, unless there is sufficient absorption so that $d \gg 1/\alpha_{\omega}$ and $d \gg 1/\alpha_{2\omega}$. For the NiO samples used in our measurements, this is clearly not fulfilled as their thicknesses of 36 and 50 µm are on the order of $1/\alpha_{\omega}$. From the observation of efficient SHG in transmission of both of these samples, we can conclude that the collinear process is the main source of SH light also in reflection geometry. For collinearly generated SHG it is, however, natural to observe emission in transmission geometry which is presented in this chapter.

5.4.1 Sample geometry dependence of the SHG response

Figure 5.7 shows the SHG response acquired in transmission geometry over a time interval of 25 ns after excitation for two different crystal slab thicknesses. Using 1200 nm as probe wavelength,
5.4 Transmission geometry measurements

Figure 5.7: SHG response to optical excitation in collinear geometry acquired at 1200 nm. The oscillations show a recovery in amplitude centered at 10.3 and 13.7 ns for the 36 and 50 µm sample, respectively. This is coincident with the observation of phase discontinuities at these times, that also occur at 5.15 and 6.85 ns. Pump-probe traces show similarity to every other time segment, while consecutive segments appear as mirrored (indicated by arrows). Notice that in the photo-excited 50 µm sample, the SHG intensity temporarily rises above the equilibrium value. Reprinted from reference [61].

The SHG shows pronounced oscillations with a frequency of about 1 GHz, as reported previously for some measurements performed in a reflection geometry [39]. No signs of oscillations in the 50 GHz range can be observed in our measurements. The SHG yield in this configuration is in fact up to two orders of magnitude larger than in the reflection geometry. As the refractive index for the second-harmonic \( n_{2\omega} \approx 2.4 \) implies a Fresnel reflectivity of 17% and the absorption length is comparable to the sample thickness for the frequencies considered here, this implies that the major part of observed SHG in reflection geometry is in fact due to internal reflection of the collinearly created second-harmonic light. Moreover, the data shown in figure 5.7 feature recurrences of the envelope amplitude as well as phase discontinuities that are especially remarkable in the 36 µm thick sample. The observation of these phase discontinuities suggests that the recovery of amplitudes is not caused by a beating as suggested in reference [39] but rather by a reflection.

There is a remarkable correlation between the crystal thickness and the observed recurrence times. The times at which the phase discontinuities occur correspond to integer multiples of a round trip time \( T_{rt} = 2d/v_g \) which we can solve for a phenomenological group velocity of \( v_g = (7.1 \pm 0.1) \) km/s.

5.4.2 Probe wavelength dependence in transmission geometry

In figure 5.8 we also investigated the dependence of the observed dynamics on probe wavelength in a transmission geometry in the 36 µm thick sample. A pronounced dependence of the oscillatory frequency and phase on probe wavelength can be observed over a wavelength range between 1140 and 1400 nm. Figure 5.8 a) shows frequencies estimated from the Fourier transform based on the
Figure 5.8: b) SHG response to optical excitation in transmission geometry for various probe wavelengths in the accessible wavelength range. A common feature of all traces is a time inversion symmetry with respect to $t = 5.15 \text{ ns}$ indicated by a broken line. A strong frequency dependence of the induced oscillations is observed. a) The maximum positions of their Fourier transforms over the first 5.15 ns are shown together with the resulting frequencies based on the simulation and following equation 5.17. A modified version of the figure can be found in reference [61].

first 5.15 ns after excitation. Phase discontinuities appear for each wavelength at 5.15 ns, after which the dynamics display mirror-symmetric behavior that manifests as an apparent reversal of the direction of the time axis.

A general remark concerning the overall magnitude of the SHG signal is advised. Although the data shown in figure 5.5, 5.6, 5.7 and 5.8 are taken at fluences between 40 and 50 mJ/cm$^2$, there are large discrepancies in their modulation amplitudes. These amplitudes vary depending on the position on the sample. A repetition of the reflection measurements shown in figure 5.5 in the same experimental configuration as the transmission measurements in figure 5.8 yields the same frequencies and phases but with a modulation amplitude that is almost one order of magnitude smaller. We therefore regard the overall scaling of the modulation amplitude as poorly reproducible, and it may be strongly influenced by small changes in alignment or local sample properties such as surface contamination.
5.5 Modeling the SHG response to optical excitation of a semi-transparent slab crystal

In the experiments shown above in section 5.3 and 5.4 we made the following observations:

• The modulation amplitude of the SHG response shows linear dependence on excitation density - no indication of threshold behavior could be observed.

• We did not observe a dependence on excitation pulse-length.

• Both frequency components in the SHG response depend on probe wavelength.

• The static and time-dependent response depend on crystal dimensions.

Taken together, these observations are strong evidence that coherent acoustic phonons are a possible origin of the observed oscillations in the SHG. In particular the close resemblance of the fast oscillation frequencies and stimulated Brillouin frequencies from equation 3.6 and considering that the phenomenological group velocity of \( v_g = (7.1 \pm 0.1) \text{ km/s} \), that was derived from the observation of phase discontinuities in section 5.4.1, is in good agreement with the sound velocity in NiO found in ultrasound measurements [103].

Interestingly, to our knowledge, no derivation of the modulation of SHG by strain in spatially confined media has been given to this day. We therefore use this section to introduce a general method to simulate such responses and apply it to the case of NiO. In chapter 3 we discussed strain generation by the most frequent case of acoustic phonon generation, thermoelastic coupling. For NiO it is reasonable to assume that this coupling is going to be at least one of the major contributions to strain generation since the material is absorbing at 800 nm and in the experiments fluences of up to 50 mJ/cm\(^2\) were applied. We can hence calculate the absolute strain profile using equation 3.2 and literature values for NiO given in table 5.1.

<table>
<thead>
<tr>
<th>( \rho ) [g cm(^{-3})]</th>
<th>( v_s ) [m s(^{-1})]</th>
<th>K [GPa]</th>
<th>( \beta ) [10(^{-5}) K(^{-1})]</th>
<th>( C_V ) [J cm(^{-3}) K(^{-1})]</th>
<th>( t_d ) [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.81[15]</td>
<td>7050</td>
<td>193.8[103]</td>
<td>4.2[104]</td>
<td>0.59[105]</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table 5.1: Elastic and thermal parameters of NiO used to calculate strain in the simulation. The bulk modulus \( K \) is based on ultrasound measurements on a crystal in (111) surface orientation [103]. The parameter \( t_d \) gives the diffusion time constant used in the simulation.

In chapter 3 we have already seen the simplified strain modulation of the linear susceptibility in equation 3.4

\[
\Delta \chi^{(1)}(z, t) = 2(n - i\kappa) \frac{\partial n}{\partial \eta_{33}} \bigg|_{\eta_{33}=0} \eta_{33}(z, t),
\]
where \( n \) and \( \kappa \) are the real and imaginary parts of NiO’s refractive index. For simplicity we also assume that the temperature changes have no direct effect on \( \chi \) which is a valid assumption as the induced temperature change only reaches up to 8 K for the maximum applied fluences and the heat capacity from table 5.1.

In a similar manner, we can also parameterize possible changes in the second-order susceptibility \( \chi^{(2)} \) with respect to changes in temperature and strain

\[
\Delta \chi^{(2)}(z, t) = \frac{\partial \chi^{(2)}(z, t)}{\partial T} \frac{\Delta T}{T=RT} \left( 1 - e^{-t/t_m} \right) e^{-t/t_d} + \frac{\partial \chi^{(2)}(z, t)}{\partial \eta_{33}} \eta_{33}(z, t),
\]

(5.2)

where RT indicates room temperature, \( t_m \) denotes the demagnetization time, which is in AFM compounds typically few ps [106], and \( t_d \) is the diffusion time constant which lies in the ns regime.

The second order susceptibility \( \chi^{(2)} = \chi^{(2)}_{\text{core}} \) is assumed to depend on the antiferromagnetic order parameter \( l \), which is related to magnetoelastic lattice distortions [40], see section 2.2. This in turn depends on the temperature, and Fiebig et al. [40] gave an expression for the temperature dependence

\[
\chi^{(2)}(T) \propto \left( 1 - T/T_N \right)^{2\beta},
\]

(5.3)

with critical exponent \( \beta = 0.33 \) [107]. The local temperature changes due to optical excitation in our experiment are on the order of several K at room temperature, which again justifies a linear expansion in \( \Delta T \).

A dependence of \( \chi^{(2)} \) on strain can arise from at least two physical origins. One possibility is a strain-induced change in the energies of the \((3d)^8\) states of Ni\(^{2+}\) that may alter the double-resonance condition of SHG in NiO. Another possibility is magnetoelastic effects that more directly change the sublattice magnetization \( l \). Both of these possibilities are at present beyond our abilities to quantify, and so we simply incorporate \( \partial \chi^{(2)}/\partial \eta_{33} \) as a parameter in our model. A schematic overview of the proposed mechanism is shown in figure 5.9.

5.5.1 Propagation matrix based calculation of SHG

For a full quantitative simulation of the time-dependent SHG in NiO, we have to deviate from the standard treatment of stimulated Brillouin scattering [86] due to the limited crystal size and the nonlinear nature of coupling between fields. Instead, we apply a two-step time-resolved propagation matrix calculation. This approach is suitable for our experimental conditions as nonlinear coupling is weak and the beams are not phase-matched in NiO, see section 2.2.4. In the first step the local fundamental fields inside the crystal are determined, while in a second step the emitted SHG is calculated based on the local source terms arising from these fields.

To implement temporal and spatial variations, the crystal volume is divided along the longitudinal direction in \( N \) slices of each a few nanometer thickness (well below the scale of optical wavelengths) whose optical properties are given by equation 3.4 and 5.2. Restricting the
5.5 Modeling the SHG response to optical excitation of a semi-transparent slab crystal

Figure 5.9: a) The optically induced strain in the weakly absorbing 36 \( \mu \text{m} \) thick NiO slab in real space at four different times. Nearly step-like strain discontinuities arise from both surfaces and propagate into the crystal at the speed of sound.

b) The proposed model allows for a local change of the refractive index and \( \chi^{(2)} \) as function of strain, here depicted at a time \( t_1 = 1.5 \) ns. Fundamental and SHG beams are hence subject to Brillouin scattering. Collinear phase mismatch \( \Delta k \) leads to spatial variations of the SHG intensity \( I'_2(\omega) \), here schematically depicted for the first collinear term, neglecting reflections. The major contributions to the observed dynamics arise from the strain induced perturbation of this collinearly generated second-harmonic and interference with the SHG from reflections of the fundamental field. Note that the propagation matrix method takes into account all possible reflections of fundamental light and SHG. Reprinted from reference [61].

Problem to one dimension is here permitted as the Rayleigh range is many times larger than the crystal thickness. Each slice with index \( m \) can then be treated as a source of SHG \( S_m \) due to the induced nonlinear polarization \( P_{m}^{\text{NL}} \)

\[
S_m = -\mu_0 \frac{\partial^2}{\partial t^2} P_{m}^{\text{NL}}, \\
P_{m}^{\text{NL}} = -i\chi^{(2)}_{eeem}(t)(E_{\omega,m}^+(t) + E_{\omega,m}^-(t))^2, \\
\tag{5.4}
\]

where \( \mu_0 \) is the vacuum permeability and \( \chi^{(2)}_{eeem} \) represents the magnetic dipole assisted nonlinear susceptibility according to equation 5.2. \( E_{\omega,m}^+/^- \) correspond to the right- and left-ward propagating
fundamental fields at slice $m$. The small value of the second order susceptibility $\chi^{(2)}$ allows us to describe the SHG process in the Born approximation in which the fundamental fields $E_\omega$ are independent of the SHG. This is the main requirement for this procedure to be applicable to acoustic perturbation of SHG. We can then apply the propagation matrix method to derive $E_{\omega/m}^+/-$ at each slice position and calculate the emitted second-harmonic fields as shown in the following.

Under the Born approximation we may use the propagation matrix approach \cite{90} to independently solve for the fundamental fields inside the crystal at slice $M$

\[
\begin{pmatrix}
E_{\omega}^+ \\
E_{\omega}^-
\end{pmatrix} = P_{M-1}(t) \begin{pmatrix}
E_{\omega,0}^+ \\
E_{\omega,0}^-
\end{pmatrix}.
\]  

(5.5)

Here, $P_{M-1}$ is a $2 \times 2$ matrix connecting the right- and leftward propagating fields at slice 0 with the fields at slice $M$. Fields at arbitrary slice positions can be derived by solving for the transmitted and reflected fields $E_{\omega,N+1}^+$ and $E_{\omega,0}^-$, using the boundary conditions $E_{\omega,0}^+ = E_0$ and $E_{\omega,N+1}^- = 0$. This can be achieved by using the result of the total propagation matrix $P_{M=N}$ and converting it to the scattering matrix of the slab crystal via

\[
S_N = \frac{1}{\delta} \begin{pmatrix}
\alpha \delta - \beta \gamma & \beta \\
-\gamma & 1
\end{pmatrix}
\quad \text{with} \quad P_N = \begin{pmatrix}
\alpha & \beta \\
\gamma & \delta
\end{pmatrix}.
\]  

(5.6)

We can then write the solution

\[
\begin{pmatrix}
E_{\omega,N+1}^+ \\
E_{\omega,0}^-
\end{pmatrix} = S_N \begin{pmatrix}
E_{\omega,0}^+ \\
E_{\omega,N+1}^-
\end{pmatrix},
\]  

(5.7)

and evaluate equation 5.5 to find the fundamental fields at every slice $M$.

Given that the lifetime of light inside the crystal is much shorter than $\lambda/v_s$, the time-dependent propagation matrices $P_M(t)$ can be calculated as

\[
P_M(t) = \prod_{m=M}^0 p_m(t),
\]  

(5.8)

where propagation through a single slice is given by

\[
p_m(t) = \frac{1}{1 - r} \begin{pmatrix}
1 & -r \\
-r & 1
\end{pmatrix} \begin{pmatrix}
e^{-\frac{i2\pi}{\lambda} n_m(t)} & 0 \\
0 & e^{\frac{i2\pi}{\lambda} n_m(t)}
\end{pmatrix},
\]  

(5.9)

with

\[
r = \frac{n_{m+1}(t) - n_m(t)}{n_{m+1}(t) + n_m(t)},
\]  

(5.10)

at normal incidence and where $n_m(t)$ corresponds to the time-dependent refractive index of
5.5 Modeling the SHG response to optical excitation of a semi-transparent slab crystal

slice \( m \), while \( \Delta \) represents the chosen slice thickness. Surface boundaries are included by setting \( n_0(t) = n_{N+1}(t) = 1 \).

The time-dependent solutions of \( E_{\omega,0}(t) \) correspond to the familiar results of stimulated Brillouin scattering of the fundamental beam, with the exception that we did not explicitly take into account the change in phase of the reflected fundamental light due to surface displacement. By knowing the fundamental field in time and space, it is then possible to calculate the emitted second-harmonic light by applying the propagation matrix approach to each slice as a source of SHG according to equation 5.4

\[
\begin{pmatrix}
E_{2\omega,N+1}^+ \\
E_{2\omega,N+1}^-
\end{pmatrix}
= 0 \prod_{m=N}^{0} P_{2\omega,m}(t)
\begin{pmatrix}
E_{2\omega,0}^+ \\
E_{2\omega,0}^-
\end{pmatrix}
+ \sum_{m=N}^{k+1} \prod_{m=N}^{k+1} P_{2\omega,m}(t)
\begin{pmatrix}
S_k \\
S_k
\end{pmatrix}.
\]

Equation 5.11 can be solved for the emitted SHG fields \( E_{2\omega,N+1}^+ \) and \( E_{2\omega,0}^- \) using the boundary condition \( E_{2\omega,N+1}^- = E_{2\omega,0}^+ = 0 \). With the definitions

\[
\begin{pmatrix}
A & B \\
C & D
\end{pmatrix}
= \prod_{m=N}^{0} P_{2\omega,m}(t),
\]

\[
\begin{pmatrix}
S^+ \\
S^-
\end{pmatrix}
= \sum_{k=1}^{N} \prod_{m=N}^{k+1} P_{2\omega,m}(t)
\begin{pmatrix}
S_k \\
S_k
\end{pmatrix},
\]

the solutions for SHG in transmission and reflection geometry are given by

\[
\begin{pmatrix}
E_{2\omega,N+1}^+ \\
E_{2\omega,0}^-
\end{pmatrix}
= \begin{pmatrix}
S^+ - \frac{B}{D} S^- \\
-\frac{1}{D} D S^-
\end{pmatrix}.
\]

The bandwidth of the ultrashort probe pulses can be taken into account by a weighted sum of the solutions \( |E_{2\omega,(-)^1/2}(\omega)|^2 \) over the fundamental light spectra. Strong etalon effects will arise in semi-transparent samples, thus fine spectral sampling may become necessary\(^2\).

Results of the simulation for transmitted and reflected intensities are shown in figure 5.11. On nanosecond timescales, the SHG in reflection geometry follows the behavior of the transmitted SHG, which reflects the fact that its main source is the collinear generation process and internal reflection, with additional contributions of the SHG arising from internally reflected fundamental light. The real part of the refractive index \( n(\omega) \) used in our simulations was obtained from a fit to the experimental data as discussed in appendix E and shown in figure 5.10. The remaining optical parameters employed in these calculations can be found in table E.1.

\(^2\)Time-domain simulations as shown in section 9.5 of part II intrinsically take these effects into account.
5.6 Discussion of the SHG results

According to our model, the dynamics in SHG are predominantly the result of the time-dependent second order polarization and light propagation inside the medium in the presence of coherent acoustic waves. By using the propagation matrix method the model takes into account multiple reflections of fundamental and second-harmonic fields as well as the strain waves inside the crystal. This is especially important as a major part of the SHG in the reflection geometry arises from the internal reflection from the interface on the opposite side of the crystal.

Although to obtain approximate quantitative accuracy the model includes many different effects, it is possible to gain some additional insight by considering in general the effect of strain waves on phase matching for a collinear or anti-collinear SHG process. In a uniform, non-absorbing medium, the output intensity in the first Born approximation is related to the effective length $L$ by

$$I_{2\omega} \propto \left| \int_0^L \chi^{(2)} \exp(i\Delta k z) dz \right|^2 = \frac{\chi^{(2)}_\Delta}{\Delta k} 4 \sin^2(\Delta k L/2),$$

where $\Delta k = 2k_\omega \pm k_{2\omega}$, with the sign depending on whether the fundamental and SHG beams are collinear or anti-collinear. Strain-induced modulation of the linear and nonlinear optical coefficients causes small, z-dependent changes in both $\Delta k$ and $\chi^{(2)}$. If we approximate a strain wave propagating through the crystal away from the front interface as a real-valued step-like discontinuity in both $\Delta k$ and $\chi^{(2)}$ that moves with the sound velocity $v_s$, we obtain

$$I_{2\omega} \propto \left| \int_0^{v_s t} (\chi^{(2)} + \delta \chi^{(2)}) \exp(i(\Delta k + \delta \Delta k) z) dz + \int_{v_s t}^L \chi^{(2)} \exp(i\Delta k z) dz \right|^2,$$

where we assume that beyond the discontinuity the optical constants are unperturbed, and before
5.6 Discussion of the SHG results

Figure 5.11: Simulation of SHG in the presence of optically induced propagating strain for a fluence of 50 mJ/cm² and a NiO crystal of 36 µm thickness. a) Relative change in transmitted SHG. Acoustic reflections occur every 5.15 ns and are marked as broken lines. The Fourier transform is shown in the insets for the relevant frequency domains. In transmission there are no significant contributions at higher frequencies (left inset). Large amplitude dynamics occur at lower frequencies around 1 GHz (right inset) where the solid line shows the curve given by $\omega_-$ in equation 5.17. b) Relative change in reflected SHG. A large amplitude modulation at frequencies around 50 GHz is observed. The left inset shows contributions at the frequency of Brillouin scattering of the fundamental $\omega_B = 2n\epsilon_0\omega/c$ and the curve given by $\omega_+$ of equation 5.17. These are shown as broken and solid lines, respectively. The low frequency oscillations given by $\omega_-$ in equation 5.17 are also present in reflection (right inset). Modified from reference [61].
the discontinuity the second-order susceptibility changes by $\delta \chi^{(2)}$ and the phase mismatch $\Delta k$ changes by $\delta \Delta k$. Evaluating this to first order in $\delta \chi^{(2)}$ and $\delta \Delta k$ yields

$$I_{2\omega} \propto \left| \frac{\chi^{(2)}}{\Delta k} \right|^2 \left[ 4 \sin^2 \frac{\Delta k L}{2} + 2 \left( \frac{\delta \chi^{(2)}}{\chi^{(2)}} - \frac{\delta \Delta k}{\Delta k} \right) \left( 2 \sin^2 \frac{\Delta k L}{2} + \cos(\Delta k(L - v_s t)) - \cos(\Delta k v_s t) \right) \right],$$

(5.16)

provided that for all measured times $t \ll 2\pi/\delta \Delta k v_s$. We see immediately from this expression that the intensity of the SHG is modulated in time with a frequency

$$\omega_{+/-} = \Delta k v_s = \text{Re}(2k_\omega \pm k_{2\omega})v_s,$$

(5.17)

where we explicitly take the real part of the expression for $\Delta k$ to extend our result to the more realistic case where there is a small imaginary component to both $k_\omega$ and $k_{2\omega}$. Notice the close similarity to the Brillouin scattering frequency of light at the second-harmonic frequency $\omega_B = \text{Re}(2k_{2\omega})v_s$, see equation 3.6.

The $\omega_-$ values from equation 5.17 correspond to the slow oscillations at frequencies near 1 GHz as shown in figure 5.7 and 5.8, where we show values for $\omega_-$ at various probe frequencies based on a four-parameter Sellmeier equation. The corresponding $n(\lambda)$ is shown in figure 5.10 and the parameters are given in table E.1. This parameterization is only a coarse approximation of the linear optical dispersion, since the absorption spectrum of NiO shows absorption lines in the observed spectral range that are not accounted for in this model [30]. Both the simulations and equation 5.16 predict that the onset phase of these oscillations should depend on the unperturbed value of $\Delta k$, which in turn depends sensitively on the probe wavelength. Different sample thicknesses $L$ also lead to different onset-phases for the same probe wavelength, as observed in figure 5.7. The simulation can also account for the temporary increase in absolute SHG above the equilibrium level observed in the same graph, since the strain modulation is under certain circumstances able to effectively improve the phase matching integral for higher outcoupling.

The $\omega_+$ values from equation 5.17 correspond to the fast oscillations observed in the reflection geometry. These values are plotted in the inset of the lower panel in figure 5.11 and match the measured data quite well. In order to match the magnitude of the oscillations seen in experiment, the simulations require a large magnitude of $\partial \chi^{(2)}/\partial \eta_{33}$, leading to local changes in $\chi^{(2)}(z)$ of several percent (see table E.1).

The physical origin behind this coupling is unclear, but may be found in the same magnetoelastic interaction responsible for the large temperature dependence of $\chi^{(2)}$ [40]. In principle, our observations could also be brought into agreement with a magnetoelastic or flexoelectric contribution to SHG due to $\partial \chi^{(2)}/\partial (\partial \eta_{33}/\partial z) \neq 0$ or higher orders [108]. The exact dependence on

---

[3] Using the values derived from the simulations, for collinear phase matching (appropriate for the 1 GHz oscillations in transmission geometry) $2\pi/\delta \Delta k v_s \approx 10^{-5}$, and for anti-collinear phase matching (appropriate for the 50 GHz oscillations in reflection geometry) $2\pi/\delta \Delta k v_s \approx 10^{-7}$. 

