Master's Thesis

Excitation of Surface Phonon Polaritons with an Infrared Free Electron Laser



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Declaration of Authorship

I hereby certify that this thesis has been composed by me and is based on my own work, unless stated otherwise. No other person's work has been used without due acknowledgement in this thesis. All references and verbatim extracts have been quoted, and all sources of information, including graphs and data sets, have been specifically acknowledged.

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Introduction

Selective control and manipulation of the physical properties of condensed matter has been an attractive goal for a long time. In the past years, coherent laser pulses ranging from terahertz (THz) energies up to the x-ray regime have been successfully employed to drive transient states of matter on time scales down to the femtosecond range. As has been demonstrated, in doing so, magnetic phases can be switched [1, 2, 3], the electronic structure altered [4, 5], superconductivity induced [6], or the crystal structure controlled [7, 8].

Due to their polarized nature, infrared (IR)-active optical lattice vibrations grant access to a variety of material properties in correlated systems, which has been demonstrated for the first time in 2007 [4] by a transient conductivity enhancement on the order of 10^5 . By this means, a field of investigation has opened up, which promises the possibility of ultra-fast data storage and information processing, combined with a drastic reduction in heating. However, in order to actually induce a vibrationally-driven phase transition rather than heating the material, the lattice atoms have to be forced far enough out of their equilibrium position, entering a strongly non-linear regime. This requires a coherent excitation with exceptional field strength exclusively at the optical phonon energies, which restricts the practicality of this approach in terms of frequency tunability.

An interesting alternative might be the so-called Surface Phonon Polariton (SPhP), which is a dispersive, spatially highly confined excitation composed of a photon coupled to a phonon, propagating at the surface of a polar dielectric. As any other polaritons, these modes are known to exhibit tremendous field enhancements, and therefore constitute a tunable phonon excitation with exceptional amplitudes of the atomic motion.

In a complimentary approach, SPhPs represent a very promising alternative to Surface Plasmon Polaritons (SPPs). These excitations, being the fundamental building block of nanophotonics, have been discussed to potentially revolutionize conventional electronics, especially focussing on miniaturization and high-frequency processing [9, 10, 11]. However, SPPs exhibit very high optical losses, which constitutes the major drawback of this approach. Here, SPhPs might offer a remedy to overcome this problem due to their relatively long lifetimes [12, 13].

By combining the advantages of a tunable non-linear lattice excitation granting ultra-fast control of material phases, and a low-loss, highly confined surface mode, the SPhP enables unique possibilities towards the development of novel physics with yet unknown applicabilities.

The focus of this work lies on the study of SPhPs at the interface of polar dielectric crystals, and the investigation and analysis of their main properties. Concerning the linear optical response, this is achieved via total internal reflection spectroscopy in the Otto geometry, which is an established approach to access these surface modes experimentally [14, 15]. As a SPhP active medium, firstly, the model polar dielectric Silicon Carbide (SiC) is chosen, since it exhibits only a single optical phonon mode in the THz region and hence serves as a well understood starting point for further investigations.

As a possible extension, one currently studied subject are the so called crystal hybrids, which are constructed by stacking atomic-scale layers of different dielectric crystals [16], creating a novel material with unique dielectric properties. These crystal hybrids are discussed to provide actively tunable, low-loss optical features, and hence are opening a new path in the field of THz nanophotonics. As a

second topic in this work, an Aluminium Nitride (AlN) / SiC heterostructure is investigated, as a first step towards revealing the nature of phonon polariton modes arising in multilayer systems.

Furthermore, this work presents the first measurements of the non-linear behaviour of SPhPs by means of Second Harmonic Generation (SHG) spectroscopy [17]. Similar to the rapidly growing field of non-linear plasmonics [18, 19, 20, 21, 22, 23], the SPhP enhanced higher order-behaviour could give another boost to the developments in nanophotonics. Very recently, resonant enhancement of SHG using localized SPhPs in sub-diffractional nanostructures was demonstrated [24]. In addition, the SHG response directly reports on the amplitude of the vibrational motion, allowing to assess and optimize non-linear lattice control in these materials.

The main reason that this kind of research has not been performed before on SPhPs¹, is a common lack of narrow-band excitation light sources with sufficient intensity in the mid-infrared (MIR) spectral region. Having such a device at hand, this work benefits from the Free Electron Laser (FEL) at the Fritz Haber Insitute (FHI) in Berlin, which features excellent conditions for MIR SHG spectroscopy.

The first chapter is dedicated to introduce the theoretical concepts of the investigated topics as well as the basic principles of the employed experimental techniques. Chapter 2 presents simulations of the reflectivity and SHG for the investigated sample systems. These simulations were performed using two different multilayer models. While the first can nicely describe isotropic materials, the latter is capable of taking into account the crystalline optical anisotropy of media, and has been specifically developed in this work. In particular, the anisotropic model is able to describe the experimental data with high precision.

In chapter 3, the experimental setup of the performed research is discussed. The experimental results are separated into two chapters. In chapter 4, the findings concerning the resonant SHG from SPhPs on SiC are illustrated. Last but not least, chapter 5 presents the results of the measurements realized on the AlN / SiC heterostructure, revealing the novel nature of two individual, simultaneously existing SPhP modes.

¹to the best of our knowledge

1 | Theoretical Basics

This chapter provides the theoretical background for this work. It is mainly dedicated to give a comprehensive insight into the underlying physics of the main subject of interest, the Surface Phonon Polaritons (SPhPs).