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5.6 Discussion of the SHG results

strain, however, is outside the scope of this work as the applied experimental techniques do not allow us to distinguish between different possible coupling mechanisms. Further insight could be obtained using static SHG imaging of strained crystals or by employing a strongly focused probe beam in time-resolved SHG in order to disentangle contributions arising from different depths inside the crystal.

The agreement between simulations and experimental data is not exact but they reproduce the observed frequencies, lead to effects of similar magnitude and give a quantitative explanation for the phase behavior of the oscillations. The relative magnitude of the dynamics in the reflection compared to the transmission geometry are in general somewhat underestimated. The experimental amplitudes are, however, also subject to uncertainties as they strongly depended on the exact position on the sample. We found the simulation results to be highly sensitive to small changes in the assumed linear optical properties. This sensitivity may account for some of these discrepancies. Furthermore, the large probe fluences used in these experiments far exceed the limit of small perturbation and will lead to back-action on internally reflected beams which is not taken into account.

As an alternative explanation for the observed effects, in principle a strain-induced modulation of \( n \) also leads to coherent Brillouin scattering of the second-harmonic light according to \( \omega_{\text{osc}} = 2k^2\omega_s \). For wavelengths closer to the band gap, the strain dependence of the refractive index \( \partial n / \partial \eta \) strongly increases [88], which in this case could lead to a pronounced visibility of Brillouin scattering at around 600 nm as compared to the fundamental light at 1200 nm. In the simulation, both \( \partial n / \partial \eta \neq 0 \) and \( \partial \chi^{(2)} / \partial \eta \neq 0 \) by themselves can lead to modulations at the observed frequencies and also to a small spectral contribution at the Brillouin scattering frequency of the fundamental beam, similar to the observations in Fe/AlGaAs heterostructures [89]. However, using our model, linear Brillouin scattering alone cannot explain the large magnitude of the observed modulation in SHG of up to 30% (see figure 5.5) as it would also lead to similarly strong modulations of the fundamental light, which was not observed. Furthermore, this mechanism cannot describe the observation of the low frequency oscillations.

As a final remark it might be surprising that despite the seemingly general nature of a strain induced change of the nonlinear susceptibility, the dynamic effects observed in NiO were not found in similar compounds such as CoO and KNiF\(_3\) which also rely on magnetic dipole assisted SHG. This may reflect a difference in the magnetoelectric interaction in these systems. We note, however, that in NiO these dynamics are strongly dependent on sample thickness, absorption and dispersion in \( \Delta k \). It may be that only a narrow set of experimental parameters leads to similar dynamics. As the SHG process in these compounds is highly restricted by resonance conditions, the range of these parameters is quite limited.
Part II

The ultrafast nonlinear THz response of low band gap semiconductors
Chapter 6

High-field carrier response in semiconductors

Before discussing our results concerning the development of broadband nonlinear THz-spectroscopy, we review high-field effects that are known to occur in low band gap semiconductors, which will in the following represent the testing ground for our investigations.

Much like insulators, semiconductors allow for the presence of high electric fields inside their bulk material. This is in contrast to metals whose large conductivity efficiently screens electric fields from propagation inside them. Still, at finite temperatures, semiconductors provide free carriers in the conduction and valence band that may freely follow strong fields and acquire considerably higher energies than possible inside a metal. This gained energy allows the carriers to explore remote parts of the band structure and may open up new channels of interactions that are forbidden to the equilibrium carriers by energy and momentum conservation and thus gives rise to nonlinearity of the field response. Ryder and Shockley already observed such behavior more than half a century ago in germanium and silicon [109, 110, 111]. At room temperature, they found deviations from Ohm’s law at fields as low as 1 kV/cm, see figure 6.1.

Interactions between carriers usually dominate over carrier energy transfer to the lattice, thus excess energy of e.g. conduction band electrons that gained energy in a high electric field will first establish thermal equilibrium in the carrier system and only then thermalize with the lattice. This can in some cases be described using a two-temperature model, where $T_c$ represents the carrier temperature and $T_L$ the one of the lattice. When high fields are applied, $T_c$ rises above $T_L$ and this physical regime is therefore commonly referred to as hot carrier transport [112]. It may not come as a surprise that high fields above 10 kV/cm are quite common in field effect transistors and in every day electronics one can find temperatures of $T_c > 1500$ K, thus

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Title-page part II: Electron microscopy image of a curled-up thin sheet of InSb generated by focused-ion-beam milling, courtesy of ETH ScopeM.
Chapter 6: High-field carrier response in semiconductors

Figure 6.1: The current density in $n$-type germanium as a function of electric field measured by application of 100-1000 ns long transient field pulses. Reprinted from E. Ryder [111] with permission from the American Physical Society.

hot carrier effects are of great interest for applications [112].

The most successful theory of high-field transport in semiconductors is based on solving the semi-classical Boltzmann transport equation. The statistical description of carrier population in momentum $\mathbf{k}$, position $\mathbf{r}$ and time $t$ can take into account the full single particle band structure as well as scattering rates based on arbitrary order of perturbation theory. Implementation using a Monte Carlo method allows for integration over the full phase-space volume of interacting bands in $\mathbf{k}$ and $\mathbf{r}$ and can describe all known hot electron effects including real-space transfer [112]. This is a complex computational task since all scattering rates have to be known beforehand.

Moreover, the semi-classical Boltzmann equation is valid only when conforming to the assumptions of weakly interacting particles and, even more stringent, when fulfilling the assumption of negligible quantum coherence over the relevant distances and times observed in the experiment. The latter criterion necessitates dephasing of the carrier wave-packet, that occurs on timescales of $\Delta t = \frac{\hbar}{\Delta E}$, which is basically stating the Fourier relation between time and energy and where $\Delta E$ is the energy difference to the nearest band, that is typically given by the band gap [113, 114, 115]. In bulk GaAs with a band gap of about 1.4 eV, this dephasing time is 3 fs, while for InSb, with $\Delta E = 0.17$ eV at room temperature, this corresponds to 24 fs. Below $\Delta t$ carriers are thought to act as truly free particles of mass $m_e$ [113]. Considering dynamics on these timescales and below then requires a fully quantum mechanical treatment and the semi-classical picture does no longer suffice. E.g. interband tunneling from the valence to the conduction band requires an appropriate treatment and will be discussed in section 6.1.

Nonetheless, the semi-classical model leads to several more abundant high-field effects that are worth a closer look. An example is given in section 6.2 which will discuss the ballistic transport (in contrast to drift-like motion) that can be sustained on short timescales until scattering phenomena gain dominance. Section 6.3 then discusses an important semi-classical scattering
6.1 Interband tunneling

Electric field induced interband tunneling has been described by Clarence Zener already in 1934 when he investigated the electric breakdown in insulators [117]. The theory of transfer from the valence bands to the conduction band has later been refined by Kane who gives the tunneling rate as [118]

\[
r = \frac{e^2 F^2 \sqrt{m_r/E_g}}{18\pi\hbar^2} \exp \left( -\frac{\pi \sqrt{m_r E_g^3}}{2\hbar e F} \right),
\]

where \( m_r \) is the reduced mass of the electron-hole pair in the two bands, the gap energy is \( E_g \) and \( F \) corresponds to the applied field. The underlying mechanism can be understood by the field distorting the electronic wave-functions such that there is overlap between valence and conduction band. In real space, this can be depicted as in figure 6.2 b). The phenomenon has also been coined Zener tunneling and finds wide application in Zener diodes that are used as voltage references and to stabilize power supplies.

Several recent publications reported observation of carrier tunneling in GaAs in the ultrafast regime [119, 120, 116]. As this semiconductor has a rather high direct band gap of 1.4 eV the field of 300 kV/cm that was used in reference [119] were found to be too small to lead to significant pure Zener tunneling according to equation 6.1. Kuehn et al. therefore suggested a decoherence assisted tunneling process based on the work of Kazarinov and Suris [121] on
tunneling in superlattices, i.e. in quantum cascade structures, and gave the following resonance condition for tunneling from the valence to the conduction band \[119\]

\[ r \propto \tau \left( 1 + (\Delta \omega \tau)^2 \right), \tag{6.2} \]

where \( \tau \) gives the decoherence time and \( \Delta \omega \) the detuning from the interband resonance at \( E_g \).

For excitation far below the band gap \( \Delta \omega = E_g / \hbar \), dephasing rates comparable to the interband transition frequency could then actually be beneficial for the tunneling rate. Here, dephasing is dependent not only on the scattering rates but also on loss of spatial overlap of the electronic wave-packet that in the applied field has contributions of valence and conduction band character that get further separated \[119\].

Hirori et al. related their observation of carrier tunneling in GaAs at fields of 1 MV/cm rather to field ionization of shallow donor-impurities that possess binding energies far smaller than the band gap \[120\]. We may add that Si-donors were also present in the study by Kuehn et al. \[119\]. Subsequently, Lange et al. applied atomically strong fields, i.e. fields high enough to lead to Zener tunneling according to equation 6.1, to GaAs using a meta-material resonance and likely observed actual ultrafast interband tunneling \[116\].

Kane originally applied formula 6.1 to the low band gap semiconductor InSb, but it turns out that at finite temperatures other effects dominate in the bulk material that we will discuss in the following sections.

6.2 Ballistic transport

Diffusive drift motion represents the steady state solution of the transport equation when a static electric field is applied. In this case, the average rate of momentum gain in the electric field and loss due to the scattering rate \( 1/\tau_{tot} \) balance each other. The scattering rate is given by the sum of all scattering transition rates (not considering effects arising from Pauli exclusion)

\[ \frac{1}{\tau_{tot}} = \sum_{k'} S(k, k'). \tag{6.3} \]

As shown in figure 6.3 the scattering of carriers with longitudinal optical phonons (LO) dominates the scattering rate for energies well exceeding the optical phonon energy \( h \omega_{LO} \). For InAs the scattering rate peaks around \( (100 \text{ fs})^{-1} \) which is about half of the value in GaAs and decreases for higher energies. In reality, the scattering rate further increases due to intervalley scattering at energies above the pseudo-gaps separating the electrons from the conduction band minimum at the \( \Gamma \)-point to the \( L \), \( X \) and \( K \)-valley minima and due to impact ionization for electron energies above the band gap, which will be discussed in section 6.3 and 6.5, respectively.

In contrast to this steady state regime, we can consider the case of an electric field that is
suddenly turned on. For times shorter than $\tau_{\text{tot}}$, we do not yet expect scattering to occur and the carriers of charge $q$ are accelerated freely, i.e. ballistically, in the electric field $F$ yielding for the change in quasi-momentum of the crystal carrier $[123, 124]$

$$\hbar \frac{dk}{dt} = -qF. \quad (6.4)$$

At negligible starting temperature, all carriers then move in the same direction and form a strong current that is reduced by the onset of scattering with phonons and electrons in the valence band that randomizes the direction of the carrier velocity. In the semi-classical limit, equation 6.4 can be solved for the quasi-momentum $k$ and the carrier velocity can be derived from the group velocity of a carrier in the band dispersion using $[112, 125]$

$$v = \frac{1}{\hbar} \nabla_k E(k). \quad (6.5)$$

The transition from this ballistic regime to the common diffusive transport is depicted in figure 6.4. Kuehn et al. suggested that after ultrafast THz excitation the electronic wave-packet only slowly increases its localization which reduces the scattering rate $1/\tau_{\text{tot}}$ and increases the range of validity of ballistic transport as compared to the Boltzmann transport equation $[126]$. Equation 6.5 can also account for the often complex curvature of the band structure which can

**Figure 6.3:** Scattering rates in InAs (left) and GaAs (right) due to optical phonon and impurity scattering as function of carrier energy. Reprinted from Krishnamurthy et al. $[122]$ with permission from the American Institute of Physics.
lead to effects beyond the effective mass approximation and average carrier energies exceeding 1 eV can be acquired [125]. We will later see that such a macroscopic ballistic motion of carriers can be a suitable model for the description of the response of low band gap semiconductors to few-cycle THz excitation, see section 9.5.

### 6.3 Intervalley scattering

We have seen that carriers in the conduction band may gain considerable energy when subjected to high electric fields. In a semiconductor like GaAs, whose band structure is shown in figure 6.5, electrons in the $\Gamma$-valley may easily acquire energies exceeding the 0.3 eV and 0.5 eV pseudo-gaps, i.e. the energy gaps separating the conduction band minimum at the $\Gamma$-point and the local minima at the $L$ or $X$-point. The transition between the valleys then only requires a scattering event with an optical or acoustic phonon that provides the considerable difference in momentum $\Delta k_{\Gamma \rightarrow L,X}$. The electrons scattered into the $L$-valley will find a significantly different band curvature and thus carrier mobility and an experiment will observe a negative differential resistivity around a critical field value [127]. The phenomenon is known since 50 years and has found wide application in transferred electron devices also coined Gunn diodes that are frequently used in microwave electronics [128, 129]. It is also known to occur in germanium and in InAs, which will be of interest in our experiments in section 9.4.1.

Figure 6.4: Schematic of the average carrier velocity developing in time, assuming that a strong step-function like electric field is applied starting at $t = 0$. In Si the overshoot peak in the transition from ballistic to diffusive drift motion forms on the time scale of hundreds of femtoseconds and can be up to a factor of 10 higher than in the steady state. The arrows indicate the distribution of carrier velocity directions, which is small in the beginning but increases due to scattering until the diffusive steady state solution is reached. Reprinted from K. Hess [112], copyright (1999) by John Wiley & Sons.
6.4 Bloch oscillations

When applying electric fields comparable to the peak fields inside atoms well above 1 MV/cm to semiconductors, carriers that follow the applied field according to equations 6.4 and 6.5 may be swept over the whole Brillouin zone before they get scattered by impurities or phonons. As the Bloch carriers are quasi-particles in the crystal potential, they witness the periodicity of the band at the zone edge, where they undergo Bragg reflection. This leads to charge oscillations in reciprocal as well as real space which were coined Bloch oscillations. A schematic depiction of the process is shown in figure 6.6.

The discontinuous nature of the described motion in a symmetry broken medium leads to harmonic-generation of arbitrary order which was observed in the semiconductor gallium-selenide (GaSe) by Schubert et al. [131]. It needs to be mentioned that GaSe has a band gap of about 2 eV which is hardly populated before the arrival of the high-field pulse, thus the driving THz pulse also accounts for the off-resonant excitation of interband polarization according to the mechanism described in section 6.1 in addition to the subsequent intraband acceleration described here [131]. The material was also chosen in order to avoid an incoherent effect that is likely to happen in low band gap semiconductors and is described in the following section 6.5.
6.5 Impact ionization

Impact ionization is electron-hole pair creation due to scattering by energetic carriers. In order to abide energy conservation, these carriers have to have energies in excess of the band gap energy. In addition, carrier multiplication necessitates pre-existing free carriers but may also be facilitated by a prior valence-to-conduction band tunneling process, see section 6.1. In InSb, with its band gap between 0.17 and 0.24 eV, the conduction band is partially populated already at low temperatures and the lowest static field necessary to observe the onset of impact ionization was found to be as low as 250 V/cm at a temperature of 77 K [132]. Again, the balance between field acceleration and scattering processes play a crucial role in order to give rise to high energy carriers. A schematic depiction of the process is given in figure 6.7.

Hoffmann et al. observed impact ionization in time-resolved transmission through InSb after application of single cycle THz fields of 100 kV/cm at 80 K [133]. They observed a conductivity change by application of another THz probe pulse that showed a rise time of 18 ps, as shown in figure 6.8. This rise can be identified with the energy relaxation time that depends on the applied frequency and field [134]. Kobayashi derived expressions for the energy relaxation rate based on a temperature rate-equation and found for application of 100 V/cm microwave fields relaxation times on the order of 2 ps. While Hoffmann et al. were able to apply this estimate to get meaningful results for their experimental situation [133], thermal equilibrium is not fully established on these timescales [125, 135] and a Monte Carlo calculation of the full transport equation, as discussed in the beginning of this chapter, may be more appropriate [136, 112, 135].
6.5 Impact ionization

Figure 6.7: Schematic impact ionization process in InSb. An electron is accelerated in an electric field from the conduction band minimum to position (1) (blue). Subsequently, it scatters with an electron in the heavy hole valence band (2). The depicted scattering process conserves energy and momentum by scattering the conduction band electron to (1') (orange) and promotes the valence band electron to the conduction band to (2') (red).

Figure 6.8: Time-dependent increase in absorption between 0.2-1.6 THz due to 100 kV/cm THz field-driven impact ionization in InSb at 80 K. The measurement was carried out in transmission through a 450 μm thick wafer using THz pulses generated in LiNbO₃. Reprinted from Hoffmann et al. [133] with permission from the American Physical Society.
Chapter 7

Indium antimonide and indium arsenide

Indium antimonide (InSb) and indium arsenide (InAs) were first characterized by Heinrich Welker and Herbert Weiss in the early 1950s at the Siemens research laboratories at Erlangen [137, 138, 139]. In their search for new semiconductors that can be applied for fast electronics they had the idea of mimicking the known semiconductors Si, Ge and Sn of the IVth elemental period by combining III and V period elements [137]. In InSb they found a semiconductor with particularly small direct band gap of 170 meV at room temperature that until today has one of the highest known electron mobilities\(^1\) and mean free-paths on the order of 1 \(\mu\)m [141]. InAs has very similar properties but a two times higher band gap of 340 meV.

Both materials have been widely used as infrared (IR) detectors, that mainly profit from their low band gaps. Their high electron mobility makes them superior to Si for fast electronics applications such as mobile communication and multi-GHz transistor technology. InSb based fabrication of transistors reaching up to 300 GHz has been claimed recently [142].

Their low scattering rates makes these materials also interesting for quantum research in general and offers an interesting playground in particular for ultrafast high-field science, THz applications and gives rise to many of the effects discussed in chapter 6.

7.1 Lattice structure

The III-V semiconductors form cubic lattices of zinblende structure, i.e. the two element species form interpenetrating face-centered cubic lattices. Unlike, the rock-salt structure of the paramagnetic NiO (section 1.1), in the zinblende structure each atom has four nearest neighbors of opposite species. It thus has the same configuration as the period IV elements that form the diamond lattice structure\(^2\), but the degeneracy between the two sublattices is lifted by the two

\(^{1}\text{InSb possesses the second highest mobility right after carbon-nanotubes [140].}\)

\(^{2}\text{InSb even possesses the same lattice constant as the grey }\alpha\text{-tin [143] that lies in the periodic table between elemental indium and antimonide.}\)
atomic species. This results in point symmetry 43m which is non-centrosymmetric and therefore allows for second-order processes in the electric dipole approximation as discussed in section 2.2. Its tensor symmetries up to 4th rank are shown in table 2.4.

The cubic symmetry consisting of two atomic species leads to a relatively simple phonon-dispersion diagram of 6 phonon bands in which the degeneracy of the transverse modes is only lifted along the K-direction (110) as shown in figure 7.1. The cubic lattice constants of InAs and InSb are 6.06 Å and 6.48 Å [144] with sound velocities of 4410 m/s and 3900 m/s, respectively [145, 146]. The ionic binding of the two atomic species leads to a strong dipole moment making the optical phonon modes infrared active. Optical and THz experiments only allow for direct access to the Γ-point, where the transverse and longitudinal optical modes can be found close to the frequencies observed in neutron diffraction νTO = 6.6 and 5.45 THz, as well as νLO = 7.25 and 5.9 THz, for InAs and InSb, respectively [147, 148].

![Image of InAs and InSb structure](image)

**Figure 7.1:** a) A schematic depiction of the zinblende structure of InAs and InSb showing the tetragonal configuration of each ion [149]. The calculated phonon dispersion diagram for InAs (b) and InSb (c). Reprinted from Lindsay et al. [144] with permission from the American Physical Society. Red and black curves differ by 1% in assumed lattice constant, with the larger being represented by the black line. The black circles and squares show neutron diffraction data from references [147, 148].
Additionally, two-phonon processes, where the limitation to the Γ-point is lifted by \( k_1 + k_2 \approx 0 \), were observed in far-infrared absorption [150, 151, 152, 153, 154, 155] and second-order Raman scattering [156] on InAs and InSb showing features at combination modes corresponding to critical points in the phonon-density of states throughout the Brillouin zone. The modes with strongest experimental evidence are listed in table 7.1. The effect is ascribed to electron-phonon coupling via the two-phonon deformation potential [157, 158].

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<td>TO(L) + LA(L)</td>
</tr>
<tr>
<td>10.8</td>
<td>300, 100</td>
<td>10.8</td>
<td>77, 300</td>
<td>2 TO(Γ)</td>
</tr>
</tbody>
</table>

Table 7.1: Two-phonon modes in InSb observed in the far-infrared by Abdullah et al. [154], Oetjen et al. [151] and Koteles et al. [152] as well as by Kiefer et al. using Raman scattering [156]. Mode assignment according to Abdullah and Koteles.

7.2 Electronic band structure

As shown in chapter 6, a semiconductor’s response to high fields is predominantly defined by its carrier dynamics and therefore by its electronic band structure. The latter describes single electron states, and hence, interaction with other carriers, the lattice and its dynamics can only be included on average or using a perturbative treatment, where interaction between carriers and phonons can be accounted for using deformation potentials [159]. Ngai and Johnson [157] applied this treatment to InSb using two-phonon deformation potentials and found that they lead to two-phonon absorption as described in the previous section.

Calculated band structures for InAs and InSb based on a sophisticated Heyd-Scuseria-Enzerhof implementation of density functional theory [160] are shown in figure 7.2. Both band structures show strong similarity. Spin-orbit splitting leads to a strong separation between the light and heavy-hole valence bands and a split-off band\(^3\). The InSb gap energies are reduced by about a factor of two compared to InAs. Detailed values are given in table 7.2.

In strong electric fields, the small band gap of InSb favors carrier multiplication due to impact ionization (section 6.5). In both materials carriers suffer from a more than ten-fold increase in effective mass after being scattered to the L-valley. Intervalley scattering (section 6.3) therefore

\(^3\)Additionally, InSb shows pronounced sub-band spin-splitting of the conduction and light-hole bands that are related to the lack of inversion symmetry in the zincblende structure [160].
Table 7.2: Experimental conduction and valence band parameters of InAs and InSb as tabulated in reference [160]. All effective band masses $m^*$ are given in units of electron mass [$m_e$]. Light-hole and heavy-hole masses are indicated with $lh$ and $hh$, respectively. The pseudo-gap gives the energy separating the conduction band minimum at $\Gamma$ and the $L$-valley.

leads to a strong decrease in conductivity. Although, the light holes show similar band masses as the conduction band carriers, they are hardly populated due to the presence of the heavy-hole band and do not significantly contribute to the conduction. Kane expected Zener-tunneling (section 6.1) to occur in these materials due to their low gap energies [118], however, this has not yet been observed experimentally at fields up to 100 kV/cm and impact ionization and intervalley scattering appear to dominate the response in this regime [125, 133, 163, 164].

![Figure 7.2: Calculated electronic band structure of InAs (a) and InSb (b). The red lines indicate the spin-split conduction band, while heavy ($hh$) and light ($lh$) hole bands are shown in blue. The split-off band (SO) is shown in orange and higher electronic bands are depicted in black. Reprinted from Kim et al. [160] with permission from the American Physical Society.](image)

**7.3 Phonon-plasmon coupled modes**

The small band gaps of InAs and InSb lead at room temperature to significant thermal carrier populations of the conduction band that can follow externally applied fields and contribute to the
polarization of the material in the DC and THz range. The semiclassical Drude-Sommerfeld model is, despite its simplicity, the most commonly used description of conductivity in semiconductors. Here, the carrier contribution to a material’s electric field response can be treated by just two characteristic quantities, the plasma frequency $\Omega_p$ and scattering frequency $\gamma_p$. In this model, the plasma frequency is related to intrinsic parameters of the material through

$$\Omega_p = \sqrt{\frac{e^2 N_e}{\epsilon_0 \epsilon_\infty m^*}},$$

(7.1)

where $e$ is the electron’s charge, $\epsilon_0$ the vacuum permittivity, the effective high frequency dielectric function $\epsilon_\infty$ and $m^*$ represents the effective mass of the carrier in the band. For simplicity we here give the expressions for electrons in the conduction band, but all equations also hold true for holes in the valence band.

In the III-V semiconductors relative motion between anions and cations is associated with an electric dipole moment making these phonon modes infrared active and leading to an additional Lorentz oscillator contribution to the transverse dielectric function. For the combined Drude-Lorentz system, a common description is given by [166]

$$\epsilon = \epsilon_\infty \left(1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2} - \frac{\Omega_p^2}{\omega^2 + i\gamma_p \omega}\right),$$

(7.2)

where $\omega_{LO}$ and $\omega_{TO}$ give the longitudinal and transverse phonon frequencies in the center of the Brillouin zone, $\gamma_p$ gives the corresponding damping, $\Omega_p$ gives the plasma frequency of the Drude carriers with damping $\gamma_p$ and $\epsilon_\infty$ represents the high frequency dielectric function that is determined by the higher lying electronic transitions.

Equation 7.2 is often used to fit material parameters to optical transmission or reflection data. Without damping of the plasma oscillations and not considering the phonon mode, equation 7.2 would lead to a negative dielectric function for frequencies below the plasma-edge frequency $\Omega_p/\sqrt{\epsilon_\infty}$. In this range the material behaves as a metal.

The dielectric response can also be represented by its action on a longitudinal electric potential that gets screened by the dielectric function according to $\phi'(k,\omega) = \phi(k,\omega)/\epsilon(k,\omega)$ [167]. Experimentally this can be realized e.g. in Electron Energy Loss Spectroscopy (EELS) by passing charges through dielectric material. This coined the term loss function that is also meaningful in optics, where $k \approx 0$, and where it is defined as

$$L(\omega) = -\text{Im} \left[ \frac{1}{\epsilon(\omega)} \right] = \frac{\epsilon''(\omega)}{\epsilon'^2(\omega) + \epsilon''^2(\omega)}.$$

(7.3)

The loss function $L$ shows strong features where the magnitudes of the components of $\epsilon(\omega)$ and

---

4See for example reference [165] for a detailed description of the model.

5$\epsilon_\infty^*$ corresponds to the interband and vacuum contribution to the permittivity, but for low plasma frequencies also accounts for phonons.
thus the screening of a longitudinal potential is small. Without damping, divergences appear at frequencies where $\epsilon(\omega) = 0$ and therefore lead to divergences at the plasma-edge frequency and the longitudinal phonon frequency for systems described by equation 7.2. For plasma frequencies in the vicinity of the phonon modes, these zero-crossings shift as the modes start to influence each other forming the coupled phonon-plasmon modes $L_-$ and $L_+$. This leads to the characteristic phenomenon of avoided crossing shown in Figure 7.3.

Figure 7.3: Coupled plasmon-phonon modes in n-GaAs. By increasing the donor concentration and thus $N_e$, the plasma frequency approximately increases $\propto \sqrt{N_e}$. Interaction of the longitudinal plasmon and phonon modes leads to avoided crossing following the peaks of the loss function in equation 7.3. Reprinted from Chandrasekhar et al. [168] with permission from the American Physical Society.

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$^6$Corrections due to non-parabolicity of the conduction band for high carrier concentrations are also included in the graph.
Chapter 8

Nonlinear THz-spectroscopy

The THz-range can be loosely defined as the electromagnetic spectrum between 0.1 and 30 THz which extends into the range of what historically used to be called the far infrared. The definition is mostly of a technical nature, as it lies between the accessible range of fast electronics and the realm of infrared optics and lasers. Spectroscopy in this range has, however, been possible since the dawn of modern physics and chemistry in the late 19th century when spectrometers made from gratings or rock salt prisms as well as thermopile or bolometer detectors were available [169]. Section 1.2 for example shows spectra acquired using such techniques. Nonetheless, until the end of the 20th century, light sources emitting radiation in this region were commonly based on broadband thermal emission by heated material such as silicon carbide or mercury discharge lamps [170]. These methods therefore only provide very limited spectral intensity compared to the overall output and a reflection or transmission signal at these frequencies is on top of the strong thermal background at room temperature ($300 \text{K} \frac{k_B}{h} \approx 6 \text{ THz}$) difficult to detect with high sensitivity.

Still, spectroscopy in the THz range has been an important tool of experimental solid-state physics, as many elementary excitations are located there. Examples include infrared active phonons, magnetic and antiferromagnetic resonances as well as collective excitations associated with broken symmetry ground states [53]. But the deficiency of previous THz sources limited experiments to the mere observation of features in this regime while other experimental parameters such as temperature, pressure or doping were altered. This is where new intense THz sources can provide significant insight. Strong THz fields can resonantly excite lattice motion or quasiparticle population with unprecedented amplitude and specificity. In particular, nonlinear THz-spectroscopy in the time domain offers to study coupling of several degrees of freedom and could allow to clarify the causal link of observations that may otherwise appear coincidental.

The recent development of ultrafast laser systems and light conversion techniques enables the generation of few-cycle THz pulses of extreme electric fields on the order of MV/cm. Such fields are comparable to atomic fields imposed on valence band carriers, meaning that for example in InAs a field of $E_a \approx 6 \text{ MV/cm}$ shifts the valence band electron on the same energetic level as the
conduction band electron of a neighboring atom. Thus, fields of this magnitude will be suitable to drive most materials into a regime far from equilibrium.

The following section 8.1 will describe two mechanisms of high-field THz generation that have been used in this work. We will later discuss a broadband detection technique that is able to measure the electric fields in a phase-resolved manner in section 8.2.2 and are going to describe how a field measurement can be used to observe the complex refractive index of a material in section 8.3. In section 8.4 the nonlinear THz-spectroscopy setup is described where we employed an asymmetric two-pulse 2D measurement scheme.

## 8.1 Generation of high-field THz pulses

Numerous different methods of THz generation are presently known and here we intend to only discuss the most relevant ones for our experiments in more detail. A comprehensive overview over the various techniques and their abilities is given in reference [53]. For the generation of the very highest MV/cm electric fields in the THz range there are only two basic classes of techniques available. One is the accelerator based generation of short, high energy electron bunches that emit THz radiation either by transmitting through a suitably designed undulator or via transition radiation emitted when entering and exiting a thin foil [171, 172, 173]. These techniques are highly scalable and achieve fields beyond 100 MV/cm, while undulator designs are in addition also tunable. Unfortunately, experiments are limited to large scale facilities and are often cumbersome to combine with other ultrafast techniques as synchronization to other light sources such as ultrafast lasers is not easily achieved.

The second class of techniques is by far more abundant and is based on the amplified mode-locked laser that provides pulses of optical light down to 10 fs with a peak power on the order of 0.1 TW. THz radiation can be generated from these pulses by nonlinear conversion in non-centrosymmetric crystals such as optical rectification (OR) and difference frequency generation (DFG), or by generation of ultrafast currents on the timescale of the optical pulse. The latter phenomenon is the main mechanism in biased photoconductive switches [174], inverse spin-Hall effect emitters [175] and THz generation in two-color gas plasmas [176].

OR and DFG are both based on the same nonlinear $\chi^{(2)}$ three-wave mixing process and distinction between them mostly arises from different experimental implementation, i.e. putting either one or two beams onto the nonlinear crystal. In fact, OR is commonly modeled as intrapulse difference frequency generation [177, 178]. The highest free-space fields of 108 MV/cm were achieved using DFG in GaSe in the multi-THz range [179], while OR in the organic compound DSTMS\(^1\) was reported to reach peak fields as high as 83 MV/cm [180]. The current-based techniques are more difficult to scale up and reach somewhat lower maximum fields, but using the two-color gas plasma technique 4.4 MV/cm [181], 8 MV/cm [176], and very recently 16 MV/cm [182], were reported by different groups.

\(^1\)DSTMS abbreviates 2,4-N,N-dimethylamino-4‘-N’-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate.
8.1 Generation of high-field THz pulses

In practice these singular field records were found to be difficult to provide to experiments on a daily basis and few experiments on condensed matter using fields far exceeding 1 MV/cm have been published so far, with the exception of the mature multi-THz GaSe based techniques [131, 183, 184, 185] and very recently also in the THz range using organic generation crystals [186, 187].

For our experiments, fields in the range of 100 kV/cm were found to be sufficient and we employed OR in DSTMS as well as two-color plasma THz generation which will be described in the following sections.

8.1.1 Optical rectification in organic crystals

OR is a nonlinear process of second order, thus the description of its nonlinear polarization follows the discussion of the general nonlinear processes in section 2.2.1. For OR we are only concerned with the efficient coupling via the tensor $\hat{\chi}^{(2)} = \hat{\chi}_{xx}$ that links two incoming electric fields to the nonlinear electric polarization $P_i^{(2)} = \hat{\chi}_{ijk}^ {(2)} E_j(\omega_1, t) E_k(\omega_2, t)$. For these applications, the nonlinear susceptibility is often represented by the electro-optic coefficient $r$ and the two quantities are related via the refractive indices of the IR fields [188, 177]

$$\chi_{ijk}^{(2)}(\omega_{\text{THz}}; \omega_{\text{IR}}) = -\frac{1}{2} n_j^2 n_k^2 r_{jki}(\omega_{\text{IR}}; \omega_{\text{THz}}).$$

(8.1)

Based on their non-centrosymmetric molecular building blocks, organic crystals can provide particularly high electro-optic coefficients approximately 50 times larger than the zincblende crystals such as GaP that are commonly used in nonlinear optics [177, 189, 190, 178, 53]. Commercially available crystals of this class are called DAST$^2$, DSTMS and OH$^3$ and show point symmetry $m$, $m$ and $mm2$, respectively [177].

Analogous to sum frequency generation in section 2.2.3, the nonlinear polarization oscillating at the difference frequency $\Delta \omega$ of two fields each of amplitude $E_0$ is given in scalar notation by $P^{(2)}(\Delta \omega) = \chi^{(2)} E_0^2 e^{i \Delta \omega t}$. In contrast to DFG, for OR the two incoming fields are degenerate, thus their difference leads to a DC component. However, short optical pulses possess considerable bandwidth of typically $\Delta \nu \approx 10$ THz and for transform limited pulses all contained frequency components can mix to induce nonlinear polarizations at frequencies $[0, \Delta \nu]$. Hence, in a non-centrosymmetric medium (as discussed in section 2.2.2) all frequencies in this interval are present. The reason why they are not always observed is due to propagation which is described by the coupled wave equations (see appendix B). This behavior is closely related to phase matching in sum frequency generation, see section 2.2.4, but gives a different criterion for optimum generation. For OR this reads

$$n^{(\text{THz})} \approx n^{(\text{IR})}_g,$$

(8.2)

---

$^2$4-N,N-dimethylamino-4′-N′-methyl-stilbazolium tosylate

$^3$2-[3-(4-hydroxystyryl-5,5-dimethylcyclohex-2-enyldene)malononitrile

$^4$For a definition see references [52, 191].
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i.e. the group velocity of the IR beam \( v_g = c/n_g \), where \( n_g \) is the group index, needs to match the phase velocity of the THz pulse.

The organic crystals mentioned above show very similar values of the electro-optic coefficient but possess a different frequency dispersion and absorption. Unfortunately, the region where phase matching can be achieved lies in the range between 1200-1500 nm and does not extend to the fundamental output frequency of the Ti:sapphire laser at 800 nm. Therefore prior frequency conversion using an optical parametric amplifier becomes necessary. The electro-optic coefficient of DSTMS is nonetheless large enough that even without matching the phase-condition, significant field strengths can be achieved [192].

In addition to effects arising from beam propagation, conversion efficiency is lowered by absorption of the generated THz fields and the infrared pump, and the delicate crystals may suffer damage from the latter.

![Figure 8.1](image)

**Figure 8.1:** The THz field emitted by a 590 µm thick DSTMS crystal after being excited by (70 ± 5) fs long 1500 nm OPA pulses. a) The blue line indicates measurements using EO detection in 100 µm GaP (see section 8.2.1), the orange line was detected using air biased coherent detection (ABCD, see section 8.2.2). b) The main emission of DSTMS lies between 1 and 5 THz, while ABCD shows significant high frequency components up to 14 THz. The broken line indicates the ideal sampling sensitivity of a 70 fs pulse.

8.1.2 Two-color plasma generation of THz fields

Efficient broadband THz generation in air can be achieved by focusing an intense laser beam into air and superimposing it with its second-harmonic field. Unlike OR, two-color plasma generation of THz fields is not based on the second order susceptibility. For several years the process was suspected to be of four-wave-mixing nature and proportional to \( \chi^{(3)} \) [193, 194], but it is now understood that the main contribution to THz emission arises from asymmetric field-induced
8.1 Generation of high-field THz pulses

The two-color field induced current in N$_2$ as given by equation 8.5. Here, the phase between fundamental 1200 nm beam and its second-harmonic is set to $\phi = \pi/2$. The induced current $J_e(t)$ shows a distinct DC component whose onset is achieved on the timescale of the pulse envelope leading to broadband THz emission. Implemented according to references [199, 160].

The process can be modeled fully quantum mechanically [197] but can also be accounted for using a semi-classical description that is instructive for deriving some of the characteristics of THz emission [200]. Bound electrons of the gas molecules are subjected to the strong optical fields of the ultrashort pulses. But while the impinging photons typically have energies on the order of 1 eV, the ionization potential of N$_2$ is $U_i = 15.6$ eV [201]. Ionization is still allowed via processes that can be characterized as multiphoton-absorption and tunneling and the regimes are commonly distinguished based on the Keldysh parameter [202] $\gamma = \frac{\omega \sqrt{I_\omega}}{\sqrt{2U_i}}$, where $I_\omega$ is the incoming light intensity at frequency $\omega$. For general laser fields this distinction has to be further refined [201, 203], but it is widely accepted that for $\gamma \ll 1$, which is the case for THz plasma generation, the process is of tunneling character leading to broad distributions of free electron energies [203]. The ionization rate $w(t)$ can then be calculated in the quasi-static Ammosov-Delone-Krainov model for tunneling in alternating fields [204]

$$w(t) = \frac{\alpha}{\epsilon(t)^\delta} e^{-\frac{\beta}{\epsilon(t)}}, \quad (8.3)$$

where $\alpha$, $\beta$, and $\delta$ give molecule specific parameters for the gas and $\epsilon(t)$ is the electric laser field in atomic units $E(t)/\epsilon_a$. In the oscillating two-color field, equation 8.3 will lead to a carrier density that increases step-wise following

$$\dot{\rho}_e = w(t) [\rho_{mol} - \rho_e], \quad (8.4)$$

where $\rho_{mol}$ and $\rho_e$ give the molecular and free electron densities, respectively. After the time of

\footnote{For constants and definitions see reference [205].}
ionization $t'$, carriers can now freely follow the two-color field and a current builds up according to [160, 206]

\[
v(t, t') = -\frac{e}{m_e} \int_{t'}^t E(t'')e^{-\frac{(t''-t')}{\tau}} dt'',
\]

\[
J_e(t) = -e \int_{-\infty}^t v(t, t') \rho_e(t') dt',
\]

where $e$ and $m_e$ are the electron’s charge and mass, respectively, and $\tau$ accounts for scattering with ions. The field is emitted due to the current $E \propto \dot{J}_e(t)$. The nonlinearity of the current resulting from equation 8.5 arises from the step-like release of new carriers due to tunneling that get accelerated in the asymmetric two-color light field. The phase relation of the second-harmonic and fundamental beams are therefore crucial and the strongest rectifying component of the current is induced for a phase of $\phi = \pi/2$ [207, 160].

There exists now a broad experimental foundation for this model. A strong argument was found in the threshold behavior of plasma ignition [195] above which the emitted field follows the scaling law [194]

\[
E_{THz} \propto \sqrt{I_{2\omega}I_\omega}
\]

Equation 8.6 is valid until the onset of saturation due to dephasing of the optical fields.

Although the model is successful in describing the fundamental scaling relations and polarization dependences, the above description is, however, not the full story since for example dephasing occurs due to Kerr self-phase modulation which not only has negative impact on the emission but can also lead to filamentation. The dynamic balancing between this Kerr-induced beam self-focusing and ionization-induced beam defocusing can increase the effective generation volume [208] and also increases the generated spectrum to higher frequencies due to beam steepening [209]. The photo-currents induced in this way were found to scale according to $J_e(t) \propto \lambda E(t) \rho_e(t)$, which suggests more intense emission for longer laser carrier wavelengths [181]. This scaling law could to some extent be reproduced [210] but was suggested to be only valid for rather specific conditions due to the complications introduced by Kerr nonlinearities [209].
8.2 Time-domain detection of electric fields

8.2.1 Electro-Optic detection (EO)

Electro-optic detection, in short EO sampling, is a particularly sensitive technique to quantitatively measure transient electric fields based on the Pockels effect. In materials with a non-vanishing electro-optic coefficient $r$, co-propagating IR and THz fields can strongly interact via the second-order susceptibility $\chi^{(2)}$ that can effectively lead to a change in the observed refractive index $\Delta n_{IR}$ between two perpendicularly polarized components of the IR field. The mechanism can also be understood in the framework of sum- and difference frequency generation process, i.e. three-wave-mixing, as previously discussed for SHG in section 2.2 and for OR in section 8.1.1 [211].

In the quasi-static picture, it is however straightforward to derive the induced difference in intensity based on the DC Pockels effect

$$\Delta n_{IR}(t) = n_{IR}^3 r E_{THz}(t). \quad (8.7)$$

For simplicity, the Pockels effect is here given in scalar notation, in general the EO coefficient is a tensor, see equation 8.1. For a more detailed discussion of this effect see references [53, 212] and [213]. The relative difference in intensity detected between two polarization channels in

---

**Figure 8.3:** The THz field emitted by a plasma source driven by 0.9 mJ, (70 ± 5) fs OPA pulses. a) The blue line indicates measurements using EO detection in 100 µm GaP, the orange line was detected using air biased coherent detection (ABCD). b) The emitted spectrum is broadband and limited by the detection bandwidth of the GaP crystal as well as by the sampling pulse-length in ABCD. The broken line indicates the sampling sensitivity of a 70 fs pulse. The dip in the spectrum around 6.1 THz is caused by PTFE absorption.
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**Figure 8.4:** Schematic of an EO detection setup depicting vertically polarized IR and THz beams and the definition of the angles $\alpha$ and $\beta$. The subsequent quarter-wave plate at an angle of around 45° leads without THz-field to circular polarization that balances the detected vertical and horizontal polarization components to $\Delta I = 0$.

Electro-optic sampling using a probe beam of wavelength $\lambda_{IR}$ and intensity $I_{IR}$ is given by [212]

$$\frac{\Delta I(t)}{I_{IR}} = \frac{\pi n_{IR}^3 r_{41} L}{\lambda_{IR}} [\cos \alpha \sin 2\beta + 2 \sin \alpha \cos 2\beta] E_{THz}(t),$$  \hspace{1cm} (8.8)

where the material specific properties are the probe refractive index $n_{IR}$, crystal length $L$ and electro-optic coefficient $r_{41}$. The angles $\alpha$ and $\beta$ are defined between the polarization of the THz and probe beams with respect to the (001)-axis of a (110)-cut crystal as defined in figure 8.4. With the knowledge of the absolute value of $r_{41}$, equation 8.8 can be used to detect the absolute values of electric fields. Competing techniques such as ABCD detection in section 8.2.2 often lack this ability.

The method was shown to be applicable from DC to fields oscillating at frequencies reaching above 100 THz [116]. Limitations to this powerful technique mainly arise from similar requirements that have to be fulfilled for efficient OR given by equation 8.2, i.e. the group velocity of the IR sampling beam has to match the phase velocity of the THz fields. Figure 8.5 a) shows that e.g. in GaP this cannot be fulfilled over a wide spectral range around the strong infrared active phonon at 11 THz. Thin detection crystals reduce the absolute phase walk-off and extend the relative spectral sensitivity, but even for 100 $\mu$m thin GaP crystals spectral sensitivity vanishes around 7 THz, see figure 8.3. This roll-off is usually not taken into account when absolute field values are reported and thus they can be considered to be lower estimates of the actual values.

Unfortunately, all known crystals that are suitable for EO detection possess IR-active phonon modes and corresponding dispersion between 5 and 12 THz. This is were the complementary gas-based method of ABCD may offer an advantage.

### 8.2.2 Air Biased Coherent Detection (ABCD)

Similar to EO sampling, ABCD is a method capable of resolving phase and amplitude of electric fields in the time domain. In contrast to EO sampling, it is based on gaseous media instead of
non-centrosymmetric crystals and thus is not limited by IR absorption in the THz range when using non-polar gases such as pure N\textsubscript{2}. Due to the spatial isotropy of gas, $\chi^{(2)}$ vanishes and in an intensity regime below the onset of field induced tunneling, see section 8.1.2, the interaction between different light fields is solely mediated by the third-order nonlinearity $\chi^{(3)}$ [214]. For intense probe beams at a frequency $\omega \gg \omega_{\text{THz}}$, the underlying four-wave mixing process can be approximated by

$$E_{2\omega} \propto \chi^{(3)} E_{\text{THz}} E_\omega E_\omega \propto \chi^{(3)} E_{\text{THz}} I_\omega.$$  

Thus, the combination of probe and THz beams leads to emission of SHG of the probe, also coined THz-field induced second-harmonic generation (TFISH) [215]. This process can also be considered as field induced breaking of inversion symmetry of the gas, therefore leading to an effective second-order susceptibility $\chi^{(2)}(E) \propto \chi^{(3)} E_{\text{THz}}$. From this consideration and equation 8.9 it is evident that a measurement of the emitted SHG intensity gives information about the THz field amplitude but is lacking information about the sign of $E_{\text{THz}}$ and thus the phase.