In 1907, the first solution and analysis of Maxwell's equations with "surface" character was found by Zenneck [25]. It consists of a polarized plane electromagnetic wave, and is highly confined at the planar interface of vacuum and a solid material with finite electric conductivity. This solution is essentially the same as the result that emerges from the theoretical study of SPhPs, highlighting the universal validity and wide application variety of the Maxwell equations.

Therefore, in order to understand the nature of these surface excitations, this chapter starts with a description of the necessary fundamentals of light-matter interaction (section 1.1), based on Maxwell's formulas. With this, SPhPs and their coupling mechanisms to light in free space will be discussed in the second section (1.2).

Furthermore, this work employs reflectivity and Second Harmonic Generation (SHG) spectroscopy in order to measure and quantify the linear and the SHG signal driven by SPhPs. While the theory for reflectivity and transmittance in multilayer systems is elaborated in chapter 2 together with the respective simulations, in this chapter in section 1.3, the basic concepts of non-linear optics are provided. Finally, section 1.4 outlines the main features of a Free Electron Laser (FEL), which is used as an excitation light source in this work.

1.1 Basics of Solid State Optics

This section treats the fundamental mechanisms of the interaction of light with matter, which are relevant for the description and understanding of SPhPs. After summarizing the most important properties of Maxwell's equations in matter, the effect of total internal reflection is discussed in section 1.1.2. Finally, in section 1.1.3, the dielectric permittivity of a polar crystal is derived and its importance for SPhPs is explained.

1.1.1 Maxwell's Equations in Matter

In a polarizable, magnetizable, conducting and charged material, the Maxwell equations can be written in the following form [26]:

$$\vec{\nabla} \cdot \vec{B} = 0 \tag{1.1}$$

$$\vec{\nabla} \times \vec{E} = -\vec{B} \tag{1.2}$$

$$\vec{\nabla} \cdot \vec{D} = \rho \tag{1.3}$$

$$\vec{\nabla} \times \vec{H} = \vec{D} + \vec{j},\tag{1.4}$$

where ρ is the charge density, \vec{j} the current density, \vec{H} the magnetic field strength, \vec{B} the magnetic field, \vec{D} the electric displacement and \vec{E} the electric field. The following relations connect \vec{B} with \vec{H} and \vec{E} with \vec{D} :

$$\vec{B} = \mu_0 \left(\vec{H} + \vec{M} \right) \longrightarrow \mu \mu_0 \vec{H} \tag{1.5}$$

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} \longrightarrow \epsilon \epsilon_0 \vec{E}, \tag{1.6}$$

where \vec{M} and \vec{P} denote the material properties magnetization and electric polarization, respectively, ϵ denotes the dielectric permittivity and μ the magnetic permeability. The arrows indicate equality in a linear approximation, i.e. when the response of the material \vec{P} to the external field \vec{E} can be described by the first-order electric susceptibility χ :

$$\vec{P} = \epsilon_0 \chi \vec{E}. \tag{1.7}$$

The dielectric permittivity and the electric susceptibility are connected by the following equation (eq.):

$$\epsilon = 1 + \chi. \tag{1.8}$$

In general, optical quantities like the dielectric permittivity are frequency dependent, complex tensors. In an isotropic material, the tensor reduces to a scalar and the following representation is suitable, where the separation into real and complex part attributes to the dispersive ϵ_1 and absorptive part ϵ_2 in the material:

$$\epsilon(\omega) = \epsilon_1(\omega) - i\epsilon_2(\omega), \tag{1.9}$$

which is also referred to as dielectric function.

The Maxwell equations can be solved by plane waves of the form

$$\vec{E} = \vec{E}_0 e^{i\left(\omega t - \vec{k}\vec{r}\right)} \tag{1.10}$$

$$\vec{B} = \vec{B}_0 e^{i\left(\omega t - \vec{k}\vec{r}\right)},\tag{1.11}$$

where \vec{k} is the propagation wave vector. For a propagating electromagnetic wave in a material with refractive index *n* and absorption index *k*, the dispersion relation has the form

$$|\vec{k}| = -\frac{\omega}{c}\tilde{n} \approx -\frac{\omega}{c}\sqrt{\epsilon},\tag{1.12}$$

where $\tilde{n} = n - ik$ denotes the complex refractive index. In the second step, the following connection to the dielectric function was applied:

$$\tilde{n}^2 = \mu \epsilon \approx \epsilon. \tag{1.13}$$

In general, $\mu = 1$ holds for all non-magnetic materials, and in optics, this approximation is usually employed in any case. Considering linearly polarized light propagating along z with the magnetic field vector pointing in the y direction, Maxwell's equations yield the following connection between the \vec{E} and the \vec{H} field:

$$E_x = \frac{k_z}{\omega\epsilon_0\epsilon} H_y,\tag{1.14}$$

whereas the other \vec{E} field components are zero. This means $\vec{E} \perp \vec{H} \perp \vec{k}$, which is true for plane electromagnetic waves propagating in isotropic materials. In anisotropic media, generally, $\vec{E} \perp \vec{k}$ is not fulfilled [27].



Figure 1.1: Illustration of the Fresnel reflection and refraction at an interface between two media with different indices of refraction n_1 and n_2 for *p*-polarized incident light. In the picture, $n_1 < n_2$, i.e. the light enters an optically denser medium, which is the case of external reflection.

1.1.2 Total Internal Reflection

When light passes through a plane interface from medium 1 to medium 2 with complex indices of refraction \tilde{n}_1 and \tilde{n}_2 , respectively, the Snellius law gives:

$$\tilde{n}_1 \sin \theta = \tilde{n}_2 \sin \phi, \tag{1.15}$$

where θ denotes the angle between surface normal and incoming light in medium 1 and $\tilde{\phi}$ is the complex angle between surface normal and refracted light in medium 2. The real and imaginary part of the complex index of refraction \tilde{n} are the refractive index n and the absorption coefficient k, respectively, i.e. $\tilde{n} = n - ik$. In the case of incidence from an optically less dense medium 1 to a more dense medium $2 (n_1 < n_2)$, $\tilde{\phi}$ is real. However, when the materials are changed, i.e. $n_1 > n_2$, an angle θ_T exists, where the transmitted wave is refracted at 90 ° to the surface normal. This angle is called the critical angle of total internal reflection and amounts to

$$\theta_T = \arcsin\left(\frac{n_2}{n_1}\right). \tag{1.16}$$

For incoming angles $\theta > \theta_T$, the reflectivity is 1. Nonetheless, the complex part of ϕ is larger than zero, and mathematically, this yields a so called evanescent wave, which propagates along the surface and decays exponentially into both media. Physically, the evanescent wave assures the fulfilment of the boundary conditions of the Maxwell equations, which requires continuity of the parallel components of the \vec{E} and the \vec{H} field.

It is instructive to calculate and visualize the field components of the evanescent wave, which exhibit a rather peculiar shape. By looking at the Fresnel reflection of a plane incoming wave at the interface



Figure 1.2: \vec{E} fields for internal reflection from ZnSe (n = 2.4) to vacuum at $\nu = 900 \text{ cm}^{-1}$. The critical angle of total internal reflection lies at 24.63°. The incident light is plotted in green, the reflected light in brown, and the refracted wave in blue. The latter is evanescent for incident angles above the critical angle of total internal reflection, which is the case in (b) and (c).

between two optically different media ($n_1 \neq n_2$), the field components of incident, reflected and transmitted light $\vec{E_i}$, $\vec{E_r}$ and $\vec{E_t}$, respectively, become in the case of *p*-polarized incident light

$$\vec{E}_i = (\cos\theta, 0, \sin\theta) E_{i0} e^{-i\tilde{k}_1 (x \sin\theta - z \cos\theta)}$$
(1.17)

$$\vec{E}_r = (-\cos\theta, 0, \sin\theta) E_{r0} e^{-i\vec{k}_1 (x \sin\theta + z \cos\theta)}$$
(1.18)

$$\vec{E}_t = (\sin\tilde{\phi}, 0, \cos\tilde{\phi}) E_{i0} e^{-i\tilde{k_2} (x\sin\tilde{\phi} - z\cos\tilde{\phi})}, \qquad (1.19)$$

where $\tilde{k}_1 = |\vec{k}_i| = |\vec{k}_r| = \frac{\omega}{c}\tilde{n}_1$, $\tilde{k}_2 = |\vec{k}_t| = \frac{\omega}{c}\tilde{n}_2$, the time dependence $e^{i\omega t}$ was omitted, and the incident angle θ is real. The situation is visualized in figure (fig.) 1.1. The ratios of the field amplitudes of reflected and transmitted light are given by the Fresnel coefficients for *p*-polarized light [26]:

$$\frac{E_{r0}}{E_{i0}} = \frac{\tilde{n}_2 \cos \theta - \tilde{n}_1 \cos \tilde{\phi}}{\tilde{n}_2 \cos \theta + \tilde{n}_1 \cos \tilde{\phi}} = \frac{\tan \left(\theta - \tilde{\phi}\right)}{\tan \left(\theta + \tilde{\phi}\right)}$$
(1.20)

$$\frac{E_{t0}}{E_{i0}} = \frac{2\,\tilde{n}_1\cos\theta}{\tilde{n}_2\cos\theta + \tilde{n}_1\cos\tilde{\phi}} = \frac{2\,\sin\tilde{\phi}\cos\theta}{\sin\left(\theta + \tilde{\phi}\right)\cos\left(\theta - \tilde{\phi}\right)}.\tag{1.21}$$

By this means, the complete \vec{E} fields can be calculated, which are plotted in fig. 1.2 for a ZnSe / vacuum interface, at three different angles in (a), (b), and (c). For angles larger than θ_T (see (b) and (c)), the evanescent wave appears on the vacuum side (z < 0), exhibiting a circular shape with poles at those points, where the \vec{E} field on the other side (z > 0) has its minima. Even though the \vec{E} field has components not just in x- but also in z-direction, there is no energy flow in z-direction, as it should be expected, since 100% of the incoming wave is being reflected. By calculating the Poynting vector, it can be shown that the energy flows only along the interface in x-direction [28].

As it can be seen already from fig. 1.2, the penetration depth d_{evan} of the evanescent wave depends on the incident angle:

$$d_{evan} = \frac{\lambda}{2\pi\sqrt{\epsilon_1 \sin^2\theta - \epsilon_2}},\tag{1.22}$$

with λ being the wavelength of the incident light.

When a third, absorbing medium is brought close to the interface between medium 1 and 2, the evanescent wave begins to leak into medium 3, where a fraction gets absorbed. Hence, the reflection is no more total, which is why this effect is called Attenuated Total Reflection (ATR) [28]. Since the absorption is very sensitive to the optical properties of medium 3, ATR is used as a spectroscopic technique [29, 30, 31]. By measuring the amount of reflected light scanning the incident angle and the wavelength, the absorption resonances of some material of interest can be studied.

In this work, ATR is used to couple to SPhPs and by this means study their resonance behaviour. Since SPhPs turn out to only exist in polar crystals, these and their optical properties are discussed in the following section.