To retrieve this phase, several schemes based on heterodyne detection adding a second-harmonic local oscillator to the experiment were proposed [215, 214, 216, 217]. For this, one can employ second-harmonic emitted by a laser induced plasma [215], add an external BBO\textsuperscript{7}-source of second-harmonic or apply a high-voltage bias around the interaction focus of the THz and probe fields that eventually coined the term air biased coherent detection [214]. The latter is superimposing a field bias $E_{\text{DC}}$ on top of the applied THz field and is by far the most common implementation of this technique. Retrieval of the phase then goes as follows

$$I_{2\omega} \propto \left[ \chi^{(3)} I_\omega (E_{\text{THz}} + E_{\text{DC}}) \right]^2,$$

$$\propto \left[ \chi^{(3)} I_\omega \right]^2 \left( (E_{\text{THz}})^2 + (E_{\text{DC}})^2 + 2E_{\text{THz}} E_{\text{DC}} \right).$$  

\footnote{Beta barium borate $\beta$-BaB\textsubscript{2}O\textsubscript{4}}

\begin{figure}[h]
\centering
\begin{subfigure}{0.4\textwidth}
\includegraphics[width=\textwidth]{fig8a}
\caption{The refractive index of GaP shows strong dispersion around the phonon mode at 11 THz.}
\end{subfigure}\hfill
\begin{subfigure}{0.4\textwidth}
\includegraphics[width=\textwidth]{fig8b}
\caption{The electro-optic coefficient of GaP also shows dispersion around the phonon resonance, but is almost constant over the range of available IR frequencies. At 1200 nm, the coefficient $r_{41} = 1.0$ pm/V. Reprinted from Casalbuoni et al. [213].}
\end{subfigure}
\caption{8.5: a) The refractive index of GaP shows strong dispersion around the phonon mode at 11 THz. b) The electro-optic coefficient of GaP also shows dispersion around the phonon resonance, but is almost constant over the range of available IR frequencies. At 1200 nm, the coefficient $r_{41} = 1.0$ pm/V. Reprinted from Casalbuoni et al. [213].}
\end{figure}
Bias electrodes

\[ \Delta I = I(E_{DC}) - I(-E_{DC}) \]

**Figure 8.6:** Schematic of an air biased coherent detection setup. Probe and THz beams are focused between the bias electrodes in a gas-atmosphere with corresponding \( \chi^{(3)} \). An extended volume in this overlap region contributes to the signal. The bias field is alternated to allow measurement of \( \Delta I_{2\omega} \) according to equation 8.11. The field induced SHG is filtered from the intense probe beam and detected using either an avalanche photo-diode (APD) or a photomultiplier-tube (PMT).

From equation 8.10 we see that in addition to a phase-independent offset intensity, the emission now has a contribution that is sensitive to the sign of the THz and bias field. By flipping the polarity of the bias field we can then measure the intensity difference

\[
\Delta I_{2\omega} = I_{2\omega}(E_{DC}) - I_{2\omega}(-E_{DC}),
\]

\[
\propto \left( \frac{2}{\chi^{(3)}} I_\omega \right)^2 |E_{DC}| E_{THz}.
\]  

Equation 8.11 therefore allows for a phase-resolved measurement of \( E_{THz} \) much like expression 8.8 does for EO sampling. A schematic of the measurement is shown in figure 8.6. More details on the experimental implementation can be found in appendix G.

The above expression also describes how the typically weak emission of second-harmonic intensity can be increased in order to increase the signal-to-noise ratio. The emitted intensity scales with \( I_2^2 \), but saturates and becomes unstable above the threshold of plasma formation [214]. The bias field is typically limited by the electric breakdown of the gas medium to fields around 10 kV/cm in air. Unlike plasma-generation of THz, see section 8.1.2, the ABCD process is a proper four-wave-mixing interaction, thus the emitted second-harmonic scales with \( (\chi^{(3)})^2 \) which allows to tremendously increase the emission by using alkane gas media [218] as shown in figure 8.7. At ambient conditions, alkane gases with chain lengths longer than butane become liquid, rendering butane the medium of choice for easy handling. For pressures above ambient condition, phase-matching of the nonlinear process plays a role again and can clamp the emitted intensity. Luckily, optimal conditions are found to be very close to ambient pressure for typical focusing geometries [218].

Looking at equations 8.10 and 8.11 it may be tempting to calibrate the absolute THz field
Figure 8.7: Detected second-harmonic intensity versus the third order susceptibility $\chi^{(3)}$ of various alkane gases. Using butane as gas medium leads to a 100-fold increase in SHG over $N_2$. Reprinted from Lu et al. [218] with permission from the OSA.

by a comparison to the applied bias field whose magnitude is known. However, the underlying generation volumes of SHG inside the Rayleigh ranges of the two beams, where the probe and THz fields lead to significant contributions to the signal, as well as the overlap volume of the bias field and probe focus, provide large uncertainties. Inhomogeneities in the spatial intensity profile of the probe beam are difficult to take into account and in particular in the regime of imperfect phase-matching, that commonly occurs at ambient pressure, estimations of the absolute field values are hence strongly obscured.

Despite this drawback, the technique offers superior spectral sensitivity over a range covering the THz-gap between 5 and 10 THz as shown in figure 8.3 which towards higher frequencies is only limited by the pulse-length of the probe beam [214]. This limitation can be further pushed to higher frequencies by active beam steepening as was carried out in references [219, 164].

8.3 THz time-domain spectroscopy (TDS)

By using methods such as EO sampling (section 8.2.1) or ABCD (section 8.2.2) to measure a material’s response to a broadband electric field pulse in amplitude and phase, time-domain spectroscopy can offer an almost model independent measurement of the complex refractive index in the THz-range. This presents a great advantage over techniques such as Fourier-transform spectroscopy (FTIR) that only measure the spectral amplitude and have to rely on Kramers-Kronig relations for the derivation of the full complex refractive index of a material [220].

In order to determine either the complex reflectivity or transmission coefficients, TDS requires two time-domain measurements of a phase-stable THz pulse once interacting with the material of interest $E_1(t)$ and in addition a reference measurement in the absence of the sample $E_0(t)$. In transmission, the reference is typically given by a measurement without the sample, where the
Figure 8.8: Schematic setup of reflective and transmissive THz time-domain spectroscopy in 0° normal-incidence geometry. About 2/3 of the generated THz field is transmitted through the Si-wafer and is subsequently focused onto the sample. Its reflection is then re-collimated by the same mirror and travels back to the silicon beamsplitter where about 1/2 of the remaining field is reflected towards detection.

Field instead propagates in vacuum or nitrogen. Pure nitrogen environments are a reasonably good approximation of vacuum in the THz range \( n_{N_2}(\omega) \approx 1 \). In a reflection geometry, the reference measurement may be carried out by putting a reference mirror in place of the sample. Underlying is the assumption that the mirror is a very high quality reflector such as bare gold of high surface quality that achieves \( \hat{r} \approx -1 \). The two time-domain fields can be converted to the frequency domain using Fourier transformation to gain the complex fields \( \hat{E}(\omega) \). The sample’s measured transfer functions are then given by

\[
\hat{r}_{T}(\omega) = \frac{\hat{E}_{1}(r)(\omega)}{E_{0}(r)(\omega)} = |r(\omega)|e^{i\varphi(\omega)}, \quad \hat{t}_{T}(\omega) = \frac{\hat{E}_{1}(t)(\omega)}{E_{0}(t)(\omega)} = |t(\omega)|e^{i\varphi(\omega)}. \tag{8.12}
\]

Here, \( \hat{E}_{0}(\omega) \) and \( \hat{E}_{1}(\omega) \) are the complex Fourier transformations of the detected time-domain fields in reflection or transmission. Subsequent evaluation is then only based on the Fresnel equations and the sample dimensions and the problem is greatly simplified in normal-incidence geometry which can easily be achieved experimentally as shown in figure 8.8 and applied in section 9.2.

An inherent characteristic of materials that feature strong THz resonances is that they are also strongly absorbing in this spectral region. Measuring such opaque materials can only be achieved in reflection geometry or in thin films, that are either free-standing or on transparent substrates. For homogeneous bulk crystals in 0°-incidence geometry, the refractive index can be directly inverted

\[
\hat{n}_{T}(\omega) = \frac{1 - \hat{r}_{T}(\omega)}{1 + \hat{r}_{T}(\omega)}, \quad \rightarrow \hat{n}(\omega) = \frac{1 - \hat{r}_{T}(\omega)}{1 + \hat{r}_{T}(\omega)}. \tag{8.13}
\]
8.3 THz time-domain spectroscopy (TDS)

The inversion for thin samples in transmission or reflection is less straightforward and depends on the thickness $d$ of the material and substrate layers that can be described e.g. using the propagation-matrix method described in section 5.5.1 and 9.3.2. For a free-standing homogeneous slab sample we can find

$$\hat{t}_T(\omega) = \frac{4n_\text{e} \frac{1}{c} \omega d}{(\hat{n} + 1)^2 + (\hat{n} - 1)^2 e^{\frac{i2\omega d}{c}}}.$$  (8.14)

For measurements of thick samples in transmission, the multiple etalon-reflections can often be separated in time. In this situation it suffices to limit the detection time to the first transmitted pulse. In the frequency-domain this is equivalent to only taking into account the first order transmission and the transfer function reads

$$\hat{t}_T(\omega) = \frac{4n_\text{e} \frac{1}{c} \omega d}{(\hat{n} + 1)^2}.$$  (8.15)

Although expression 8.14 and 8.15 cannot be solved for $\hat{n}$ directly, the refractive index can be found by iterative optimization of its two components and thickness $d$ employing e.g. a genetic algorithm.

Using this technique, experimental difficulties mainly arise from limited sample quality. As typical THz focus diameters are around 500 $\mu$m, evaluation of equations 8.13, 8.14 and 8.15 requires a large homogeneous sample volume. Long-time drift of the THz source and fluctuations in the water vapor concentration can also lead to significant errors as acquisition of a spectrum can take up to several hours. Drift is particularly problematic when sample and reference traces are acquired subsequently and are not frequently alternated. In reflection geometry the experimental implementation of the reference measurement poses a significant complication as the exact surface position needs to be reproduced by the mirror in order to not cause significant phase errors [221]. In section 9.2 we will introduce a method that greatly simplifies this reference measurement, but can only be applied for a very specific class of materials.

For time-resolved measurements, this treatment is in general insufficient and an interaction model based approach to describe the underlying physics in the time domain is advised [222, 223]. On long timescales, i.e. for time delays exceeding the detection time interval, the concept of refractive index can be regained by a time-dependent description as $n(\omega, t)$ [224, 225, 226]. A special example is given by Huber et al. [227] who evaluated the dielectric function equivalently to equation 8.14 to observe the transition time to a photo-induced semi-equilibrium state of electron-hole-density.$^8$

In addition, the Fresnel equations are based on the underlying assumption of linear response to electric fields, including the independence of all spectral components. For pulsed THz sources reaching fields up to the MV/cm-scale, it is possible to leave this regime and effects emerging from such THz-field nonlinearities present the main focus of the following chapters.

$^8$More precisely, they observed the upper bound of such a transition time given by the intrinsic temporal resolution of the measurement.
8.3.1 Experimental setup for time-resolved reflective THz-spectroscopy

Figure 8.9 shows the experimental implementation of a normal-incidence reflective THz time-domain spectrometer based on two-color plasma THz generation (section 8.1.2) and ABC-detection (section 8.2.2) with the addition of optical excitation using a separate tunable OPA output.

The nitrogen-purged setup is fed by two outputs of a twin-OPA pumped by a 17 mJ/pulse 800 nm beam at 93 fs pulse-length. The laser system is described elsewhere [53]. The 1 mJ/pulse signal of output HE1 is tuned to 1200 nm at $(70 \pm 5)$ fs pulse-length [199] and subsequently split, where 90% of the intensity is used for two-color plasma THz generation of field $E_1$ using an 8” off-axis parabolic mirror (OAPM) and a 100 µm thick BBO (section 8.1.2). The residual 10% of the power is used for ABC-detection (section 8.2.2). The THz beam is filtered for optical light using a thin band of Teflon as scatterer as well as Si attenuation. Collimation is carried out using an OAPM and the beam is focused onto the sample with a 4” OAPM. The second OPA output HE2 can be employed for optical excitation of the sample. A 1 m focusing lens allows to transmit the beam through a hole in the focusing THz OAPM, realizing a spot size on the sample of $(1.88 \times 1.65)$ mm² (FWHM). This ensures laterally homogeneous excitation of the sample over the 300 µm spot size of the THz beam. The optical beam can be delayed by a motorized stage to vary the excitation delay $\tau$. 

![Figure 8.9: Broadband normal-incidence reflective THz time-domain spectrometer for time-resolved measurements (not to scale). The environment is purged with nitrogen to reduce THz absorption by water vapor.](image)
8.4 2D THz-spectroscopy

Unlike the mature multi-dimensional infrared spectroscopy [228, 229, 230, 231] that was enabled by the rise of the Ti:sapphire technology in the 1990s, two-dimensional THz-spectroscopy is a very young experimental technique whose first results were published in 2009 [232].

A short, but possibly comprehensive list of experimental work using 2D THz-spectroscopy is given by the following references that were published since then [232, 233, 234, 183, 184, 185, 235, 236, 237, 155, 238, 239].

Again, this was sparked by technological development. This time, the conversion of ultrafast laser pulses to THz fields in nonlinear crystals such as GaSe and LiNbO$_3$ (section 8.1.1) provided THz fields of sufficient magnitude and stability to acquire nonlinear 2D maps consisting of on the order of $10^4$ single measurements that are necessary to carry out meaningful Fourier transformations in two dimensions.

Using time-domain detection methods as described in section 8.2, 2D THz-spectroscopy allows detection of the nonlinear response of all beams involved in a phase-resolved manner, thus, it can provide a measurement of the full information contained in the electromagnetic interaction.

Experimentally, this can be realized in a geometry where the beams propagate collinearly onto the sample and into the detection either in transmission or reflection geometry. Transmission was the geometry of choice for all multidimensional THz experiments so far. The fields can be delayed relative to each other with excitation time $\tau_i$ and are measured at a sampling time that is referred to as realtime $t$. To extract the nonlinear field components from such measurements, experiments have to be carried out with all combinations of fields $E_i$ on and off, which is commonly achieved by simple mechanical chopping. In the case of two fields $E_1$ and $E_2$ the nonlinear response can be extracted by carrying out three separate measurements and calculating the difference

$$E_{NL}(t, \tau) = E_{12}(t, \tau) - E_1(t, \tau) - E_2(t, \tau),$$

(8.16)

where $E_1$ and $E_2$ correspond to the single fields detected after interaction with the sample for which the other beam was blocked (before reaching the sample). $E_{12}$ represents the combined field response. In the linear regime, this difference always yields 0, however, any of the strong field effects described e.g. in chapter 6 lead to a deviation from this behavior.

8.4.1 Experimental setup for 2D THz-spectroscopy

We choose to study the nonlinear response in reflection geometry allowing for broadband measurements of bulk polar semiconductors. Experimentally, this is realized in an asymmetric collinear THz-pump/THz-probe experiment as depicted in figure 8.10.

In close similarity to the setup discussed in section 8.3.1, the nonlinear THz-spectrometer presented here is fed by two outputs of a high power twin-OPA. The signal of output HE1 is tuned to 1200 nm at $(70 \pm 5)$ fs pulse-length [199] and is subsequently split where 90% of the
intensity is used for two-color plasma THz generation of field $E_1$ using an 8” OAPM and a 100 µm thick BBO (section 8.1.2). The residual 10% of the power is used for ABC-detection (section 8.2.2). The second OPA output HE2 provides a 1.5 mJ/pulse signal at 1500 nm at $(70 \pm 5)$ fs and gets optically rectified using a 6 mm aperture 590 µm thick DSTMS crystal to generate $E_2$ (section 8.1.1). The optical beam can be delayed by a motorized stage to vary the excitation time $\tau$ between $E_1$ and $E_2$. Both THz beams are filtered for residual optical light using thin sheets of Teflon as scatterers and Si/Ge attenuation.

While the plasma THz beam is collimated using an OAPM, the rectified beam is propagating based on its source divergence. Both beams are focused onto the sample using 4” OAPMs. The beam diameters of $E_1$ and $E_2$ at the focus position can be measured using a two-dimensional bolometer array⁹ and are found to be 300 µm and 560 µm (FWHM), respectively¹⁰.

The field $E_2$ can be attenuated using two consecutive wire-grid polarizers WG1 and WG2. While $E_1$ is transmitted through the beamsplitter BS, $E_2$ is reflected by it onto the sample. The reflected field components that get transmitted through BS are then recollimated and the reflection from the Si beamsplitter is afterwards detected using ABCD in horizontal geometry with a sampling beam delayed by realtime $t$.

---

⁹The NEC IR/V-T0831 is an uncooled THz imager, 320 × 240 pixels, with a pitch of 23.5 µm.

¹⁰The camera sensitivity is, however, increasing towards higher frequencies.
The properties of the beamsplitter BS in figure 8.10 have not yet been specified. In our experiments in section 8.4 we choose to use for this purpose a wire-grid THz polarizer from Tydex Optics\textsuperscript{11} with a line density of 1200 mm\textsuperscript{-1} and an extinction ratio of 350 to 400. Its wires are deposited on a high-density polyethylene substrate of refractive index $n_{\text{HDPE}} = 1.52$ and thickness\textsuperscript{12} $(80 \pm 8) \mu$m. The orientation is set to vertical wire alignment, such that the horizontally polarized $E_1$ is almost fully transmitted, while the predominantly vertically polarized field $E_2$ is reflected. Only the horizontal components of the fields reflected off the sample are transmitted by the wire-grid BS towards the detection. The crossed polarization and different amplitudes and spectra of $E_1$ and $E_2$ make this an asymmetric 2D THz-spectroscopy setup.

\textsuperscript{11}TydexOptics / Domostroitelnaya str. 16 / 194292 St. Petersburg / Russia
\textsuperscript{12}The thickness was measured with ABCD using the THz phase delay and the value of $n_{\text{HDPE}}$. 
Chapter 9

Time-resolved THz-spectroscopy

9.1 Introduction

As THz time-domain spectroscopy is intrinsically time-resolved, it is straightforward to implement pump-probe measurements following the transmission \( \hat{t} \) or reflection coefficient \( \hat{r} \) as function of time after ultrafast excitation.

Being able to optically induce changes to the material’s reflectivity allows us to perform self-referencing measurements of the refractive index in certain semiconductors as will be discussed in section 9.2. Reflective THz TDS of large crystals can provide a convenient means to carry out broadband measurements on strongly absorbing materials, but large sample volumes can lead to strong limitations for time-resolved experiments which is addressed in section 9.3. Finally, we will discuss the novel technique of broadband 2D THz-spectroscopy, here applied to low band gap semiconductors, which is able to identify competing high-field effects occurring in these systems in section 8.4.

Parts of the results presented in section 9.2 and 9.3 have been published in the following manuscript:

L. Huber, F. Kapsalidis, and S. L. Johnson,  

9.2 Reflective THz time-domain spectroscopy: 
The photo-screening method

For standard reflective time-domain spectroscopy as described in section 8.3 the extracted complex refractive index may be erroneous due to the sample misplacement with respect to a reference mirror. As this reference corresponds to the measurement of the incoming field on the sample,
it is of equal importance for the derivation of the refractive index as the sample measurement, and the procedure requires to reproduce both exact placement and orientation. For example a longitudinal misplacement by $\Delta z = 1 \, \mu\text{m}$ leads to a temporal shift between signal and reference of about $\Delta t = 7 \, \text{fs}$, which corresponds to a phase shift of more than $10^\circ$ at frequencies of 10 THz. This phase directly enters the evaluation of the refractive index in equation 8.13 and leads to systematic errors of the dielectric function.

To carry out broadband TDS measurements it is therefore advised to take extreme care in placement and stabilization of the sample and the reference mirror. However, measurements on semiconductors may allow for a different approach: One could apply an intense laser pulse that is strong enough to induce a transient state possessing a plasma frequency far beyond the observed frequency range. Thus, using this photo-screening method we intend to briefly induce a metallic state that intrinsically sits at the exact position of the sample whose equilibrium reflectivity can be measured one laser pulse later. Figure 9.1 gives an indication for the methods ability to screen all relevant features in the range between 1 and above 10 THz.

![Reflectivity spectra acquired on InSb under equilibrium conditions (blue) and 3 ps after intense excitation using 1500 nm OPA pulses with fluences of 1 mJ/cm². The excited area of $(1.88 \times 1.65) \, \text{mm}^2$ (FWHM) is large compared to the 300 $\mu\text{m}$ (FWHM) THz focus size. The spectra show a large set of rotational water absorption lines and additional narrow absorption at 6.1 THz due to the PTFE scatterer that are present in both measurements. The solid black line shown at the top indicates the reflectivity from the Drude-Lorentz model (equation 7.2) for a $10\times$ higher plasma frequency than for the equilibrium material. A feature that could be expected from the lower coupled plasmon-phonon mode $L_-$ is too strongly screened to be observed.](image)

Figure 9.1: Reflectivity spectra acquired on InSb under equilibrium conditions (blue) and 3 ps after intense excitation using 1500 nm OPA pulses with fluences of 1 mJ/cm². The excited area of $(1.88 \times 1.65) \, \text{mm}^2$ (FWHM) is large compared to the 300 $\mu\text{m}$ (FWHM) THz focus size. The spectra show a large set of rotational water absorption lines and additional narrow absorption at 6.1 THz due to the PTFE scatterer that are present in both measurements. The solid black line shown at the top indicates the reflectivity from the Drude-Lorentz model (equation 7.2) for a $10\times$ higher plasma frequency than for the equilibrium material. A feature that could be expected from the lower coupled plasmon-phonon mode $L_-$ is too strongly screened to be observed.
To achieve this, we apply intense optical excitation of 1 mJ/cm\(^2\) of 1500 nm OPA pulses to the sample, leading to an excitation density of \(8 \times 10^{19}\) cm\(^{-3}\). The band gap of InSb is roughly 5 times lower than the photon energy, thus excitation creates electrons with excess energies requiring increased scattering time to thermalize. The process is in addition accompanied by significant impact ionization (section 6.5) and was shown to take up to 8 ps to reach a maximum in carrier density [241]. Here, we apply lower excess energy to the electrons such that intervalley scattering that can efficiently trap carriers in the \(L\)-valley (section 6.3) is expected to be of minor importance.

In the THz-range we observe no significant changes to the reflectivity after 2 ps. The applied excitation density leads to an equal density of initially hot electrons that cascade further and in a crude approximation\(^2\) may lead to up to 0.1 conduction band electrons per unit cell. This would clearly lead to highly metallic behavior in the THz range, but also to strong electron-electron scattering. In the following, we therefore intend to experimentally access if the proposed photo-screening method is a legitimate approach to serve as a reference for the refractive index of low band gap semiconductors.

### 9.2.1 Photo-screening results on GaSb, InAs and InSb

We carry out time-domain THz-reflectivity measurements on three different low band gap semiconductors: GaSb, InAs and InSb and acquire their respective field reference using the photo-screening method. The resulting frequency-domain reflectivity and phase as defined in equation 8.12 are shown in figure 9.2.

From this data we can directly access the refractive index using equation 8.13. To extract material properties that allow for a comparison to literature values, we also fit the reflectivity data using a common description of the Drude-Lorentz model given in equation 7.2. The results for the three compounds GaSb, InAs and InSb are shown in figure 9.3, 9.4 and 9.5, respectively. Fitting parameters are listed in table 9.1.

Figure 9.3, 9.4 and 9.5 show that the method gives meaningful results apart from the very lowest frequencies below 1 THz, where the magnitude of the InSb reflectivity is indistinguishable from 1 and only the phase gives valid information. The contrast between sample and reference reflectivity is in this range very small, rendering the measurement insensitive and prone to errors. In addition this part of the detected raw spectrum shows a strong slope and is thus sensitive to instabilities of the plasma emission, see figure 8.3. Noise of the signal also increases towards higher frequencies which is mainly due to reduced spectral sensitivity of the detection.

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1 See section 7.3 for the definition and section 9.3 for measurements of the coupled modes \(L_-\) and \(L_+\).

2 Assuming complete energy conversion to electrons in the \(\Gamma\)-valley without taking into account energy loss to the lattice or hole-recombination.
Figure 9.2: THz-reflectivity time-domain measurements of InSb, InAs and GaSb acquired using ABCD in the setup described in section 8.3.1. The references are based on photo-screening by intense above-band gap excitation using 1500 nm in the case of InSb and 1600 nm pump light for the other two measurements at a fluence of (1.0 ± 0.1) mJ/cm² and delays of 2-3 ps after excitation. The InSb measurement shows a higher level of residual water background but also shorter polarization lifetimes than InAs and GaSb where free polarization decay extends beyond 6 ps.

Figure 9.3: Refractive index of GaSb estimated using THz TDS and photo-screening referencing. Blue and red diamonds indicate measurements of reflectivity $r$ and phase $\phi$ based on the time-domain data shown in figure 9.2 and equation 8.13. Solid lines show fits to the complex reflectivity data based on equation 7.2.
9.2 Reflective THz time-domain spectroscopy: The photo-screening method

Figure 9.4: Refractive index of InAs as estimated using THz TDS and photo-screening referencing.

Figure 9.5: Refractive index of InSb as estimated using THz TDS and photo-screening referencing. The black squares indicate reflectivity measurements by Chochol et al. using a combination of FTIR and low-frequency TDS [242].
Chapter 9: Time-resolved THz-spectroscopy

<table>
<thead>
<tr>
<th>Material</th>
<th>$\epsilon_\infty$</th>
<th>$\nu_{LO}$ [THz]</th>
<th>$\nu_{TO}$ [THz]</th>
<th>$\gamma_{ph}$ [THz]</th>
<th>$\Omega_p / 2\pi \sqrt{\epsilon_\infty}$ [THz]</th>
<th>$\gamma_p$ [THz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb*</td>
<td>14.90 ± 0.1</td>
<td>7.13 ± 0.02</td>
<td>6.83 ± 0.02</td>
<td>0.30 ± 0.02</td>
<td>1.73 ± 0.09</td>
<td>1.85 ± 0.24</td>
</tr>
<tr>
<td>GaSb[243]</td>
<td>14.50</td>
<td>7.07</td>
<td>6.81</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GaSb[244]</td>
<td>15.1 ± 0.1</td>
<td>7.09 ± 0.01</td>
<td>6.79 ± 0.01</td>
<td>0.37 ± 0.01</td>
<td>1.8 ± 0.08</td>
<td>2.20 ± 0.15</td>
</tr>
<tr>
<td>InAs*</td>
<td>14.04 ± 0.09</td>
<td>7.17 ± 0.01</td>
<td>6.44 ± 0.01</td>
<td>0.26 ± 0.05</td>
<td>2.80 ± 0.02</td>
<td>0.39 ± 0.01</td>
</tr>
<tr>
<td>InAs[84]</td>
<td>12.3</td>
<td>7.16</td>
<td>6.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>InSb*</td>
<td>15.78 ± 0.19</td>
<td>5.70 ± 0.02</td>
<td>5.34 ± 0.02</td>
<td>0.62 ± 0.02</td>
<td>2.21 ± 0.01</td>
<td>0.30 ± 0.01</td>
</tr>
<tr>
<td>InSb[242]</td>
<td>15.68 ± 0.03</td>
<td>5.55 ± 0.01</td>
<td>5.38 ± 0.01</td>
<td>0.50 ± 0.01</td>
<td>2.21 ± 0.01</td>
<td>0.29 ± 0.01</td>
</tr>
</tbody>
</table>

Table 9.1: Fitting parameters of the Drude-Lorentz model 7.2 for various semiconductors measured in THz TDS. Our measurements are indicated by (*) and were acquired by fitting the complex reflectivity in the range between 1 and 12 THz using a genetic algorithm. Errors are estimated by fitting different subsets of the data. The plasma frequency divided by $\sqrt{\epsilon_\infty}$ gives the plasma-edge frequency where the real part of the permittivity crosses zero.

Compared to literature values, almost all fitted Drude-Lorentz parameters in table 9.1 are in agreement. The Drude parameters $\Omega_p$ and $\gamma_p$ are sensitive to exact doping and are not expected to be identical\(^3\). However, the measurements tend to overestimate the high frequency dielectric function $\epsilon_\infty$. This is likely due to the limitation of the photo-screening method. It is possible that we are measuring in a regime where screening is not fully achieved for high frequencies and the assumption of $\hat{r}_{PS}(\omega) = -1$ is not fulfilled everywhere. Despite realizing lateral homogeneity of the carrier excitation by applying a large pump beam (see section 8.3.1) longitudinally homogeneous excitation is difficult to attain and a short absorption length of the pump can cause deviations from ideal reflectivity which is further discussed in section 9.3. For InSb, where the deposited energy is particularly high compared to the small band gap, a higher total number of carriers is generated. This is likely the reason why this measurement is in very close agreement with the accepted literature value of 15.7. As a note, the applied fluences are still far below the damage threshold, but kept low to avoid excessive average heating which increases the equilibrium carrier concentration and thus the measured plasma frequency.

9.2.2 Estimation of carrier-concentration

From the Drude-Lorentz model we can further extract the carrier concentration which is an important starting parameter for the time-domain simulations in section 9.5. The plasma frequency in this model is defined by equation 7.1 that scales according to $\propto \sqrt{N_e}$. For semiconductors of low doping, the carrier concentration in the conduction band $N_e$ depends on the energy gap and temperature based on the Fermi-Dirac statistics that for small carrier

\(^3\)See the next section 9.2.2 for a more detailed discussion on this.
concentrations can be approximated by the Maxwell-Boltzmann statistics

$$N_e = n_C e^{-\frac{E_C - E_F}{k_B T}},$$  

(9.1)

where $n_C$ gives the density of conduction band states, $E_C$ and $E_F$ are the band and Fermi energy and $k_B T$ gives the thermal energy. The density of states can be approximated using the effective mass of electrons

$$n_C = 2 \left( \frac{2\pi m^* k_B T}{\hbar^2} \right)^{\frac{3}{2}},$$  

(9.2)

where $\hbar$ is Planck’s constant. Equations 9.2 and 9.1 allow for the estimation of thermal carriers in the conduction band of intrinsic semiconductors. Although all samples were bought as nominally undoped, growth processes commonly introduce unintentional doping that is also specified by the manufacturer. Estimations of intrinsic carrier concentration, the specifications by the manufacturer and our measurements are given in table 9.2. The latter rely on equation 7.1 using the effective high frequency dielectric function that includes the phonon contribution via the Lyddane-Sachs-Teller relation $\epsilon_\infty^* = \nu_{LO}^2 / \nu_{TO}^2 \epsilon_\infty$ rather than the bare $\epsilon_\infty$. This treatment is assumed to give a better approximation of the carrier density as the plasma-edge frequency lies for all samples significantly below the phonon frequency.

<table>
<thead>
<tr>
<th>Material</th>
<th>$m^*_{e,h}$ [$m_e$]</th>
<th>$E_g$ [eV]</th>
<th>$N_e^{(i)}$ [cm$^{-3}$]</th>
<th>$N_e^{(spec.)}$ [cm$^{-3}$]</th>
<th>Type</th>
<th>$N_e^{(exp.)}$ [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb [245]</td>
<td>0.4 ($h$)</td>
<td>0.73</td>
<td>4.7 · 10^{12}</td>
<td>(1 – 2) · 10^{17}</td>
<td>und. (P)</td>
<td>9.2 · 10^{16}</td>
</tr>
<tr>
<td>InAs [160]</td>
<td>0.026 ($e$)</td>
<td>0.35</td>
<td>1.3 · 10^{14}</td>
<td>&lt; 3 · 10^{16}</td>
<td>und. (N)</td>
<td>1.55 · 10^{16}</td>
</tr>
<tr>
<td>InSb [160]</td>
<td>0.014 ($e$)</td>
<td>0.17</td>
<td>1.4 · 10^{15}</td>
<td>(0.3 – 3) · 10^{15}</td>
<td>und. (N)</td>
<td>6.1 · 10^{15}</td>
</tr>
</tbody>
</table>

Table 9.2: Experimentally derived and expected values for the samples’ carrier concentration based on the fit values of table 9.1. The literature values for the gap energies $E_g$ and the effective conduction and heavy valence band masses $m^*_e$ and $m^*_h$ are indicated with $e$ and $h$, respectively. The intrinsic carrier concentration at room temperature $N_e^{(i)}$ is derived from equations 9.1 and 9.2, while the experimental findings $N_e^{(exp.)}$ are based on equation 7.1 only considering the majority carriers. The manufacturer’s specifications are given as $N_e^{(spec.)}$. The InSb sample appears to exceed these specifications by a factor of 2.

9.3 IR pump – reflective THz probe: Effects of partial penetration depth mismatch

Studies in reflection geometry allow broadband measurements on bulk grown crystals as opposed to transmission measurements on film samples that, for a large class of materials, can not be grown of comparable quality or are not available at all. In addition film samples often provide additional scattering channels due to substrate induced defects and strain or intrinsic geometric
phenomena such as Landau damping [246]. Furthermore, as was shown in the previous section, in normal-incidence the time-resolved dielectric function can be directly measured via equation 8.13 and does not rely on fitting procedures as in film transmission measurements.

A technique that combines optical excitation and reflective broadband-THz probing is therefore appealing in particular for the study of strong infrared active modes. However, in the ultrafast regime, the method may suffer from penetration depth effects arising from a mismatch between the absorption lengths of the excitation beam and the probed THz volume. For broadband THz detection this poses a particularly strict criterion, as the excitation pulse would have to exceed the THz attenuation over the whole observed spectral range. On the other hand one might presume, that due to the high refractive index of these semiconductors the by far dominant contribution to the reflected field arises from the air-material interface and gradients inside the material may only lead to minor contributions. In this section we therefore investigate the limitations of the reflective technique for ultrafast measurements of the coupled phonon-plasmon modes in III-V semiconductors by studying their loss function.

9.3.1 IR excitation – THz probe experiments

Figure 9.6 a) shows differential time-domain spectra acquired on InAs at room temperature for various delays $t'$ using the setup described in section 8.3.1 and a 1500 nm excitation fluence of 130 $\mu$J/cm$^2$. Based on a previously acquired equilibrium dielectric function using the photo-screening method (section 9.2.1), the differential reflectivity data can be converted to a transient loss spectrum using equation 7.3. This is shown in figure 9.6 b) where before excitation we can observe well defined peaks corresponding to the plasma-edge and longitudinal phonon. After excitation, the equilibrium features in the loss function disappear due to the large increase in carrier density and the coupled phonon-plasmon modes $L_-$ and $L_+$ appear. Note that for the shortest delay around 40 ps the strongly screened $L_-$-feature is found at 6.3 THz which is close to $\nu_{TO} = 6.44$ THz as expected by the Drude-Lorentz model for highly screened oscillators. The stronger plasmon-like feature $L_+$ relaxes into the observed spectral range in about 200 picoseconds and decreases further due to electron-hole recombination and diffusion.

Shortly after excitation, the equilibrium plasmon mode fully disappears and the coupled phonon-plasmon modes $L_-$ and $L_+$ begin to form as can be seen in figure 9.7. However, their formation is not finished after 2.5 ps. In fact, additional measurements at this excitation fluence did not observe formation of defined modes in the first 100 ps. This observation is much slower than previously reported by Huber et al. for GaAs [227] and InP [247]. For high values of excess energy it was observed that electron thermalization can take up to 8 picoseconds [241], nonetheless, this can not explain the current observations. Penetration depth mismatch is, however, able to cause this behavior and we are going to investigate this notion in the following.
9.3 IR pump – reflective THz probe: Effects of partial penetration depth mismatch

Figure 9.6: a) Time-evolution of relative reflectivity and phase difference from InAs after photoexcitation using 1500 nm pulses of 130 µJ/cm² fluence. The excitation induced reflectivity increases by up to a factor of 6 in the vicinity of the plasmon and phonon modes. Measurements are displaced vertically for better visibility. b) Evolution of the real and imaginary part of the loss function. New features in the spectrum appear due to the coupled modes $L_-$ and $L_+$. Loss arising from the lower phonon-like $L_-$ mode is strongly reduced by screening. Evaluation of the loss function around the LO-frequency is noisy and is here blanked for better visibility.

Figure 9.7: Evolution of the real and imaginary part of the loss function on short timescales excited with 1500 nm pulses of 10 µJ/cm² fluence. Here, the coupled modes appear on short timescales but seem washed-out and badly defined over the whole observed timescale.
9.3.2 The effect of penetration-depth mismatch on the reflective response

We can model linear effects on the reflection of THz fields introduced due to penetration depth mismatch by using the propagation matrix method that was previously applied to the problem of propagating strain in NiO in section 5.5.1. We assume that after excitation, a transient equilibrium state is realized that can locally be well approximated by a Drude-Lorentz model (equation 7.2) with plasma frequency $\Omega_p(z)$. We will briefly summarize the propagation matrix-method by the linear relation

$$
\left(\begin{array}{c}
E^+_{\omega,M} \\
E^-_{\omega,M}
\end{array}\right) = P_{M-1} \left(\begin{array}{c}
E^+_{\omega,0} \\
E^-_{\omega,0}
\end{array}\right), \quad \text{with} \quad P_M = \left(\begin{array}{cc}
\alpha & \beta \\
\gamma & \delta
\end{array}\right) = \prod_{m=M}^{0} p_m. \quad (9.3)
$$

Here, $P_{M-1}$ is a $2 \times 2$ matrix connecting the right- and leftward propagating fields at slice 0 with the fields in slice $M$. The reflected field $E^-_{\omega,0}$ can be solved for using the boundary conditions for a semi-infinite volume $E^-_{\omega,N+1} = 0$, $E^+_{\omega,0} = E_0$ and introducing a vacuum layer in front with $\hat{n}_0(\omega) = 1$. The propagation matrix $P_M(t)$ is calculated as the result of propagation through $M$ thin slices of the material of thickness $\Delta$, where propagation through a single slice is given by equation 5.9 and 5.10. Equation 9.3 can then be solved for the THz-reflectivity $r(\omega) = \frac{E^-_{\omega,0}}{E^+_{\omega,0}} = -\frac{\gamma}{\delta}$. This allows to deduce the complex loss function $\mathcal{L}(\omega)$ from $r(\omega)$ in the same way as for the experimental results.

The excitation pulse locally introduces an increase in carrier density $\Delta N_e(z)$. For our simulation we vary the penetration depth, but hold the maximum density of introduced carriers at the surface at a fixed value such that the maximum plasma frequency is $\Omega_p^{\text{max}} = 3\Omega_p^0$. The results are shown in figure 9.8.

For very short penetration depths, the equilibrium loss function is only slightly distorted towards higher frequencies and the THz pulse is mostly probing the unperturbed bulk material. For penetration depths above 5-10 $\mu$m the loss function converges to the one expected from a homogeneously excited material. In between these regimes, there is a washed-out transition showing badly defined modes. The measurement shown in figure 9.7 at an excitation wavelength of 1500 nm have been acquired in this regime [248] and the effect of the penetration depth mismatch shown here is likely to explain these observations. The measurements on long timescales in figure 9.6, nonetheless, show well defined peaks. This can be attributed to diffusion that recovers homogeneity on timescales of several hundred picoseconds. Additionally, at higher fluences, the Drude-Lorentz response is less strongly influenced by a difference in $N_e$, thus making the loss function less sensitive to excitation mismatch. This effect also allows the photo-screening method in section 9.2.1 to yield useful results. Using the idler wave of the OPA would allow to achieve penetration depths above 1.5 $\mu$m, which according to our simulations may lead to significant improvement of the response, but still hinders a direct quantitative measurement of the intrinsic loss.

\[\text{This implies that we also assume constant effective masses of equilibrium and excited carriers.}\]
Figure 9.8: The simulated real (a) and imaginary part (b) of the reconstructed loss function $L(\omega)$ of InAs based on the propagation method for various penetration depths of the excitation pulse. The arrow in b) indicates the penetration depth of a 1500 nm pulse as was used in the experiments in figure 9.7.

9.4 2D THz-spectroscopy on InSb and InAs

Nonlinear spectroscopy could be of great interest for the study of quasi-particles in correlated systems that arise from coupling of different degrees of freedom, such as electron-phonon, phonon-phonon, electron-magnon, but also electron-electron and magnon-magnon coupling. In particular measurements in a two-dimensional scheme allow to differentiate between causal relationships or mere correlations between various degrees of freedom. In the THz-range of electric fields, 2D spectroscopy has previously been realized in the time-domain at frequencies around 20 THz at MV/cm fields, where non-resonant Rabi-flopping [185, 184, 183, 235], two-phonon quantum coherences and higher-order photon coherences were observed [155, 235] as well as at frequencies around 1 THz in magnetically ordered insulators [239] and in the gas phase [238]. The latter systems show very high oscillator fidelity, much longer than the transient driving fields, which
enables to interpret these results using methods that have been established for nuclear-magnetic resonance and 2D infrared spectroscopy [231].

Many quasi-particle modes are, however, strongly broadened due to efficient coupling to other degrees of freedom, which requires to be able to evaluate 2D time-domain data in the presence of the transient driving field. Intending to develop techniques that allow to interpret this regime, we will in the following focus on the THz response of more basic systems. Plasmonic excitations in semiconductors are known to show strong THz-nonlinearities and a large amount of experimental work on field-nonlinearities in semiconductors has been carried out over the last 20 years using Fourier transform infrared-spectroscopy or phase sensitive electro-optic detection of transient THz fields. The effects of carrier multiplication in InSb (section 6.5), intervalley scattering in InAs (section 6.5) and band tunneling in GaAs (section 6.1) have been well characterized [133, 119, 249], but the immediate nonlinearities in InSb and InAs on timescales of the transient driving field were only recently addressed [126, 163, 164, 125].

In section 9.4.2, we present 2D THz experiments in the range between 1-10 THz investigating the electronic band-nonlinearities of InSb and InAs on timescales of few picoseconds. To evaluate such datasets in the temporal overlap regime, we simulate our experiments in time using the finite-difference time-domain technique (FDTD), that will be introduced in section 9.5.2 and readily treats the temporal overlap regime, can solve the equation of motion of the material response and is not limited to the perturbation limit.

9.4.1 Impact ionization and intervalley scattering in InSb and InAs

Using the experimental setup described in section 8.4.1, we started by acquiring THz-excitation – THz-probe data on InSb for long timescales. The results for excitation delays up to 200 ps are shown in figure 9.9. The DSTMS-generated excitation pulse $E_2$ was filtered using a sheet of PTFE and a 2 mm thick Germanium wafer to warrant that no residual optical light reaches the sample.

In the nonlinear signal $E_{NL}$, we observe two clearly distinguishable temporal domains of a transient response with a width of about 1.2 ps (FWHM), as well as a persistent increase of the signal with a rise-time of 7.5 ps. The integrated spectral signal corresponding to the signal $E_{12} - E_2$ can be monitored to observe the overall reflectivity. The data indicates that this total reflectivity is continuously increasing. In the spectral range between 0.5 and 7 THz an average increase in reflectivity of 12% is reached at a delay of $\tau = 20$ ps.

The continuously increasing integrated reflectivity on timescales exceeding the overlap of the pulses indicates an increase in the material’s plasma frequency (see equation 7.1). This can be achieved by either a decrease in effective mass or an increase in carrier density. The former is not allowed by the band structure of InSb (section 7.2) as the equilibrium carriers in the $\Gamma$-valley already possess the lowest available effective band mass. Hence, this strongly indicates an increase in carrier density by impact ionization (section 6.5) as was previously reported by Hoffmann et
9.4 2D THz-spectroscopy on InSb and InAs

![Graph showing 2D THz experiments on InSb for long timescales.]

**Figure 9.9**: 2D THz experiments on InSb for long timescales. The lower graph shows the nonlinear field $E_{NL}$ from equation 8.16 for cross-polarized beams relative to the peak field of $E_{12}$. The DSTMS excitation field was $E_2 = (112 \pm 8)$ kV/cm while the plasma probe field was $E_1 = (27 \pm 7)$ kV/cm. The integrated spectral signals are shown in the upper graph. The overall reflectivity of $E_1$ continuously increases after excitation on the order of $10^{-1}$. The nonlinear signal consists of a transient effect and an exponential increase. Fitting the Gaussian feature results in the parameters: $t_0 = (0.85 \pm 0.05)$ ps, $\sigma = (0.50 \pm 0.05)$ ps, and the exponential fit has a rise time of $\tau = (7.5 \pm 0.4)$ ps.

al. [133] and Ho et al. [163, 164]. Our fitted value for a rise of the persistent reflectivity signal of $(7.5 \pm 0.4)$ ps agrees with the value of 7 ps measured by Hoffmann et al.. Interband tunneling would provide an additional mechanism for electron-hole pair generation, but can be ruled out by the long timescale of the signal increase.

In InAs, we can also observe a persistent increase in overall reflectivity for fields of $E_2 = (112 \pm 8)$ kV/cm similar to the observations in InSb. However, when decreasing the applied excitation field, one can observe a transition to a different response regime that is shown in figure 9.10. For fields of $(75 \pm 5)$ kV/cm, we mainly observe a transient response where equilibrium reflectivity is almost restored after 10 ps. The nonlinear transient can be roughly approximated by an exponential decay of time-constant $\tau = (3.5 \pm 0.2)$ ps. Particularly interesting about this response is, that the overall integrated reflectivity of $E_{12} - E_2$ significantly decreases below the equilibrium values for a duration of about 6 ps.
Figure 9.10: 2D THz response of InAs on timescales up to 10 ps acquired under similar conditions as in figure 9.9 but with an excitation field \( E_2 = (75 \pm 5) \text{kV/cm} \). Here, the transient nonlinear signal (shown in red diamonds) shows a fast increase, followed by a decay with \( \tau = (3.5 \pm 0.2) \text{ps} \) (exponential fit to the nonlinear signal) and the integrated signal in the Fourier domain of the absolute reflectivity of field \( E_1 \) (blue diamonds) decreases for a duration of about 6 ps compared to the unexcited value. Afterwards, equilibrium conditions appear to be recovered.

This is a strong indication for a decrease in plasma frequency caused by an increase in carrier effective mass through intervalley scattering (section 6.3). While ballistic transport (section 6.2) also leads to a decrease in effective mass, as the conduction band curvature decreases for \( k > 0 \), the persistence of the reduced plasma frequency appears too long. Ballistic transport is connected to a band dipole moment, hence the population would recover to the conduction band on the timescale of the inverse plasma-edge frequency \( 2\pi \epsilon_\infty / \Omega_p \). Carrier heating may also lead to electron population at higher effective masses, but in thermal equilibrium, the carrier density would at the same time increase and thus not lead to a reduced plasma-frequency.

With an energy gap of 1.1 eV separating the \( \Gamma \)-valley and the next highest \( L \)-valley, intervalley scattering as discussed in section 7.2 is the most plausible mechanism. For this transition the effective mass of a sub-population of carriers changes from \( m_e^*(\Gamma) = 0.026 \) to \( m_e^*(L) = 0.29 \) \( m_e \) by more than an order of magnitude and hence the transferred carriers can no longer significantly contribute to the conductivity. These carriers are trapped there for some time until they scatter back to the \( \Gamma \)-valley with the assistance of a phonon [241]. This observation was previously made.
by Fan et al. [249] in GaAs and by Ho et al. [163] in InAs. The latter also showed that for higher fields impact ionization also contributes to the change in THz reflectivity which is in accord with our observations.