1.1.3 Dielectric Permittivity in a Polar Crystal

A crystal with $N_{u.c.}$ atoms in the primitive unit cell has 3 acoustic and $3N_{u.c.} - 3$ optical modes. For the long-wavelength limit, i.e. at the Brillouin zone center, in acoustic phonons all atoms oscillate together, whereas in optical phonons, the atoms describe an out of phase movement with specific periodicity. The latter are called optical because their resonance frequencies at the Brillouin zone center lie in the spectrum of infrared light. In order to be optically active, however, a polarization must be present, which is the case in so called polar crystals. Here, the moving basis atoms induce a time-varying dipole, which can couple to light.

Depending on the vibration direction with respect to the propagation direction, a distinction is made between longitudinal (LO) and transverse (TO) optical modes. In polar crystals such as SiC, AlN or Gallium Nitride (GaN), a gap between the two resonance frequencies ω_{TO} and ω_{LO} can be found at the zone center, which does not exist in non-polar crystals. This lifting of the degeneracy between the optical branches can be understood in terms of electric polarization induced by the atomic motion. For the TO modes, the charged atoms oscillate within parallel planes without changing the lateral distance between each other. For the LO mode, however, this distance varies over time, resulting in an additional Coulomb force along the propagation direction. Hence, the LO frequency is higher than the TO frequency [32]. The region between both frequencies is called the Reststrahlen (*German: residual rays*) band.

In order to get an expression for the dielectric function of a polar crystal, a Lorentz oscillator can be used as an approximation [33]. In this picture, the equation of motion of a single atom is

$$m\ddot{\vec{u}} + m\gamma\dot{\vec{u}} + m\omega_0^2\vec{u} = q\vec{E},\tag{1.23}$$

with the displacement \vec{u} from the equilibrium position, damping constant γ , atom mass m, charge q, resonance frequency ω_0 and the incident electric field $\vec{E} = \vec{E}_0 e^{i\omega t}$. Taking into account momentum conservation, and that for an electromagnetic wave in isotropic media $\vec{E} \perp \vec{k}$, two conclusions can be



Figure 1.3: Dielectric function of SiC in the MIR from eq. 1.27, split into real and imaginary part. Material constants are taken from [15] for SiC, i.e. with $\omega_{TO} = 796 \text{ cm}^{-1}$, $\omega_{LO} = 972 \text{ cm}^{-1}$ and $\gamma = 3.75 \text{ cm}^{-1}$. The peak of ϵ_2 lies in that case at approximately 676. $\epsilon_{\omega=0}$ denotes the dielectric function at $\omega = 0$, $\epsilon_{\infty} = 6.5$ the value in the high frequency limit and $\epsilon_A = 1$ is the dielectric constant of material A in section 1.2. ω_S denotes the crossing point of ϵ_A and ϵ_1 .

drawn: Firstly, just transverse optical modes can be excited, which leads to $\omega_0 = \omega_{TO}$, whereas ω_{LO} cannot be excited. Secondly, just phonons near the zone center are accessible, because the wavenumber of infrared photons lies in the range of 10^3 cm^{-1} , whereas phonons reach up to 10^8 cm^{-1} [33]. In other words, the wavelength of the incident light is much longer than the lattice constant. The solution of the differential eq. 1.23 is then

$$\vec{u} = \frac{q\vec{E}}{m\left(\omega_{TO}^2 - \omega^2 + i\omega\gamma\right)}.$$
(1.24)

For N oscillating atoms, the macroscopic polarization amounts to $\vec{P} = Nq\vec{u}$, and by using equations 1.24, 1.7 and 1.8, the dielectric function can be formulated as

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{Nq^2}{\epsilon_0 m} \frac{1}{\omega_{TO}^2 - \omega^2 + i\omega\gamma},$$
(1.25)

where ϵ_{∞} was written instead of 1 in order to account for the contribution of the valence electrons to the dielectric function in the high frequency limit [32]. If there are no excess charges in the material (i.e. $\rho = 0$), Gauss law (eq. 1.3) and eq. 1.6 lead to the condition

$$\epsilon \left(\vec{k} \cdot \vec{E}_0 \right) = 0, \tag{1.26}$$

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Figure 1.4: Complex index of refraction \tilde{n} of SiC from eq. 1.13, split into real (dispersive) and imaginary (absorptive) part n and k. The absorption resonance of the transvers phonon at ω_{TO} is evident. Interestingly, k > 0 up to ω_{LO} , which indicates that excitations in the material still exist for frequencies above ω_{TO} . The reflectivity from eq. 1.30, plotted in red, exhibits its typical behaviour of almost 1 in the Reststrahlen band, as it is expected for $\epsilon < 0$, describing an atomic motion compensating the electric field of the incoming electromagnetic wave. Furthermore, it is k > n, which is characteristic for this region of high reflectivity.

where the plane wave (eq. 1.10) was plugged in. This equation can be satisfied either by $\vec{k} \cdot \vec{E} = 0$ or by $\epsilon = 0$. The former corresponds to the case where $\omega = \omega_{TO}$, i.e. the dielectric function exhibits a resonance. The latter, on the other hand, describes longitudinal waves, i.e. where $\omega = \omega_{LO}$ and $\epsilon(\omega_{LO}) = 0$. By solving eq. 1.25 in this special case (where γ is approximated to be zero) the expression $\frac{Nq^2}{\epsilon_{0m}} = \epsilon_{\infty} (\omega_{LO}^2 - \omega_{TO}^2)$ can be obtained. Plugging this into eq. 1.25 finally yields

$$\epsilon(\omega) = \epsilon_{\infty} \frac{\omega^2 - \omega_{LO}^2 - i\gamma\omega}{\omega^2 - \omega_{TO}^2 - i\gamma\omega}.$$
(1.27)