In InSb, we could not observe signs of a decrease in plasma frequency on timescales above the overlap region. Although intervalley scattering is likely to be present, impact ionization dominates the THz response in this material for fields between 20 and 112 kV/cm.

### 9.4.2 Nonlinear mixing in InSb and InAs

In the last section, we identified impact ionization and intervalley scattering in the THz-response of InSb and InAs, that represent two rather well studied phenomena in these materials. But the discussion of the immediate overlap region of the two THz-pulses has so far been omitted. This is now going to be at the focus of the remainder of this work.

In figure 9.9 and 9.10, we observed an increase in the nonlinear signal at the time of the field overlap. As our experimental setup (section 8.4.1) is capable of providing phase-resolved measurements of the THz fields, we will now study the nonlinear signal in the overlap region when both driving fields and the polarization decay of the material are present.

Figure 9.11 shows an example of the data collection method described in section 8.4.1 in the overlap region on InSb using peak fields of $E_1 = (34 \pm 9)$ kV/cm and $E_2 = (52 \pm 4)$ kV/cm. The field calibration and estimation of error is discussed in more detail in the following section 9.4.3.

The single field measurement $E_1$ shows a constant phase at a given detection delay $t$, while $E_2$ varies according to its excitation delay following the diagonal $t + \tau = \text{const}$. The nonlinear component of the signal shown in the lower right reaches 13% of the magnitude of the combined signal $E_{12}$ and is thus comparable to the residual field of $E_2$ that enters the detection. The lower half of this nonlinear signal, at $\tau > 2$ ps, shows a vertical structure only slowly changing in excitation delay, which can be understood as a persistent change of the reflectivity of $E_1$ induced by $E_2$. These changes can for InSb be attributed to impact ionization (section 9.4.1) and may be classified as an incoherent contribution to the signal.

In the overlap region of the two pulses, the strong nonlinear response shows a clear dependence on the relative phase between the two fields. In particular, the response appears to be modulated at a frequency close to the equilibrium plasma-edge frequency (section 9.2.1), but also contains additional frequency components. To separate these various contributions, we can continue to study the response in the two-dimensional frequency domain.

Two-dimensional Fourier transformations of 2D THz time-domain measurements on InSb, InAs and GaSb are shown in figure 9.12, 9.13 and 9.14, respectively. Here, the 2D-frequency plane is only shown for positive frequencies $\nu_t$ corresponding to the conjugate of realtime $t$ in which the fields $E_1$ and $E_2$ evolve. The transformation along this coordinate is therefore perfectly antisymmetric. However, the spectrum is not symmetric in $\nu_\tau$ as the phase-front of pulse $E_2$ is...
Figure 9.11: 2D THz signal acquired in reflection from InSb using peak fields of $E_1 = (34 \pm 9)$ kV/cm and $E_2 = (52 \pm 4)$ kV/cm. The color indicates the signal in detected voltage (V). The nonlinear field $E_{NL}$ reaches a magnitude of 13% of $E_{12}$. As described in section 8.4.1, the nonlinear 2D THz signal is extracted from ABCD-measurements of the combined field $E_{12}$ by subtracting the sequentially measured fields $E_1$ and $E_2$. The dataset shown above consists of about $7 \times 10^4$ data points acquired using well above $10^7$ laser pulses.
9.4 2D THz-spectroscopy on InSb and InAs

**Figure 9.12**: 2D THz measurement on (100)-surface oriented InSb with peak fields $E_1 = (34 \pm 9)$ kV/cm and $E_2 = (52 \pm 4)$ kV/cm, where $E_1$ is aligned along the (010)-direction. The plot shows the same data as in figure 9.11 in percentage of the peak field of $E_{12}$. The 2D Fourier transformation is shown in (a.u.) and is based on the time-domain data shown to the left using an error-function-shaped windowing to suppress artificial high-frequency components from the boundaries. The red circles indicate the positions of potential SHG and OR of frequency $\nu_p$ that are absent in our measurement.

Features in the spectrum are in the following going to be addressed using $(\nu_t, \nu_\tau)$. For example in figure 9.12, one can observe strong features at $(\nu_p, 0)$ and $(\nu_p, \nu_p)$, where $\nu_p = 1.92$ THz. These features do not appear exactly at the plasma-edge frequency of 2.21 THz, but rather at the position corresponding to the strongest gradient in reflectivity, see section 9.2.1. In addition to these strong signals, one can observe weaker features at $(\nu_p, -\nu_p)$ and $(\nu_p, 2\nu_p)$. And, remarkably, we can also observe a faint set of features connected to the longitudinal phonon frequency $(\nu_{LO}, 0)$, dependent on both $\tau$ and $t$ and thus aligns along the diagonal in the time-plane in the same way as in the frequency-plane. The solid red lines in the Fourier plane indicate the position of the 2D spectra of the linear fields $E_1$ and $E_2$. In the nonlinear signal $E_{NL}$ these lines indicate persistent changes to the reflectivity. A persistent pump-probe effect of $E_1$ on $E_2$ for example would lead to a signal on the positive diagonal, while the opposite effect would lead to signal on the horizontal axis. For signals depending on the relative phase between the two fields, combination tones will appear in the spectrum. These may be identified by Liouville pathways of different orders in perturbation theory [235, 231], yet, for now we do not intend to follow this description since one can see from figure 9.11, that the encountered nonlinearities are in excess of 10% of the combined signal and hence beyond the perturbative regime.
Chapter 9: Time-resolved THz-spectroscopy

InAs

$$(\nu_p, 2\nu_p)$$
$$(\nu_p, \nu_p)$$
$$(\nu_p, 0)$$
$$(\nu_p, -\nu_p)$$
$$(\nu_{LO}, 0)$$

Figure 9.13: 2D-THz measurement on (100)-surface oriented InAs with fields $E_1 = (67 \pm 18)$ kV/cm and $E_2 = 60$ kV/cm. The field $E_1$ is aligned along the (010)-direction. The time-domain data is shown in percentage of the peak field of $E_{12}$. The incoming polarization of $E_2$ on the WG-beam-combiner was here set to 41°.

$$(\nu_{LO}, \nu_p)$$ and $$(\nu_{LO}, 2\nu_p)$$, where $\nu_{LO} = 5.70$ THz. Potential THz second-harmonic would appear at frequencies $(2\nu, \nu)$ as it is a real field emitted in time $t$ of twice the incoming frequency of the contributing field component of $E_2$. Optical rectification may for the same reason also be observed at $(0, \nu)$. This was observed by Lu et al. [239] in ferri-magnetic systems and is in general also symmetry-allowed in the III-V semiconductors (table 2.4), but the non-zero tensor components are $\chi^{(2)}_{ijk}$ where $i \neq j \neq k$ and therefore the second order polarization vanishes in normal-incidence on a (100)-surface.

In a measurement on InAs, similar features as for InSb can be observed. Here, the positions in the 2D spectrum appear shifted by the respective difference in plasma-edge frequency of the two materials. In the time-domain measurement shown in figure 9.13, a diagonal structure in the nonlinear signal indicates a pump-probe effect from $E_1$ on $E_2$ which is plausible as both field amplitudes are of comparable magnitude. Features at $(\nu_p, 0)$, $(\nu_p, 2\nu_p)$, $(\nu_p, \nu_p)$ and $(\nu_p, -\nu_p)$ can be observed, but the latter two show a split structure. This can be tentatively assigned to an interference fringe in the spectrum of the incoming $E_2$ introduced by the reflection from the wire-grid beam-combiner at the specific polarization angle used in this measurement. This is discussed in more detail in section 9.5.4.

In figure 9.14 we also carried out measurements on GaSb that has a majority of heavy-hole carriers of effective mass $m_h^* = 0.4 m_e$ (table 9.2). Here, the observed nonlinear response is
Figure 9.14: 2D THz measurement on (100)-surface oriented GaSb with peak fields $E_1 = (67 \pm 18) \text{kV/cm}$ and $E_2 = (112 \pm 8) \text{kV/cm}$. The field $E_1$ is aligned along the (010)-direction. The time-domain data is shown in percentage of the peak field of the combined signal $E_{12}$.

much weaker than in InSb or InAs and corresponds to slightly above 1% of the combined field signal. The response can be separated into an immediate overlap signal at $(\nu_p, 0)$ and a persistent broadband increase along the $(\nu_t, 0)$-axis. Again, the dominant spectral feature appears at the plasma-edge frequency in this material (table 7.2). The measurement also shows the noise floor of the experiment that in the time domain corresponds to a relative error of $3 \times 10^{-3}$ at the peak of the plasma THz field while the noise floor is about 5 times lower in the absence of the THz pulse. This behavior can be understood by considering the ABCD process described in equation 8.10 where $I_{\text{probe}}(E_{\text{THz}} + E_{\text{DC}})$ enters the signal quadratically and higher fields hence increase the absolute noise in the difference signal. Chopping at 250 Hz limits the error due to drifting signal, nonetheless, pulse-to-pulse fluctuations are not corrected for in this setup. This and the quadratic dependence described above make ABCD inferior to EO sampling (section 8.2.1) in terms of signal-to-noise. Measurements on GaAs were also carried out at a field of $E_2 = 120 \text{kV/cm}$ but did not show nonlinear response exceeding this noise floor.

From our observations we can conclude that the low band gap semiconductors show strong nonlinearities in their response to transient electric fields. In the 2D spectrum these present a complex structure of combination tones of the elementary infrared active excitations in the material: the plasmon-edge and phonon modes. As the signal vanishes for GaAs and is strongly reduced for GaSb in comparison to InAs and InSb these observations are likely to be connected to the gap energy and the effective mass of the conduction band carriers.
9.4.3 Field dependence of 2D THz-spectra

Further insight can be gained by studying the field dependence of the spectral response. We will briefly discuss the experimental implementation of the field strength variation as this has some implications on the observed signal.

The plasma-generated THz $E_1$ is horizontally polarized, while the DSTMS source is set to generation of vertically polarized THz fields $E_2$. The vertically aligned wire-grid beam-combiner (BS) described in section 8.4.1 therefore fully transmits $E_1$ (horizontal polarization) and fully reflects $E_2$ (vertical polarization). For the attenuation of field $E_2$ we inserted an additional wire-grid polarizer in the beam path of $E_2$. This effectively attenuates the vertical component of $E_2(x)$, but also leads to a rotated horizontal component along $E_2(y)$. Therefore, reflection from the wire-grid does not only lead to an attenuated field in vertical $x$-direction, but also to an additional $y$-component along the horizontal direction due to $p$-reflection from the polyethylene-substrate of the wire-grid and its back-surface. This creates a slightly elliptical beam where the weaker horizontal component shows interference arising from the front and back-surface of the polyethylene.

The THz overlap at the sample position was achieved using a $(300 \pm 50) \mu$m pinhole pinched into an aluminium foil at the sample position that was imaged using an OAPM behind the sample position and a two-dimensional bolometer array. The alignment was optimized for transmitted total signal.

**Figure 9.15:** 2D THz-spectroscopy as a function of vertical excitation field strength $E_2$ with $E_1 = (34 \pm 9) \text{kV/cm}$. The wire-grid polarizer angles (WG1) with respect to the vertical plane are indicated in brackets.
Calibration of the electric fields was done after the acquisition of the 2D THz-spectra which were carried out over the range of several weeks in which the OPA output power gradually dropped by 13%. This led to an inherent systematic error of these field measurements. The electric field values were detected with electro-optic sampling according to equation 8.8 in a 100 µm thick GaP crystal at the sample position using a small fraction of the 1200 nm ABCD sampling beam. The two focal-points of \( E_1 \) and \( E_2 \) were found to deviate in depth \( z \) by about 2 mm. We choose to give the mean value of the field measurements at these two positions throughout this chapter and the difference to this value as error of the measurement. This yields relative errors in the plasma field of \( \Delta E_1/E_1 = 0.26 \) and for the DSTMS field \( \Delta E_2/E_2 = 0.07 \). The spectra of \( E_1 \) and \( E_2 \) are shown in figure 8.3 and 8.1, respectively. Note that the EO sampling is not sensitive to spectral components above 7 THz thus systematically underestimates the real field in particular for \( E_1 \). On the other hand, \( E_1 \) has at the same peak field a lower spectral amplitude at the plasma-edge frequency, therefore may interact less strongly with the medium.

For the measurements on InSb we varied the vertical excitation field \( E_2 \) from 35 to 80 kV/cm by rotation of the first wire-grid polarizer (WG1) while keeping the peak field of \( E_1 \) constant at \((34 \pm 9) \) kV/cm. The time-domain data and their respective 2D Fourier transformations are shown in figure 9.15 where we can qualitatively observe a transition from a regime of well defined spectral features to a step-like increase in reflectivity for the highest fields, resulting in a broadband structure along the excitation frequency. The latter can be explained by fast carrier multiplication from impact ionization that also manifests itself in the pump-probe response on \( E_1 \) at \((\nu_{LO}, 0) \) shown in figure 9.16 b).

![Figure 9.16](image-url)

**Figure 9.16:** The field dependence of peak \((\nu_{LO}, 2\nu_p) \) (a) and \((\nu_{LO}, 0) \) (b) in InSb. While \((\nu_{LO}, 0) \) strongly increases with field, the feature at \((\nu_{LO}, 2\nu_p) \) appears to be suppressed at the same time. The graphs show the fitted amplitudes using two-dimensional Gaussian functions. Lines are shown to guide the eye.
Measurements on the weak combination tone \((\nu_{\text{LO}}, 2\nu_p)\) show a suppression of this feature at the highest fields as shown in figure 9.16. Suppression of narrow features connected to the plasma-edge frequency can, however, be expected as impact ionization leads to a swift shift of the plasma frequency and the transition from \(\nu_{\text{TO}}\) to the upper coupled mode \(L_+\) (section 9.3).

The combination tone at \((\nu_p, 2\nu_p)\) shows within the uncertainty no clear trend over the studied field strengths. The peaks \((\nu_p, \nu_p)\) and \((\nu_p, -\nu_p)\) seem to decrease with increasing fields \(E_2(x)\). This could, however, be connected to the rotated field component \(E_2(y)\) that is reduced for lower angles of WG1. The simulations in section 9.5.4 will be able to take into account this effect which presents a somewhat unnecessary experimental complication.

### 9.4.4 Separating even and odd \(E_2\)-parity components of the nonlinear signal

In the following, we will discuss an experimental method that provides additional information about the spectral features by analysis of their dependence on parity with respect to one of the excitation fields. For this we take two consecutive 2D THz measurements with inverted polarities \(E_2\) and \(\overline{E}_2\) which can experimentally be realized by simply turning the OR crystal by 180°. Separation between odd \((E^-)\) and even \((E^+)\) components of the nonlinear signal \(E_{\text{NL}}\) can then be made. A similar approach was followed for single-trace measurements by Ho et al. [163, 164]. For a 2D measurement, this requires acquisition of 5 different field combinations

\[
E^{\pm} = (E_{12} - E_1 - E_2) \pm (E_{1\overline{2}} - E_1 - E_{\overline{2}}),
\]

where \(\overline{2}\) indicates the inverted polarity of \(E_2\). Contributions following \(\propto E_2^{2n}\) which include the incoherent contributions of carrier multiplication and intervalley scattering on \(E_1\) add to the even signal, while signals \(\propto E_2^{2n-1}\) contribute to the odd signal. The time-domain data for measurements on InSb at a field strength of \(E_2 = 52\) kV/cm is shown in figure 9.17.

Results for \(E^-\) and \(E^+\) acquired on InSb and InAs are shown in the Fourier domain in figure 9.18. In \(E^+\) and \(E^-\) one can observe a separation of the spectral features in figures 9.12 and 9.13 into signals of different parity with respect to \(E_2\). The peaks at \((\nu_{\text{LO}}, 2\nu_p), (\nu_p, 2\nu_p)\) and \((\nu_{\text{LO}}, 0)\) are only contained in \(E^+\) and are thus found to be of purely even parity. This is expected for the latter peak, as incoherent contributions changing the carrier population would lead to a change in screening of the phonon-mode. The same incoherent effect also leads to a strong change of the plasma-edge frequency and therefore to the strong feature \((\nu_p, 0)\) that dominates the even parity signal.

By definition, \(E^-\) only contains the signal components that follow the phase of \(E_2\) which are experimentally found only for features at the plasma-edge frequency \((\nu_p, \nu_p), (\nu_p, 0)\) and \((\nu_p, -\nu_p)\). Remarkably, the latter feature appears only in the odd signal where the \((\nu_p, \nu_p)\) component is strongly pronounced compared to the even signal. This peak in the \(E^+\) signal of InSb and InAs at 56 kV/cm is likely caused by an amplitude drift between the polarity inverted \(E_2\) and \(\overline{E}_2\). Such an
9.4 2D THz-spectroscopy on InSb and InAs

Figure 9.17: Parity sensitive 2D THz-spectroscopy on InSb shown in the time-domain at field strengths of $E_1 = 34$ kV/cm and $E_2 = 52$ kV/cm. Relative values are given with respect to the peak field of $E_{12}$. Both measurements of $E^-$ and $E^+$ are based on the same dataset evaluated according to equation 9.4.

Experimental misbalance leads to leakage between odd and even signals which can also be observed along the 0 excitation-frequency line in the $E^-$ measurements of InAs. Leakage of the strong even parity $(\nu_p,0)$ peak may easily dominate the odd parity signal at these frequencies. Nonetheless, the odd signal $E^-$ shows clear features at $(\nu_p,\nu_p)$ and $(\nu_p,-\nu_p)$ for both semiconductors at lower fields, which get reduced and possibly shifted towards lower frequencies at fields of $E_2 = 87$ kV/cm.

Now, what can be learned from these observations? On the one hand, calculating the odd signal provides a means to suppress incoherent contributions to the nonlinear signal, as well as any coherent contributions with even parity in $E_2$. On the other hand, using a perturbative treatment in orders of $\chi^{(n)}$, the method also provides information about the order of field $E_2$ contributing to the signal.

We can briefly discuss the currently established description of these processes that is based on perturbation treatment and was in the context of phase-resolved 2D THz-spectroscopy used by Kuehn et al. [232] and Lu et al. [238, 239]. The underlying idea is that the process can be described by linear combinations of single interactions between a field and a state that can exchange quanta. According to their relation to the delays $t$ and $\tau$, the two fields $E_1$ and $E_2$ then appear as horizontal $k_1$ or diagonal vectors $k_2$ in the two-dimensional frequency plane, respectively. Examples of several nonlinear mixing processes using this depiction are shown in figure 9.19.
Figure 9.18: Odd and even parity spectra of InSb and InAs at different field amplitudes of $E_2$. The relative magnitudes are given with respect to the spectral peak signal of field $E_1$. The color scale is cut off at 6.5%, peak values beyond this value are indicated in the graph. Solid lines along the horizontal and the diagonal correspond to the spectral regions that solely follow the phase of either $E_1$ or $E_2$. Broken lines indicate combination tones of the plasma-edge and phonon features in the two different semiconductors.
9.5 Simulating the nonlinear electronic response in the time-domain

In section 9.3.2 we used the propagation matrix model to simulate linear propagation through inhomogeneous media and expanded the method in section 5.5.1 to even include nonlinear effects.
arising from weak coupling. Being derived from the wave-equation, these methods are, however, intrinsically linear and not suitable to describe a strongly-interacting system of material and fields. For that we may directly solve the time-dependent Maxwell’s equations in the presence of an interacting medium. This fundamental approach treats broadband sources and inhomogeneous and nonlinear media in a natural way.

One of the most successful approaches in order to solve this complex task is found in the finite-difference-time-domain method (FDTD) first derived by Yee\(^5\) [250]. The method solves Maxwell’s partial derivative equations in space and time on a discretized grid using central differences. For a comprehensive overview over the method and its implementation in three dimensions the reader may be referred to the book by Taflove and Hagness\(^6\) [251]. A description of a polar semiconductor’s ballistic response to electric fields for propagation in one dimension together with an FDTD implementation thereof is shown in the following.

### 9.5.1 Modeling ballistic transport in the THz range

We start with Maxwell’s \(\text{rot}\)-equations, i.e. Faraday’s and Ampère’s laws

\[
\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}. \tag{9.5}
\]

By restricting the problem to transverse electromagnetic modes with propagation in \(z\)-direction and assuming that any occurring material is non-permeable\(^6\) we get

\[
\frac{1}{\mu_0} \begin{pmatrix}
\frac{\partial E_x}{\partial z} \\
\frac{\partial E_y}{\partial z}
\end{pmatrix} = -\begin{pmatrix}
\frac{\partial H_x}{\partial t} \\
\frac{\partial H_y}{\partial t}
\end{pmatrix}, \quad \begin{pmatrix}
\frac{\partial H_x}{\partial z} \\
\frac{\partial H_y}{\partial z}
\end{pmatrix} = \begin{pmatrix}
\frac{\partial D_x}{\partial t} \\
\frac{\partial D_y}{\partial t}
\end{pmatrix}. \tag{9.6}
\]

The electric field \(\mathbf{E}\) is connected to the displacement field \(\mathbf{D}\) via the material polarization \(\mathbf{P}\), which hence contains all information about the electromagnetic properties of the material. The low band gap III-V semiconductors can in the THz-range be described by

\[
D_{x,y}(z) = \epsilon_0 \epsilon_\infty E_{x,y}(z) + P_{x,y}^{(ph)}(z) + P_{x,y}^{(e)}(z), \tag{9.7}
\]

where \(\epsilon_\infty\) gives the background permittivity due to high frequency excitations. \(P^{(ph)}\) is the polarization arising from the polar optical phonon which in the time-domain follows the differential equation

\[
\frac{\partial^2 P^{(ph)}}{\partial t^2} + \gamma_{ph} \frac{\partial P^{(ph)}}{\partial t} + \omega_{ph}^2 P^{(ph)} = \left(\omega_{LO}^2 - \omega_{TO}^2\right) \epsilon_\infty E_{x,y}. \tag{9.8}
\]

The definitions are given in equation 7.2, where \(\left(\omega_{LO}^2 - \omega_{TO}^2\right)\epsilon_\infty\) corresponds to the oscillator strength. \(P^{(e)}\) represents the polarization due to free carriers. While the first two terms in 9.7 are here implemented as linear responses, the electronic polarization is going to show field

\(^5\)The method is therefore often referred to as Yee’s method.

\(^6\)For InSb this assumption may have to be reconsidered for higher fields [242].
dependence. In the dipole approximation, the change in polarization can be written in terms of the group velocity $v$ of the many-particle electronic wave-packet

$$(9.9)$$

$$ \dot{P}^{(e)} = -N_{e} ev. $$

The group velocity is defined through its dispersion relation given by the band structure. We can thus write [125]

$$ v(k) = \frac{1}{\hbar} \frac{\partial \mathcal{E}(k)}{\partial k}, \quad (9.10)$$

where $\mathcal{E}(k)$ represents the energy dispersion of the dominant carrier band, which is the conduction band for the semiconductors considered here. It is straightforward to implement further contributing bands. For Bloch electrons, the equation of motion in the electric field $E$ can be written as (see section 6.2) [123, 124, 125]

$$ \hbar \ddot{k} + \gamma_{e} \hbar k = -eE, \quad (9.11)$$

where $\gamma_{e}$ is the electronic scattering rate. In reality, the scattering rate is a function of $\mathcal{E}$ and thus of $k$ as shown in figure 6.3, but is here approximated as constant. Equations 9.7 to 9.11 capture the physical concept of ballistic transport (section 6.2) and can even lead to Bloch oscillations (section 6.4) but do not include scattering phenomena arising from electron-electron scattering (section 6.5), electron-phonon scattering (section 6.3) or interband tunneling (section 6.1). Implementation of these additional effects would require a sub-division of the electronic population that is best achieved using a Monte-Carlo approach [112].