The real and imaginary part ϵ_1 and ϵ_2 , respectively, are plotted in fig. 1.3. By setting $\omega = 0$ and renaming $\epsilon(\omega = 0)$ to $\epsilon_{\omega=0}$, the Lyddane-Sachs-Teller relation is obtained [34]:

$$\frac{\epsilon_{\omega=0}}{\epsilon_{\infty}} = \frac{\omega_{LO}^2}{\omega_{TO}^2}.$$
(1.28)

The following section will discuss SPhPs at the interface of a polar crystal with a non-absorptive dielectric (with dielectric constant ϵ_A). As will be shown, SPhPs are limited by a cut-off frequency ω_S , which is the frequency where the real part of the dielectric function ϵ_1 crosses the negative value of ϵ_A , as shown in fig. 1.3. In order to get an expression for the frequency ω_S , the dielectric function (eq. 1.27)

is solved at $\epsilon_1(\omega_S) = -\epsilon_A$, which yields (using eq. 1.28):

$$\omega_S = \omega_{TO} \sqrt{\frac{\epsilon_A + \epsilon_{\omega=0}}{\epsilon_A + \epsilon_{\infty}}}.$$
(1.29)

From eq. 1.13, the complex index of refraction can be calculated, which is plotted in fig. 1.4. Since in the Restrahlen band ϵ_1 is negative, n is almost zero (non zero contribution comes from the damping). The reflectivity of a material with refractive index \tilde{n} for normal incidence is [33]:

$$R_{\perp} = \left| \frac{\tilde{n} - 1}{\tilde{n} + 1} \right|^2 = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2},\tag{1.30}$$

which is also shown in fig. 1.4. As eq. 1.30 suggests for $n \rightarrow 0$, the reflectivity is maximal in the Restrahlen band. This is analogous to the high reflectivity of metals below the plasma edge, i.e. where $\epsilon_1 < 0$, which means that \tilde{n} is purely imaginary [35].



Figure 1.5: Illustration of a surface electric dipole excitation with a wavenumber k close to zero at the interface of a non-dispersive (A) and a dispersive (B) medium (both isotropic). \vec{P} denotes the polarization, and the red and green circles indicate the wave of surface charges at the interface produced by the polarization wave. The resulting electric field \vec{E} is drawn in orange. To this surface phonon excitation, a p-polarized photon can couple, forming together a SPhP.

1.2 Surface Phonon Polaritons

As will be shown in the following section, a very special solution to the Maxwell equations are the so called surface polaritons, which can be understood as a mixture of a surface electric dipole excitation and a photon in a strongly confined area at the interface between two media. First, we will take a closer look at a general surface electric dipole excitation [36]. Afterwards in section 1.2.1, the dispersion relation of SPhPs for an isotropic medium will be derived, and in section 1.2.2, SPhPs on uniaxial crystals are discussed. Finally, the Otto geometry as a coupling configuration is presented in section 1.2.3.

In figure 1.5, an interface between a non-dispersive, dielectric medium A and an isotropic dielectric medium B is depicted, where the interface extends in the x-y-plane. The blue arrows indicate the polarization \vec{P} of a transverse electric dipole wave propagating in the x-direction. If this excitation is considered in the bulk, no effective charge density will be present. At an interface, however, the polarization wave creates local charge densities, which oscillate in the same fashion as \vec{P} and produce circular electric fields, depicted in orange. The field strength decays with increasing distance from the surface since the overall field sums up to zero, which localizes the excitation at the surface. Furthermore it has just x- and z-components, since the propagation direction was taken to lie in the x-direction (this implies no restriction due to the isotropy of material B).

By looking at the boundary conditions from the Maxwell equations

$$\vec{D}_{\perp}, \ \vec{B}_{\perp}, \ \vec{E}_{\parallel}, \ \vec{H}_{\parallel}$$
 continuous (1.31)

and recalling that $\vec{D} = \epsilon_0 \epsilon \vec{E}$, the following condition for the existence of the surface electric dipole excitation must hold:

This is a first evidence that SPhPs can only exist in the Reststrahlen band, where $\epsilon_B < 0$. In fact, the solution to eq. 1.32 gives exactly the cut-off frequency ω_S , also shown in figure 1.3.

Furthermore, this picture allows a qualitative insight into the polarization of surface excitations. Since the oscillating dipoles create \vec{E} -fields only in the *x*-*z*-plane, a coupled photon will necessarily have

its \dot{H} -field in the *y*-direction. Hence, coupling of incident light with the surface dipole excitation is only expected for *p*-polarized light (also called transverse magnetic (TM) wave, since the magnetic field stands perpendicular on the plane of incidence). This restriction to p-polarized light can be shown mathematically by solving the Maxwell equations for *s*-polarized light, which yields no solution [37].

Before continuing with SPhPs, bulk phonon polaritons in a polar crystal will be introduced briefly, i.e. the coupling between a phonon and a photon propagating through the bulk of a material. In order to achieve the dispersion relation, the dielectric function of a polar crystal (eq. 1.27) is substituted into the square of the dispersion relation of light (eq. 1.12), which yields [32]

$$k^{2} = \frac{\omega^{2}}{c^{2}} \epsilon_{\infty} \frac{\omega^{2} - \omega_{LO}^{2} - i\gamma\omega}{\omega^{2} - \omega_{TO}^{2} - i\gamma\omega}.$$
(1.33)

This is a quadratic equation in ω^2 , which means that for every k, two branches exist. This function is visualized in figure 1.6 together with the dispersion relation of SPhPs, which will be derived in the following section.

1.2.1 Dispersion Relation for Isotropic Crystals

A single interface of an isotropic crystal with a second dielectric is the most simple configuration, in which the SPhP can be discussed. Therefore, the full derivation of the dispersion relation for this special case is given in the following, before the more complex cases of a non-isotropic crystal and the Otto geometry are are dealt with.

Derivation A plane surface wave is chosen to propagate along the x-direction on a x-y-surface and to be a TM wave, which gives the explicit form

$$\vec{E} = \vec{E}_{0\pm} e^{i(\omega t - k_{x\pm}x \mp k_{z\pm}z)},$$
(1.34)

where the subscript \pm stands for $z \ge 0$, i.e. for the two half spaces filled by material A and B (see fig. 1.5). Since the k component parallel to the interface k_x must be continuous, in the following it will be written $k_{x+} = k_{x-} = k_x$. When this wave is plugged into the three dimensional wave equation

$$\Delta \vec{E} = \frac{\epsilon_{\pm}}{c^2} \vec{\vec{E}},\tag{1.35}$$

the relation $k_{z\pm} = \sqrt{\frac{\omega^2}{c^2}\epsilon_{\pm} - k_x^2}$ is obtained. In order to get an actual surface wave, however, the \vec{E} -field should vanish for increasing distance to z = 0. This is only achieved for complex $k_{z\pm}$, because by this means the z part in the exponent of eq. 1.34 gets real and hence results in an exponential decay in both z directions (for correctly chosen signs). Therefore, with the definition

$$\kappa_{\pm} \coloneqq ik_{z\pm} = \sqrt{k_x^2 - \frac{\omega^2}{c^2}\epsilon_{\pm}},\tag{1.36}$$

where κ_{\pm} are meant to be real and positive (to be shown), eq. 1.34 becomes

$$\vec{E} = \vec{E}_{0\pm} e^{i(\omega t - k_x x)} e^{\mp \kappa_{\pm} z}.$$
 (1.37)



Figure 1.6: Dispersion relations for bulk phonon polaritons (eq. 1.33) and for SPhPs (eq. 1.44). In the Reststrahlen band, no bulk phonon polaritons can exist, and the reflectivity is almost 1. SPhPs, on the other hand, just exist in this region up to the cut-off frequency ω_S . Parameters for vacuum and SiC are the same as specified in fig. 1.3.

In order to get expressions for the vector components of the \vec{E} -field and by this means also extract the dispersion relation, the Maxwell equations 1.2 and 1.4 for a plane wave in a material with $\rho = 0$, $\vec{j} = 0$ are taken

$$\vec{\nabla} \times \vec{E} = -i\omega\mu_0 \vec{H} \tag{1.38}$$

$$\vec{\nabla} \times \vec{H} = i\omega\epsilon\epsilon_0 \vec{E},\tag{1.39}$$

where the time derivative was carried out explicitly. Now, either \vec{H} from eq. 1.38, or \vec{E} from eq. 1.39 can be substituted into eq. 1.39 or 1.38, respectively. This yields for the \vec{E} -field

$$\Delta \vec{E} + \frac{\omega^2}{c^2} \epsilon \vec{E} - \vec{\nabla} \left(\vec{\nabla} \vec{E} \right) = 0, \qquad (1.40)$$

where the identities $\mu_0 \epsilon_0 = c^{-2}$ and $\vec{\nabla} \times (\vec{\nabla} \times \vec{E}) = \vec{\nabla} \cdot (\vec{\nabla} \cdot \vec{E}) - \Delta \vec{E}$ were used. Since a TM wave is considered, the \vec{E} -field has no *y*-component. It then can be easily verified that the *x*-component of the \vec{E} -field from eq. 1.40 satisfies

$$\frac{\partial^2 E_x}{\partial z^2} + \frac{\omega^2}{c^2} \epsilon E_x - \frac{\partial^2 E_z}{\partial x \partial z} = 0.$$
(1.41)

When eq. 1.37 is plugged into this equation, the following relation between the field components is obtained:

$$E_{0\pm_z} = \mp i \frac{k_x}{\kappa_\pm} E_{0\pm_x}.$$
(1.42)

Applying again the boundary condition for the displacement \vec{D} ($\epsilon_+ E_{0+z} = \epsilon_- E_{0-z}$) and the boundary condition for \vec{E} ($E_{0+x} = E_{0-x}$) yields the following relation:

$$\frac{\kappa_+}{\epsilon_+} = -\frac{\kappa_-}{\epsilon_-}.\tag{1.43}$$

Since κ_+ , κ_- and ϵ_+ are positive, ϵ_- has to be negative. Substituting eq. 1.36 into this equation finally gives the dispersion relation for a SPhP:

$$k_x = k_{SPhP} = \frac{\omega}{c} \sqrt{\frac{\epsilon_+ \epsilon_-}{\epsilon_+ + \epsilon_-}}.$$
(1.44)

This is plotted in figure 1.6 together with the dispersion relation for bulk phonon polaritons (eq. 1.33). Similar derivations can be found in [38, 39]. It is worth emphasizing that this dispersion (eq. 1.44), although derived for surface phonon polaritons, is also valid for the well studied Surface Plasmon Polaritons (SPPs), i.e. the coupling between a photon and a collective electron oscillation.

When this relation (eq. 1.44) is substituted into eq. 1.36, the necessary condition on the dielectric functions of the materials for the existence of the surface wave (eq. 1.37) can be extracted:

$$\kappa_{\pm} = \frac{\omega}{c} \frac{|\epsilon_{\pm}|}{\sqrt{-(\epsilon_{+} + \epsilon_{-})}} \longrightarrow \epsilon_{-} < -\epsilon_{+}, \tag{1.45}$$

since κ_{\pm} have to be real. Hence, SPhPs can only exist within the Reststrahlen band between ω_{TO} and ω_S , i.e. where $\epsilon_{-} < -\epsilon_{+}$, as it also becomes clear from fig. 1.6.