### 9.5.2 Finite-difference time-domain calculation (FDTD)

The coupled differential equations above can be translated into a one-dimensional central finite-difference description of the fields $E$, $D$ and $H$ on a grid in time $t$ and space $z$ separated by steps $\Delta t$ and $\Delta z$, respectively. In the transverse electromagnetic field approximation only perpendicular fields in $x$ and $y$ direction are of concern. The ordering of fields on the FDTD grid is depicted in figure 9.20. Staggered time and space is indexed using $l$ and $n$, respectively.

---

7This is merely a simplification and not a requirement of the FDTD method.
The Yee algorithm commonly starts with the calculation of $\mathbf{H}(k)$ and $\mathbf{D}(k)$ by a finite-difference approximation of equation 9.6

$$
H_{x}^{l+\frac{1}{2}}(n-1/2) = H_{x}^{l-\frac{1}{2}}(n-1/2) + \frac{\Delta t}{\mu_0 \Delta z} \left( E_{y}^{l}(n) - E_{y}^{l}(n-1) \right),
$$

$$
H_{y}^{l+\frac{1}{2}}(n-1/2) = H_{y}^{l-\frac{1}{2}}(n-1/2) - \frac{\Delta t}{\mu_0 \Delta z} \left( E_{x}^{l}(n) - E_{x}^{l}(n-1) \right). \tag{9.12}
$$

And we can calculate the displacement $\mathbf{D}$ due to the magnetic field

$$
D_{x}^{l+1}(n) = D_{x}^{l}(n) - \frac{\Delta t}{\Delta z} \left( H_{y}^{l+\frac{1}{2}}(n+1/2) - H_{y}^{l-\frac{1}{2}}(n-1/2) \right),
$$

$$
D_{y}^{l+1}(n) = D_{y}^{l}(n) + \frac{\Delta t}{\Delta z} \left( H_{x}^{l+\frac{1}{2}}(n+1/2) - H_{x}^{l-\frac{1}{2}}(n-1/2) \right). \tag{9.13}
$$

To continue the series we also need to derive the electric field for the next time-step $E^{l+1}$ from these quantities and the description of the material polarization based on equation 9.7. We start with calculating the various contributions to the polarization. The Lorentz-oscillator can be implemented by introducing the displacement current $J = \partial \mathbf{P}/\partial t$. Equation 9.8 can then be rewritten [252]

$$
J_{ph;x,y}^{l+\frac{1}{2}}(n) = \left[ \frac{2 - \gamma_{ph} \Delta t}{2 + \gamma_{ph} \Delta t} \right] J_{ph;x,y}^{l-\frac{1}{2}}(n) - \left[ \frac{2 \omega_{ph}^2 \Delta t}{2 + \gamma_{ph} \Delta t} \right] P_{ph;x,y}^{l} + \left[ \frac{2 \epsilon_{\infty} (\omega_{LO}^2 - \omega_{TO}^2) \Delta t}{2 + \gamma_{ph} \Delta t} \right] E_{x,y}^{l}(n). \tag{9.14}
$$

The phonon polarization at time step $(l+1)$ then becomes

$$
P_{ph;x,y}^{l+1}(n) = P_{ph;x,y}^{l}(n) + \Delta t J_{ph;x,y}^{l+\frac{1}{2}}(n). \tag{9.15}
$$

The carrier induced polarization can be calculated by an iterative process in order to determine the $k$-vector of the electron population as proposed by Yu et al. [125]. Equation 9.11 can be translated to

$$
k_{x,y}^{l+1}(n) = (1 - \gamma_{e} \Delta t) k_{x,y}^{l}(n) + \frac{\epsilon \Delta t}{\hbar} E_{x,y}^{l}(n). \tag{9.16}
$$

Yet, the difference $(k^{l+1} - k^{l})$ in equation 9.16 is not centered on time step $l$ at which field $E^{l}$ is evaluated and therefore $k^{l+1}$ can only give an approximation of the correct value. A correct central difference formulation is given by [125]

$$
k_{x,y}^{l+1}(n) = \left[ \frac{1 - \gamma_{e} \Delta t}{1 + \gamma_{e} \Delta t} \right] k_{x,y}^{l-1}(n) + \left[ \frac{\epsilon \Delta t}{\hbar (1 + \gamma_{e} \Delta t)} \right] \left( E_{x,y}^{l+1}(n) + E_{x,y}^{l-1}(n) \right). \tag{9.17}
$$

Nonetheless, since $E^{l+1}$ is not yet known, the approximation in equation 9.16 is useful as it can be applied to derive an approximate value of the missing electric field. From equation 9.9 we can calculate the polarization, based on the electronic wave-packet velocity $v$ that can be estimated using the electron wave-vector from equation 9.16 in equation 9.10. To simulate
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nonlinear dynamics, this procedure requires a realistic band structure as given in the following section 9.5.3. For the carrier polarization based on equation 9.9 this yields

\[ P_{l+1}^{e,x,y}(n) = P_{l}^{e,x,y}(n) - N_e \epsilon \Delta t \left( v_{x,y}^{l+1}(n) + v_{x,y}^{l-1}(n) \right), \]  

(9.18)

where, again, the central difference behavior was enforced. We can now write down the approximate electric field for \( l + 1 \) (equation 9.7)

\[ E_{x,y}^{l+1}(n) = \frac{1}{\epsilon_0 \epsilon_\infty} \left( D_{x,y}^{l+1}(n) - P_{ph,x,y}^{l+1}(n) - P_{e,x,y}^{l+1}(n) \right), \]  

(9.19)

Equations 9.17, 9.18 and 9.19 can now be iterated to converge to the correct field value. In a numerical implementation, we can only treat a finite spatial grid and thus have to introduce suitable boundary conditions for the recursive FDTD description given above. A useful choice for these in one dimension is given by the perfectly absorbing boundary condition that prohibits energy flow back into the observation volume. Assuming we choose a grid that fulfills \( \Delta t = \Delta z/(2c) \), where the edges of the observed volume are in vacuum \( (n = 1) \), a perfectly absorbing boundary is achieved by enforcing at grid point \( n_{end+1}^l \) the same magnitude of field that entered the last grid point of the volume at the next to last time step \( n_{end-2}^l \). The same can be applied to the remaining edge. These boundary conditions force the vacuum at the edges to behave homogeneously. In contrast, e.g. the Dirichlet boundary condition \( E_{x,y} = 0 \) would turn the simulation volume into a perfect cavity. The treatment in more than one dimension requires more sophisticated methods [253].

The procedure can be implemented as a single loop in time \( \Delta t \) over equations 9.12 to 9.19 acting on spatial arrays that represent all relevant physical quantities. To simulate a reflection or transmission experiment, the dynamic polarization arrays can be initialized with zeros. A source of predefined fields \( E_{src}(t) \) and \( H_{src}(t) \) can then be injected at a position \( n_{src} \) and the fields evolve in time and space with a well defined velocity of information, travelling here at \( c = \Delta z/(2\Delta t) \).

To acquire reflected and transmitted fields in one dimension, it is straightforward to monitor the fields that arrive at the edges of the calculated spatial volume. An exemplary FDTD simulation on InAs at a fixed time step is shown in figure 9.21. To increase numerical efficiency, the coefficients in equations 9.12 to 9.19 (shown in square brackets) can be pre-calculated. However, they may also be implemented as time-dependent functions by adding corresponding update equations.

---

\[ ^8 \text{This bootstrapping method was derived by Yu et al. [125] that also applied the method to ballistic transport in InSb.} \]
Figure 9.21: FDTD simulation for nearly cross-polarized fields $E_1 = 40 \text{ kV/cm}$ and $E_2 = 60 \text{ kV/cm}$ using the experimental field conditions discussed in section 9.5.4 that are impinging on an InAs sample (shaded area). The fields are shown as solid red lines at a positive delay of $\tau = 1.4 \text{ ps}$, at which the majority of field $E_2$ is already reflected, but right before $E_1$ interacts with the material. The solid blue line indicates the wave vector components of the conduction band carriers. The fine black line depicts the dissipated energy to the material.

9.5.3 Tight-binding model of the band structure

In order to solve equation 9.10 for the carrier velocity for arbitrary field polarizations and propagation directions, we use a tight-binding calculation of the band structure of InAs and InSb written and kindly provided by Georg Winkler and Quansheng Wu\textsuperscript{9}. The model has previously been employed to simulate the impact of strain on conductivity \cite{254} and for microscopic semiconductor structures in external electric fields \cite{255}. The tight-binding method is closely related to the linear combination of atomic orbitals in molecular physics and approximates the band structure by minimizing the total-energy of a system described by a superposition of atomic wave-functions \cite{84}.

Results of the tight-binding calculation for the relevant conduction and hole bands of InSb are shown in figure 9.22. The calculations predict bulk effective masses at the $\Gamma$-point of 0.0159 and 0.0295 $m_e$ for InSb and InAs. These values are slightly higher than the experimental room temperature literature values from table 9.2. To account for the observed plasma frequency according to equation 7.1, the simulations were carried out at adjusted values of the carrier concentration $N_e$ of $7.66 \cdot 10^{15}$ and $19.7 \cdot 10^{15} \text{ cm}^{-3}$ for InSb and InAs, respectively.

For numerical efficiency we limited the implementation of equation 9.10 to treating only the

\textsuperscript{9}Both are affiliated with the Institute for Theoretical Physics and Station Q, ETH Zurich.
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Figure 9.22: Tight-binding calculation of the light-hole (LH), heavy-hole (HH) and conduction bands (CB) in InSb for a projection in (100), i.e. in the $\Gamma \rightarrow X,K$-plane using the critical point nomenclature of the face-centered cubic lattice. The conduction band shown here has been averaged over the two spin-split conduction bands and shows band-minima at $\Gamma$ and along the $X$ and $K$-directions. The lower lying $L$-valley does not lie in this plane and can therefore not be reached in the experimental geometry by purely ballistic transport.

Conduction band carriers in the plane described in figure 9.22. The wave-packet velocity in $k_x$ and $k_y$ directions was pre-calculated from the band structure according to equation 9.10. For this, we generated two sampling grids, a fine one for the innermost 10% of the conduction band around the $\Gamma$-point and a coarser grid covering the full Brillouin zone. The latter is only used for $k$-vectors exceeding the fine grid. To allow for arbitrary query points of $k_x$ and $k_y$, the grid is interpolated using two-dimensional cubic interpolation.
9.5.4 Field-driven nonlinear electronic response using the FDTD-method

Following the FDTD implementation in section 9.5.2 including the band dispersion relation known from the tight binding calculation in the previous section 9.5.3, we simulated the parity-sensitive nonlinear fields $E^+$ and $E^-$ in the same way as the experiments were taken, i.e. by simulating the response for the different field combinations in equation 9.4. The source fields $E^{src}_1$ and $E^{src}_2$ were for numerical efficiency based on the analytic functions

$$E^{src}_1(y) = A_1 e^{-\left(\frac{t-t_0}{t_1}\right)^2} \cos(\omega_1(t-t_0) + \phi_1),$$
$$E^{src}_2(x) = A_2 e^{-\left(\frac{t-t_0+\tau}{t_2}\right)^2} \left[\cos(\omega_2(t-t_0+\tau) + \phi_2) + B \cos((\omega_3(t-t_0+\tau) + \phi_3))\right].$$

(9.20)

We first fitted these functions to the ABC-detected fields in figure 8.3 and 8.1 to achieve a good approximation of the spectrum and in a second step fitted the phases to the electro-optically detected fields at the sample position$^{10}$. The slight ellipticity of attenuated fields $E_2$ that was present in our experiments and was previously discussed in section 9.4.3 could be taken into account by treatment of the non-vanishing substrate $p$-reflectivity of the wire-grid beam-combiner. While assuming perfect $s$-reflectivity $\hat{r}(x) = -1$ along the vertically aligned wires, the $p$-reflectivity $\hat{r}_{HDPE}(y)$ is given by multiple Fresnel reflections from an 80 $\mu$m thick high-density polyethylene substrate of refractive index $n_{HDPE} = 1.52$ at about 45$^\circ$.

Results of the simulated $E^+$ and $E^-$ are shown in figure 9.23 and table 9.3 for InSb using the experimental input fields $E_1$ and $E_2$ with amplitudes of 34 and 52 kV/cm for the experimental polarization conditions. The magnitude of the odd nonlinear signal $E^-$ of 12% of the combined field $E_{12}$ in the time-domain matches within the errors the experimentally observed 13%. This is rather remarkable as we do not take into account the population changing interactions, but it indicates that ballistic transport is likely the dominant effect at these field strengths. In the Fourier plane, we find close resemblance to the experimental data. All experimentally observed peaks are reproduced by the simulation with a comparable relative strength as shown in table 9.3 with the exceptions of the peaks at $(\nu_p,0)$ in the odd signal and $(\nu_p, \nu_p)$ in the even signal, that are likely caused by imperfect inversion of field $E_2$$^{11}$. The two dominant peaks $(\nu_p,0)$ and $(\nu_p, \nu_p)$ are underestimated by 35% to 50%. The combination tones at $(\nu_p, 2\nu_p)$ and $(\nu_{LO}, 2\nu_p)$ are, however, in the simulation both overestimated by a factors of 3.7 and 2.8, respectively.

These discrepancies can be attributed to the incoherent contributions of impact ionization and intervalley scattering which change the plasma-edge frequency observed by $E_1$ and $E_2$ leading to positive contributions to $(\nu_p,0)$ and $(\nu_p, \nu_p)$ and hence also to the overall nonlinear response in the time-domain. The additional decoherence of the field-driven electronic wave-packet induced

$^{10}$The fields are shown in figure 8.3 and 8.1.

$^{11}$Imperfect inversion results in a mixing of the odd and even signal.
9.5 Simulating the nonlinear electronic response in the time-domain

**InSb**

![Figure 9.23](image)

**a)** Simulated odd $E^-$ and even $E^+$ parity signals based on the FDTD implementation of the ballistic band structure dynamics in InSb using the realistic fields applied in the experiment. **b)** Experimental results reprinted from figure 9.18 for comparison. The shown colorscales are given relative to the spectral maximum of the field $E_1$.

Figure 9.23: a) Simulated odd $E^-$ and even $E^+$ parity signals based on the FDTD implementation of the ballistic band structure dynamics in InSb using the realistic fields applied in the experiment. **b)** Experimental results reprinted from figure 9.18 for comparison. The shown colorscales are given relative to the spectral maximum of the field $E_1$. 
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Table 9.3: Comparison of the magnitude of the nonlinear response in InSb between experiment and simulation as shown in figure 9.23. The experimental fields were $E_1 = (34 \pm 9)$ kV/cm and $E_2 = (52 \pm 4)$ kV/cm. The errors of the simulated values correspond to the difference between simulations at the nominal fields and the upper bound of the error bars. All entries refer to the peak values and are given in percent, with the amplitudes $A$ given relative to the spectral maximum $A_{1}^{\text{max}}$ of field $E_1$. Amplitudes of even and odd signals are indicated with (+), (−), respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{\text{max}}/E_{12}^{\text{max}}$</th>
<th>$A^+ (\nu_p,0)$</th>
<th>$A^- (\nu_p,\nu_p)$</th>
<th>$A^-(\nu_p,-\nu_p)$</th>
<th>$A^+(\nu_p,2\nu_p)$</th>
<th>$A^+(\nu_{\text{LO}},2\nu_p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>13</td>
<td>39</td>
<td>8.5</td>
<td>2.0</td>
<td>1.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Simulation</td>
<td>12 ± 2</td>
<td>25 ± 3</td>
<td>4 ± 2</td>
<td>1.3 ± 0.5</td>
<td>7 ± 1</td>
<td>2.5 ± 0.3</td>
</tr>
</tbody>
</table>

in this way can lead to a reduction of the ballistic contribution to the nonlinear signal leading to the lower experimental values for the magnitudes of $(\nu_p,2\nu_p)$ and $(\nu_{\text{LO}},2\nu_p)$. These effects are not taken into account in our calculation as well as experimental drifts and the aforementioned imperfect balancing between $E_2$ and $E_2^{y}$ leading to leakage between $E^-$ and $E^+$. In addition, our calculations did not take into account effects arising from field gradients, which are inherent to the 2D THz method. Here, we only simulated the maximum effect in the focal spot. One may in particular expect that effects of higher order in $E_1$ than in $E_2$ are likely to be poorly reproduced by our simulation as the focus of beam 1 is almost a factor of 2 smaller than of beam 2.

A comparison to the data taken on InAs is shown in figure 9.24. The split structure of the features $(\nu_p, -\nu_p)$ and $(\nu_p, \nu_p)$ in the experiment can also be observed in the simulation. There, it is caused by the interference in the $E_{2,y}$-component reflecting from the wire-grid substrate. The phonon peaks predicted by the simulation are not observed in the measurement at $E_2 = 56$ kV/cm, however, they are visible at slightly higher fields as shown in figure 9.18. Again, we assign the observation of odd $(\nu_p,0)$ and even $(\nu_p,\nu_p)$ features to leakage. As for InSb, we do not observe the odd features at $(\nu_{\text{LO}},\nu_p)$ that are predicted by the simulation. This is likely due to the limited spectral sensitivity at these frequencies. However, we may have observed an indication of this spectral feature in the data shown in figure 9.12.

The strong nonlinearity arising through the conduction band polarization is also reflected in very large excursions of the average electron population in the band structure. The simulated trajectory of the mean conduction band $k$-vector is shown for the front-surface of the material under the experimental field conditions in figure 9.25 a). Average conduction band electron energies above the gap energy of 0.17 eV at room temperature can transiently be achieved. The maximum excursion in $k$ reaches a value above 3% of the zone-edge wave-vector $k_{ZB}$ in the $\Gamma \rightarrow X,K$ plane. This is less than the 10% estimated by Yu et al. using an equivalent calculation in the same material for fields of 100 kV/cm [125]. However, their measurements were carried out at 10 K and hence at a strongly reduced conduction band population and the correspondingly lower plasma resonance frequency while using an excitation frequency of 1 THz which can then
9.5 Simulating the nonlinear electronic response in the time-domain

**Figure 9.24:** a) Simulated odd $E^-$ and even $E^+$ parity signals based on the FDTD implementation of the ballistic band structure dynamics in InAs using the realistic fields applied in the experiment. b) Experimental results reprinted from figure 9.18 for comparison. Although, the phonon peaks in the simulation are not observed in the measurement for $E_2 = 56 \text{ kV/cm}$, they are visible at slightly higher fields as shown in figure 9.18.
apply more work on the conduction band carriers. At room temperature we also observe the onset of impact ionization, which at lower temperatures is a less restrictive limitation [119].

Figure 9.25 b) shows simulations of the integrated odd signal of fully crossed polarized beams at \((\nu_p, \nu_p)\) and the even signal at \((\nu_p, 2\nu_p)\) as function of the azimuthal sample angle \(\phi\). The angle is defined between the polarization of field \(E_1\) and the \(\Gamma \rightarrow X\)-axis. Along the symmetry axes \(\Gamma \rightarrow X\) and \(\Gamma \rightarrow K\) the odd signal vanishes, while the even signal shows only little angular dependence. The maximum of the odd signal is reached at an azimuthal angle of \(\phi = 22.5^\circ\).

Figure 9.26 b) shows simulations at fully crossed polarization for such a sample angle. By comparison to figure 9.26 a), which shows the simulation for fully parallel fields, it is evident that the main contribution to the experimentally observed odd signal is due to the small fraction of parallel polarized light caused by the polyethylene substrate of the wire grid polarizer.

Assuming this can be corrected in the future to make the beams truly cross polarized in the experiment, the odd signal should provide a sensitive measure for the anisotropy of the band structure. The even signal then measures the amount of deviation from band harmonicity. This is schematically depicted in figure 9.27, where different potential symmetries are compared. For large excursions from the \(\Gamma\)-point in non-parabolic bands that are driven e.g. by field \(E_2\), the lateral band curvature at wave-vector \(k_2\) differs from the equilibrium value and thus the effective mass experienced by \(E_1\) changes, leading to a nonlinear response. For isotropic potentials and along the symmetry points of arbitrary band shapes, as shown in figure 9.27, this response is
9.5 Simulating the nonlinear electronic response in the time-domain

Figure 9.26: a) FDTD-simulated odd $E^-$ and even $E^+$ parity signals using fully parallel fields $E_1$ and $E_2$. b) Simulations for perfectly cross-polarized fields $E_1$ and $E_2$ aligned along a sample angle of $\phi = 22.5^\circ$, right in between the symmetry axes. Here, one can find significant odd signal arising from the local radial curvature of the conduction band along the trajectory as indicated in figure 9.25 b). For angles aligned along one of the symmetry axes $\Gamma \rightarrow X$ and $\Gamma \rightarrow K$, at rotation angles of $\phi = 0^\circ$ or $45^\circ$, the odd signal fully vanishes.
symmetric in the sign of $k_2$ leading to a purely even signal in a 2D measurement. However, e.g. along the $\Gamma \rightarrow W$ direction, the orthogonal band curvature experienced by $E_1$ differs for positive and negative excursions of $k_2$ and thus gives rise to a nonlinear signal of odd parity, which is schematically shown in figure 9.27 b) and found in our simulations in figure 9.25 b).

![Figure 9.27: Orthogonal band curvature contributions to the even and odd signal. a) The red surface depicts a fully parabolic band $E_B = a k^2$, with $k_r = (k_x^2 + k_y^2)^{1/2}$, as found for truly free carriers. The yellow band has a quartic correction term $E_B = a k^2 - b k^4$ leading to anharmonicity, and the blue band in addition shows anisotropy with $E_B = a k^2 - b k^4 - c(k_x^4 + k_y^4)$. b) The excursion of the carrier wave-packet $k_2$ is induced by the field $E_2$. The orthogonal field $E_1$ then experiences different band curvatures for increasing magnitudes of $k_2$ which is shown here for $k_2$ along the high-symmetry directions $\Gamma \rightarrow X, K$ and along $\Gamma \rightarrow W$.]

9.6 Discussion of the 2D THz-spectroscopy results

In this chapter, we have showed reflective 2D THz-spectroscopy in the range of 1-10 THz on the prototypical nonlinear electron systems InSb and InAs for field-strengths between 20 and 120 kV/cm. The spectral bandwidth of the experiment was able to cover both relevant infrared active plasmon and phonon-modes. The experimental asymmetry introduced by the two different THz sources, different beam diameters and nearly cross-polarization geometry corresponds to a two-beam nonlinear spectroscopy experiment, where beam $E_2$ purely interacts with the plasmon-mode, while $E_1$ responds to both plasmon and phonon excitations. Although, this is reminiscent of a pump-probe experiment, the similar magnitude of applied fields prohibits treatment as such.

Experimentally, we observe strong nonlinear signals with timescales on the order of 7 ps that
can be attributed to carrier multiplication and transient population of secondary conduction band valleys, that have previously been observed [133, 163]. These effects represent a background for the observation of another strong nonlinear time-domain signal on the overlap timescale of the two beams reaching up to 13% of the magnitude of the combined fields. While this signature has been observed by Ho et al. [163, 164], we extend their measurements in a two-dimensional scheme that allows to study the detailed phase dependence of this coherent response. Two-dimensional Fourier transformations of these measurements reveal a complex internal structure of these nonlinearities leading to a large set of combination tones of the plasma-edge and longitudinal phonon frequencies.

Carrier dynamics in semiconductors are generally rather well understood and relevant phenomena are listed in chapter 6 of this work. Low band gap semiconductors hence present an interesting model systems to develop an understanding of 2D THz-spectra. To evaluate such data-sets in the temporal overlap regime, we simulate our experiment in time using the finite-difference time-domain technique. For this, we assume on top of the incoherent slower effects such as impact ionization a coherent, i.e. ballistic, motion of the conduction electrons in the band structure as proposed by Yu et al. [125]. We extend their treatment by a full two-dimensional band-structure dynamics simulation and additionally treat contributions from a phonon oscillator. While it is straightforward to implement additional bands, they do not yield considerable contributions to the signal for InSb and InAs. This is likely to be different for the p-type semiconductor GaSb shown in figure 9.14.

Without free parameters and without introducing additional coupling, the electronic band nonlinearities arising from ballistic transport can explain the order of magnitude and all features observed in the nonlinear THz response at early times. This also includes the nonlinear signals at phonon frequencies which can be understood by a dynamically changing screening of these modes.

The experimental separation into signals of odd and even parity in \( E_2 \) provides further information about the symmetry of the coupling mechanism and e.g. allows to assign Liouville pathways to the various peaks. The observation of the feature at \( (\nu_{LO}, 2\nu_p) \) would, however, require perturbation theory of at least fifth order in the electric fields.

In our experiments, we did not fully suppress the \( E_{2,y} \) field component which is according to our simulations shown in figure 9.26 the main contribution to the observed odd peaks \( (\nu_p, -\nu_p) \) and \( (\nu_p, \nu_p) \) in our measurements. However, it is straightforward to realize fully orthogonal polarization by adding a third wire-grid polarizer as shown in figure 8.10 as WG2. For perfectly crossed polarization, the peaks in the 2D spectra can be assigned to the symmetry of the band curvature along the trajectory as shown in figure 9.25 b), 9.26 b) and discussed in detail in figure 9.27. A numerically efficient implementation of the FDTD routine would enable to fit conduction band properties to the observed fields. 2D THz-spectroscopy may hence allow to investigate more exotic electronic systems that show high mobility such as Weyl-semimetals [256, 257, 258, 259].

While the latter has not been shown experimentally, the close resemblance of experiment
and simulation gives confidence in the magnitude of the extracted values of conduction band \( k \)-vectors, which are beyond the validity of Kane’s \( k \cdot p \)-band valley models \cite{162} and justifies our implementation of the full tight-binding band structure. Simulations of the spin-split bands further suggest a strong odd contribution to the nonlinear signal arising from the non-degenerate conduction band which could be observed in strong magnetic fields.

We may add, that while Ho et al. \cite{164} assigned a broad structure in the odd-parity nonlinear THz reflectivity of InAs at around 3.2 THz to a two-phonon absorption peak (2TA, see table 7.1), we did not observe comparable features in our 2D spectra. However, the plasmonic response in experiment and simulation was found to show inner structure depending on the spectrum and phase of the THz pulses, that can lead to similar observations, as observed for the effects of the wire-grid beam-combiner.

The treatment of ballistic transport discussed here also covers the physics of Bloch oscillations (section 6.4), which in the (100)-orientation leads to odd-harmonic generation for fields on the MV/cm-scale, but the underlying coherent transport approximation breaks down at room temperature already at fields in excess of 80 kV/cm when there is a considerable change in carrier population. Modeling such behavior may be best realized by a Monte-Carlo implementation of carrier transport \cite{112} inside the FDTD description.
Conclusions and outlook

In this work, we set out to gain a deeper understanding of ultrafast nonlinear electromagnetic probes applied to the study of solid-state material. For this we carried out two major studies, one was based on a nonlinear optical probe that enables to follow a material’s order parameter, while the second experiment explored the capabilities of phase-resolved nonlinear spectroscopy in the THz range.

Part I aimed to improve the understanding of previous observations made in the prototypical antiferromagnet NiO using time-resolved second-harmonic generation. Based on these findings, the material was suggested to provide a coherent gateway to a non-thermal state of magnetic ordering of large fractional magnitude via an ultrafast change in magnetic anisotropy.

We therefore investigated magnetization dynamics in NiO using a complementary direct probe of antiferromagnetic order. Picosecond-time-resolved non-resonant magnetic x-ray diffraction was employed as a tool to study sublattice magnetism after ultrafast optical excitation and our findings suggested that the dynamics in NiO observed with the previously used optical probe do not directly reflect dynamics of the antiferromagnetic order parameter.

This warranted a re-investigation of the experimental observations that were leading to the interpretation in the first place, namely magnetic-dipole sensitive second-harmonic generation. The extended data presented here supplement prior investigations and reveal some aspects that are inconsistent with the previous explanation for the ultrafast dynamics of SHG in NiO. Our studies prove an acoustic origin of the dynamics, which becomes particularly apparent in the observation of echoes that depend on the acoustic path-length, as well as the probe wavelength dependencies.

Our simulations of this process present, to our knowledge, the first treatment of second-order stimulated Brillouin scattering in non-ideally phase-matched crystals leading to the two signature frequencies $\omega_{\pm} = \text{Re}(2k\omega \pm k^2\omega)v_s$. The process thus gives rise to slow oscillations and higher frequencies that resemble linear stimulated Brillouin scattering but are shifted by phase mismatch.

These findings show that nonlinear probes can lead to rather complex results when used under conditions of non-ideal phase matching and low absorption, where assignment of the detected intensity to the nonlinear susceptibility cannot readily be made. We propose that
Conclusions and outlook

experimental evaluation of such probes should always be accompanied by considerations of the signal’s generation process with the implications of inhomogeneous ultrafast excitation.

Despite the increasing complexity, nonlinear methods are able to provide an unparalleled sensitivity in the search for new physics in ultrafast solid-state science. In part II of this work, we therefore investigated the novel method of broadband 2D THz-spectroscopy. The technique can combine the process of driving intrinsic excitations, relevant e.g. in inducing an order transition, while at the same time probing the very same and associated modes.

Even in an excitation regime far away from driving permanent changes, the method can provide information about the curvature and symmetry of the energy landscape in which the modes reside. Yet, in this work we were merely setting the stage for such experiments by first attempting to improve the understanding of the 2D THz method itself. For this, we performed reflectivity measurements and simulations on low band gap III-V semiconductors that represent well-understood polaron systems which show an early onset of electric field-linearity.

Experimentally, we find that the previously observed strong nonlinear responses in InSb and InAs at very early times are composed of combination tones of the intrinsic excitations in the 2D spectrum. Observing the full phase information and having control over the polarity of the excitation fields allowed us to further differentiate between the parity of the spectral features. This might be of particular interest for disentangling strongly damped excitations.

For our simulation, we solved Maxwell’s equations in the presence of a polaronic medium using Yee’s algorithm. The calculated field-driven ballistic transport led the mean conduction band population into regions distant from the equilibrium Γ-point by as far as 3% of the zone-edge wave vector. The simulations were able to reproduce the magnitude as well as all observed spectral features and their parity. The nonlinear observations in the 2D spectra, including features at the phonon frequency, are thus found to be purely based on plasmonic anharmonicity and their explanation does not require additional coupling between the material’s intrinsic excitations. Nonetheless, the spectra and their symmetries were found to contain information about the local curvature of the band structure along the carrier trajectories.

This could be applied as a means to study ultrafast high-field transport in static magnetic fields and to more exotic electronic systems such as Weyl semimetals. Apart from observing electronic band dynamics, the framework can also be applied to magnetic materials and in particular for systems that show coupled degrees of freedom, such as multiferroics and systems showing strong inter-phononic coupling. As we have shown in this work, evaluation of 2D spectra can also be meaningful in the temporal overlap region of the excitation fields, which enables to study strongly damped systems, that can e.g. be found in ferro-electrics.

Key to the application of this technique to a broader class of materials is to achieve field strength in excess of the MV/cm range. In the light of the findings presented in this thesis, it appears essential to develop comprehensive time-dependent analysis tools in order to achieve a solid understanding of signals gained from nonlinear probes.
Appendix

A Conventions

\[ c = \frac{1}{\sqrt{\mu_0 \epsilon_0}} \]
\[ \epsilon = 1 + \chi, \]
\[ \epsilon = \epsilon' + i \epsilon'', \]
\[ n = \sqrt{\epsilon}, \]
\[ n = n' + i \kappa, \]
\[ k = \frac{\omega}{c} n \text{ and } k = k' + ik'' \]
\[ \sigma = \sigma' + i \sigma'', \]
\[ \sigma_1 = \omega \epsilon''. \]

B Coupled-wave equation in absorbing media

For homogeneous media without free charges \( \nabla \cdot \mathbf{E} = 0 \), but allowing for absorption, the general form of the nonlinear wave equation can be written as [79, 63, 52]

\[ \nabla^2 \mathbf{E} = \mu_0 \left( \omega \epsilon_0 \epsilon'' \frac{\partial \mathbf{E}}{\partial t} + \epsilon_0 \epsilon' \frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{\partial^2 \mathbf{P}^{NL}}{\partial t^2} \right). \]  

(B.1)

To solve equation B.1 we can start with a plain wave ansatz

\[ \mathbf{E}(\mathbf{r}, t) = \sum_i \left[ \mathbf{E}_i(\mathbf{r}) e^{i \mathbf{k}_i \cdot \mathbf{r}} \right] \cdot e^{-i \omega_i t}, \]  

(B.2)

and by carrying out the temporal derivatives, the partial differential equation B.1 reduces to only spatial dependencies.

We now want to investigate the coupled wave equations for the case of three wave mixing. For
this, we assume that only coupling up to second order occurs and that the field $E$ breaks up into three contributions $E_i(\omega_i)$ oscillating at different frequencies $\omega_a$, $\omega_b$ and $\omega_c$. These fields are coupled via the nonlinear polarization $P_{\text{NL}}$ as discussed in section 2.2.1. In order to fulfill energy conservation, only commensurate sets of frequencies fulfilling $\omega_a = \omega_b + \omega_c$ for arbitrary combinations of $a, b, c$ can contribute. By using the dispersion relation $\omega^2 = c^2 k'^2 / \epsilon'$ and the ansatz B.2, the coupled differential equations for the three beams can be written as [79, 191, 52]

\[
(\nabla^2 + k'^2 a)E_a = i \frac{\omega_a^2}{c^2} \epsilon_a'' E_a - 2 \frac{\omega_a^2}{c^2} \hat{\chi} E_b E_b^*,
\]

(B.3)

\[
(\nabla^2 + k'^2 b)E_b = i \frac{\omega_b^2}{c^2} \epsilon_b'' E_b - 2 \frac{\omega_b^2}{c^2} \hat{\chi} E_c E_a^*,
\]

(B.4)

\[
(\nabla^2 + k'^2 c)E_c = i \frac{\omega_c^2}{c^2} \epsilon_c'' E_c - 2 \frac{\omega_c^2}{c^2} \hat{\chi} E_a E_b^*,
\]

(B.5)

For SHG these simplify to

\[
(\nabla^2 + k'^2 \omega)E_\omega = i \frac{\omega^2}{c^2} \epsilon'' \omega E_\omega - 2 \frac{\omega^2}{c^2} \hat{\chi} E_{2\omega} E_{\omega}^*,
\]

(B.6)

\[
(\nabla^2 + k'^2 2\omega)E_{2\omega} = 4i \frac{\omega^2}{c^2} \epsilon''_{2\omega} E_{2\omega} - 4 \frac{\omega^2}{c^2} \hat{\chi} E_{\omega}^2.
\]

(B.7)

C Polarization dependence of the time-resolved signal

We also went on to investigate the polarization dependence of the time-resolved SHG response in NiO. A static polarization dependence of the SHG signal from a part of the sample that is presumably a single structural domain is shown in figure C.1. Based on reference [18] we can tentatively assign the observed pattern to a coherent combination of either a single structural domain contracted in surface normal direction (coined $T_1$) with a dominant spin domain, or a random spin domain distribution in one of the other 3 structural domains. However, using probe beam sizes on the order of 100 $\mu$m, most of our time-resolved measurements were carried out looking at a set of various structural domains that can contribute coherently or incoherently, as was exhaustively discussed in reference [18]. We studied the dependence of the SHG response at 1300 nm fundamental wavelength as function of pump polarization using an excitation wavelength of 1180 nm and found no strong dependence as shown in figure C.2 b). We observe, however, significant ellipticity of 0.6 at delays of 4 ps. Studying the effect of circular polarization by introducing a $\lambda/4$-wave-plate did not impact the SHG response significantly. As in the case of 800 nm pumping and 1200 nm probing [38], we detect strong four-wave-mixing at $t_0$. Its polarization dependence is shown in figure C.2 c).
C Polarization dependence of the time-resolved signal

Figure C.1: Polarization dependence of detected SHG intensity on a sample spot showing particularly well defined features. Blue triangles indicate measurements for parallel probe polarization and analyzer transmission, thus they are related to $\chi^{(2)}_{xxy}$. The red ones indicate $\chi^{(2)}_{xyy}$ in crossed polarization detection geometry. The solid lines show fits for the SHG intensity based on the assumption that the measurement is looking at a pure $S_{1}$-domain in a structural ($T_{1}$)-domain, as given in reference [18].

Figure C.2: a) The dependence of the detected SHG at 1300 nm in transmission geometry as function of fundamental beam polarization without analyzer. The signal shows less modulation than the data shown in black in figure C.1 indicating several domains as sources of SHG. b) Relative drop in SHG at a probe polarization of $120^\circ$ at 4 ps after excitation as function of 1180 nm pump polarization. The results are fitted with an ellipse of $\epsilon = 0.6$. c) The four-wave-mixing process at $t_0$ shows a particularly strong dependence of the change in signal on pump polarization with a maximum around $\phi_0 = 30^\circ$, i.e. crossed polarization. Fitted using $a \cos (\phi_2 + \phi_0)^2$. 
D Surface generated strain in a confined medium

Equation 3.2 gives the solution for strain induced by impulsive optical excitation. Its dimensionless spatial and temporal evolution $F(z,t)$ for thin crystals is then given by

\[
F(z,t) = f(z) \left( 1 - \frac{1}{2} f(v_s \tau(t)) \right) - \frac{1}{2} f(|z - v_s \tau(t)|) \\
\cdot \text{sgn}(z - v_s \tau(t)) \\
+ f(d) \left( \frac{1}{2} f(d - z + v_s \tau(t)) - \frac{1}{2} f(|d - z - v_s \tau(t)|) \right) \\
\cdot \text{sgn}(d - z - v_s \tau(t)),
\]

with the initial spatial distribution of thermoelastic stress

\[
f(z') = e^{\alpha(2d - z')} + \text{Re}^{\alpha z'},
\]

and the effective time $\tau(t)$

\[
\tau(t) = \begin{cases} 
  t \mod(d/v_s), & \text{if } t \mod(2d/v_s) \leq d/v_s \\
  -t \mod(d/v_s) + d/v_s, & \text{otherwise}.
\end{cases}
\]

This definition of $\tau(t)$ emphasizes the time inversion symmetry with respect to the acoustic reflections occurring at multiples of $d/v_s$.

E Optical parameters employed for the SHG simulation

The absorption of NiO in the visible and near-infrared range is strongly affected by impurities such as excess oxygen [30]. In order to determine an absorption spectrum for the simulation that suits the NiO crystals measured in our experiments, we used a polynomial fit to a known spectrum [30] $\alpha_0(\omega)$ and adjusted for the specific impurity concentration by fitting $\alpha(\omega) = a\alpha_0(\omega) + b$ to a set of three direct absorption measurements that we carried out for $\lambda = 600, 800$ and 1200 nm, yielding $\alpha = 284, 355$ and 427 cm$^{-1}$, respectively. The absorption spectrum employed for the model is shown in figure 5.10. These measurements also yielded a real part of the refractive index of about $n = 2.35 \pm 0.05$. Due to the limited surface quality of our samples, we were not able to measure the dispersion in a static experiment with sufficient precision to predict the observed frequencies in the SHG response.
Combining the two parts of this thesis, we also carried out tests on the SHG response of THz excited NiO. For this we placed the 50 µm thick NiO sample in the focal position of the ABC-detection branch in figure 8.10 and used the plasma-generated THz pulse for excitation. We did not carry out a field calibration for these measurements and the environment was only partially purged. The 1200 nm probe pulse was attenuated to 5 µJ. Results of these measurements are shown in figure F.1.

We carried out several measurements of different polarization combinations between IR probe and THz field as well as with and without the analyzer Glan-Laser prism. The static NiO-SHG signal was about 0.53 (a.u.) and THz-modulation increased this signal by up to a factor of 3. The measurements show pronounced ringing which can be ascribed to the NiO slab etalon and water lines of the THz field. A very similar experiment on NiO has been published in reference [260], which, however, shows by far inferior signal to noise as the data presented here. The plot also shows a measurement in air acquired under the same conditions as the blue trace of NiO which is equivalent to the pure air TFISH-signal as discussed in the ABCD method section 8.2.2.

In the context of the ABCD method the origin of the signal observed in NiO can be easily understood. NiO’s $\chi^{(3)}$ is in contrast to its $\chi^{(2)}$ considerable, as was already seen by the strong four-wave-mixing signal between 800 nm and 1200 nm in chapter 5 and shown e.g. in figure C.2 c). It therefore provides a much more efficient nonlinear medium than e.g. air which, obscures whatever dynamics the $\chi^{(2)}$, and thus the magnetic order, may show. Due to the mixture of TFISH and magnetic SHG, both non-phase-matched, the spectra cannot readily be assigned to any internal excitations and we refrain from interpretation. This is a severe but unfortunately general limitation of the THz-excitation - SHG probe technique which may only be resolved by measurements on thin films or by a comprehensive simulation and symmetry analysis of the tensor elements giving rise to $\chi^{(2)}$ and $\chi^{(3)}$.
**Figure F.1:** b) SHG intensity after plasma-generated THz excitation of NiO. Traces are offset for better visibility. The broken lines indicate the baseline of the respective signals. The long duration of the SHG modulation arises from water lines. a) The spectrum of the modulated signal at crossed infrared and THz polarization (with analyzer) shown in yellow shows strong interferences fringes arising from the 50 µm thick slab etalon. The broken black line shows the spectrum between times -0.2 to 0.8 ps.
Figure G.1: The ABCD gas cell that was employed for the experiments in chapter 9, constructed by Filippos Kapsalidis during his Master’s project. Reprinted from his thesis [199]. The drawing shows a 4” OAPM, in our experiments a 2” OAPM was used.

G Electrical schematics of the ABC-detection

The experimental ABCD setup used for our experiments, that was only schematically depicted in section 8.2.2, is shown in figure G.1. The 100 $\mu$J, $(70 \pm 5)$ fs, 1200 nm probe beam is focused using a 15 cm lens and enters the detection cell through a window after which it transmits through a hole in the parabolic mirror that focuses the THz. The latter enters the cell through a 3” high-resistivity Si window from the side. Both beams are focused in between the 3 mm thick copper electrodes that are mounted using insulating plastic holders in a plate-capacitor geometry rather than the often used wire geometry. More details and plans can be found in Filippos Kapsalidis’ Master thesis [199].

As described in section 8.2.2, the ABCD method requires two measurements at inverted high-voltage bias fields $V_{DC}^+$ and $V_{DC}^-$ to acquire a signal that is equivalent to EO sampling (section 8.2.1). For this we employed a TREK 2220 high-voltage (HV) amplifier, which has a fixed amplification factor of 200 $V_{out}/V_{in}$ and a rise time of about 100 $\mu$s. The output voltage is delivered to the detection cell with an SHV-jack. The phase of the connector is then directly attached to one of the electrodes, while the other electrode is put to ground via the cell which in turn is grounded to the table.

Frequent alternation of the bias is favorable as it reduces drift noise. We therefore chose to synchronize the HV-amplifier to the 1 kHz-laser and reduced the frequency using a simple flip-flop implementation. Using either the TTL-trigger from a delay generator that is fed by the
laser-trigger directly or using the phase-locked output trigger of a Thorlabs mechanical chopper
MC2000, this scheme was used for a phase stable HV-bias at 1/2 or 1/4 of the laser frequency.
To achieve a symmetric bias switching from -2 kV to 2 kV, the frequency reduced TTL signal
needed to be offset and amplified, which was realized by the electronic schematics shown in figure
G.2.

The TREK 2220 HV amplifier also provides a proportional copy $\propto 1/200$ of its amplified
output that is acquired alongside the detected ABCD signal on a shot-to-shot basis. Based on
equation 8.10 and 8.11 this can be used to correct for bias fluctuations and synchronization
glitches. Note, however, that when using a gated-integrator for the ABCD signal, synchronization
with the HV proportional signal might be delayed by 1 laser trigger ($S_{HV}(t + 1)$ then corresponds
to $S_{ABCD}(t)$).

Figure G.2: Schematic of the TTL alternator that generates an alternating signal with up to
10 V amplitude at half the input frequency and without DC component in order
to drive the TREK 2220 HV-amplifier for ABC-detection. Certainly not the best,
but definitely some way to do it. The inset shows the voltage at the 3 color-coded
nodes for suitably chosen values of P1 and P2.
List of publications


167
• T. Huber, M. Ranke, A. Ferrer, L. Huber, and S. L. Johnson,
  Coherent phonon spectroscopy of non-fully symmetric modes using resonant terahertz excitation.

  Coherent Structural Dynamics of a Prototypical Charge-Density-Wave-to-Metal Transition.

  Coherent dynamics of structural symmetry during the ultrafast melting of a charge density wave.

  Large-Amplitude Spin Dynamics Driven by a THz Pulse in Resonance with an Electromagnon.
Curriculum vitae

*Omitted in the electronic version.*

Conference contributions

- *Two-dimensional THz-spectroscopy on the low band gap semiconductors InSb and InAs,*
  Poster at the annual NCCR-MUST meeting, Grindelwald, Switzerland, January 2017.

- *Gas-based time-resolved THz time-domain spectroscopy for the study of nonequilibrium
electron-phonon interaction in semiconductors,*
  Poster at the International Conference on Ultrafast Phenomena XX, Santa Fe, New Mexico,
  July 2016.

- *Time-resolved differential time-domain spectroscopy in the range of 1-10 THz,*
  Poster at the annual NCCR-MUST meeting, Engelberg, Switzerland, January 2016.

- *Coherent acoustic perturbation of SHG in NiO,*
  Poster at the International Conference on Ultrafast Structural Dynamics, Zurich, Switzerland,
  June 2015.

- *A gas based time-domain spectrometer spanning the THz gap,*
  Poster at the annual NCCR-MUST meeting, Engelberg, Switzerland, January 2015.

- *The influence of optically induced strain on SHG in NiO,*
  Poster at the annual NCCR-MUST meeting, Engelberg, Switzerland, January 2014.
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