It must be noted, though, that in general, material B can have a damping γ , and hence ϵ_{-} is complex. In that case, the condition eq. 1.45 needs to be modified to read $Re(\epsilon_{-}) < -Re(\epsilon_{+})$.

Discussion From the expression for κ_{\pm} (eq. 1.45), the penetration depth *d* into both half spaces can be calculated, i.e. the depth, at which the field amplitude has decayed to $\frac{1}{e}$:

$$d_{\pm} = \frac{1}{|\kappa_{\pm}|} = \frac{c}{\omega |\epsilon_{\pm}|} \left| \sqrt{\epsilon_{+} + \epsilon_{-}} \right|.$$
(1.46)

The penetration depth (eq. 1.46) is plotted in fig. 1.7 (a) in both *z*-directions, where for the material A the penetration depth with and without damping is shown. The penetration depth into the polar crystal B is rather short compared to material A (plotted for vacuum), but never vanishes. Into material A, a resonance behaviour can be observed at ω_{TO} .

In order to get an expression for the propagation length L along the x-direction, the dispersion (eq. 1.44) must be split into real (propagating) and imaginary (decaying) part $k_x = k_{x_1} + ik_{x_2}$. With this, the propagation length can be expressed as

$$L = \frac{1}{2 |k_{x_2}|}.$$
 (1.47)

The group velocity v_q of the SPhP is given by

$$v_g = \left(\frac{\partial k_{x_1}}{\partial \omega}\right)^{-1},\tag{1.48}$$



Figure 1.7: General properties of SPhPs: (a) Penetration depth in μ m (eq. 1.46) of a SPhP at the interface of vacuum (*A*) and SiC (*B*). The penetration depth into material *A* is shown with (blue) and without (green) damping, the penetration depth into material *B* is plotted in red. Close up views show the behaviour close to ω_{TO} and ω_S . In the latter, the penetration depths into both materials converge (for the damped case). (b) shows the propagation length (eq. 1.47), (c) the group velocity (eq. 1.48) and (d) the decay time of a SPhP at the interface of vacuum (*A*) and SiC (*B*) (parameter specification see fig. 1.3).

and finally, this yields for the decay time $\tau = \frac{L}{v_g}$ [39]. All three quantities are also plotted in figure 1.7 (b), (c), and (d).

In order to get a better understanding of the nature of SPhPs, it is very instructive to take a closer look at the \vec{E} -fields. By applying eq. 1.42, an explicit form of the vector components is obtained [14]:

$$\vec{E}_{\pm} = E_0 \begin{pmatrix} 1\\0\\ \mp \frac{ik_x}{\kappa_{\pm}} \end{pmatrix} e^{i(\omega t - k_x x)} e^{\mp \kappa_{\pm} z}, \qquad (1.49)$$

with amplitude E_0 , which will be set to 1 for simplicity. In figure 1.8, a 3D plot of the *x*-component is shown. It can be nicely seen, how the decay into both materials changes with frequency. The slight oscillatory behaviour (best visible at ω_{TO}) arises due to the damping, which results in a small imaginary part in the *z* exponent. The figure was plotted for the stationary case (x = 0 and t = 0).

The complete \vec{E} field (eq. 1.49) at different frequencies is shown in fig. 1.9 as vector plots in the x-z-plane at t = 0, $\gamma = 3.75$ cm⁻¹. A similar picture for surface plasmons can be found in [40]. By this means, several features are clearly visible: First, the propagation length (in x-direction) decreases for increasing



Figure 1.8: Normalized *x*-component amplitude distribution of the \vec{E} -field of a SPhP as a function of frequency. For z > 0, the \vec{E} field extends into material A (vacuum), for z < 0 into the polar crystal B. The high spatial confinement to the surface is nicely visible. Just for frequencies close to ω_{TO} , the field extends further into the vacuum, as seen in fig. 1.7. Parameters for vacuum and SiC as in fig. 1.3.

frequency, and the field extension in *z*-direction depends on the frequency for both materials. Secondly, the field has both sources and sinks at the interface which are starting and ending points for circular field lines, as depicted qualitatively in fig. 1.5. For higher frequencies, the distance (wavelength) between those points decreases. This particular shape is familiar from the evanescent wave depicted in fig. 1.2, giving a good intuitive understanding of the strong coupling mechanism.

Finally, for frequencies close to ω_S (noticeable already in 1.9c), the expected shape of a surface electric dipole excitation is obtained, whereas close to ω_{TO} (1.9a), the field points mainly normal to the surface for z > 0 and in plane for z < 0 with almost no curvature in the field lines. This is, at least for z > 0, the exact shape expected for a TM plane wave. Hence, operating closer to ω_{TO} results in an electromagnetic wave-like character of the polariton, whereas closer to ω_S , the dipole excitation character predominates.

1.2.2 SPhP Dispersion Relation in Uniaxial Crystals

When generalizing from an isotropic to a non-isotropic material, the scalar dielectric function ϵ has to be replaced by a tensor $\bar{\epsilon}$, which, in general, has diagonal elements $\bar{\epsilon}_{ii}$ and off-diagonal elements $\bar{\epsilon}_{ij}$, with i, j = x, y, z:

$$\bar{\epsilon} = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{xy} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{xz} & \epsilon_{yz} & \epsilon_{zz} \end{pmatrix}.$$
(1.50)



Figure 1.9: \vec{E} fields of a SPhP at the interface between vacuum (z > 0) and SiC (z < 0) at four different excitation energies inside the Reststrahlen region. The transition from a TM wave at energies close to ω_{TO} to a dipole excitation at energies close to ω_S can be nicely seen. Parameters for vacuum and SiC as in fig. 1.3.



Figure 1.10: Demonstration of the three possible configurations for a SPhP propagating on the surface of a uniaxial crystal. Geometry A is called *ordinary*, while B and C are *extraordinary* because there, the SPhP depends on the crystal anisotropy. A uniaxial crystal as illustrated in B is called *c*-cut.

However, by rotating the crystal such that its main axes coincide with the principle axes of the physical system, the off-diagonal terms can be set to zero. Furthermore, for the special case of uniaxial crystals, only one principle axis, i.e. the *c*-axis, differs from the other two. This means that $\bar{\epsilon}$ does only contain the two components ϵ_{\parallel} and ϵ_{\perp} , which correspond to the directions parallel and perpendicular to the *c*-axis, respectively.

Considering a SPhP on a uniaxial crystal, three configurations have to be distinguished, which are illustrated in fig. 1.10. For case A, the c-axis lies in the surface plane pointing in the y-direction, and the SPhP propagates perpendicular to the c-axis, in the x-direction. Here, the \vec{E} fields lie in the x-z-plane, and therefore the SPhP depends only on ϵ_{\perp} . This situation is referred to as *ordinary*, since it is exactly the same as for an isotropic crystal with dielectric function ϵ_{\perp} . The dispersion relation hence reads

$$A: \qquad k_x^o = \frac{\omega}{c} \sqrt{\frac{\epsilon_\perp \epsilon_+}{\epsilon_\perp + \epsilon_+}},\tag{1.51}$$

where ϵ_+ represents again the scalar dielectric function of the adjacent isotropic medium.

The cases B and C, on the other hand, depend on both dielectric components, and are called *extraordinary*. In configuration B, the *c*-axis is perpendicular to the interface, and hence \vec{E} couples to both ϵ_{\parallel} in the *z*-direction, and ϵ_{\perp} in the *x*-direction. The dispersion relation is then given by [41, 42]

$$B: \qquad k_x^{e1} = \frac{\omega}{c} \sqrt{\epsilon_+ \epsilon_{\parallel} \frac{\epsilon_\perp - \epsilon_+}{\epsilon_{\parallel} \epsilon_\perp - \epsilon_+^2}}.$$
(1.52)

Such uniaxial crystals, which have their *c*-axis pointing perpendicular to the surface, are called *c*-cut.

In case C, the c-axis lies again in the interface plane, but is also parallel to the propagation direction \vec{k} . Therefore, the \vec{E} field points into ordinary and extraordinary crystal directions and involves both components of $\bar{\epsilon}$. In that configuration, the dispersion relation is given by [41, 42]

$$C: \qquad k_x^{e^2} = \frac{\omega}{c} \sqrt{\epsilon_+ \epsilon_\perp \frac{\epsilon_\parallel - \epsilon_+}{\epsilon_\parallel \epsilon_\perp - \epsilon_+^2}}.$$
(1.53)

These three dispersion relations are plotted in fig. 1.11, where ϵ_{\perp} and ϵ_{\parallel} have been simulated with eq. 1.27 using *TO* and *LO* frequencies for hexagonal, uniaxial 6H-SiC given by [43], and γ and ϵ_{∞} are taken from [15], as specified before. For the ordinary SPhP (green), the cut-off frequency ω_S^o has been



Figure 1.11: SPhP dispersion relations in uniaxial 6H-SiC for the three different configurations *A*, *B*, and *C* given by equations 1.51, 1.52, and 1.53, respectively. The chosen uniaxial crystal is 6H-SiC, with frequencies $\omega_{TO}^{\parallel} = 788 \text{ cm}^{-1}, \omega_{LO}^{\parallel} = 964 \text{ cm}^{-1}, \omega_{TO}^{\perp} = 797 \text{ cm}^{-1}$, and $\omega_{LO}^{\perp} = 970 \text{ cm}^{-1}$, taken from [43].

calculated with eq. 1.29. It lies directly on the peak k value, which can be expected to be analogous for the cut-off frequencies of the extraordinary SPhPs.

For 6H-SiC, the resonance frequency splitting between ordinary and extraordinary crystal direction is rather small ($\sim 4\%$ of the average Reststrahlen band), which is why the three different dispersion relations are quite similar. In a first approximation, this allows the description of SPhPs in weakly anisotropic crystals as it is done in section 1.2.1, as if the active medium was an isotropic crystal. In order to achieve a more accurate description of the physics in anisotropic crystals such as 6H-SiC, a matrix method can be applied, which is done in section 2.2.

1.2.3 Coupling of Light to SPhPs in the Otto Geometry

In order to describe the coupling behaviour to SPhPs, the incident medium is chosen to be a nonabsorptive material with dielectric function ϵ_A , and the SPhP propagates at the surface of medium Bwith dielectric function ϵ_B . When plotting the dispersion relation k_x of such a SPhP (eq. 1.44) together with the dispersion of light q_A (eq. 1.12) in medium A, see fig. 1.12, it becomes clear that the dispersions have no crossing point. For this two-layer system this means that SPhPs cannot be excited, and they are, vice versa, non-radiative.

The crossing of dispersion relations, however, is required in order to fulfil energy and momentum conservation simultaneously. In order to achieve coupling to SPhPs, several techniques can be applied. For instance, a periodic line grating can be cut into the surface, which was already done for SPPs in 1969 [44] and more recently, also for plasmons on metal tips [45]. By this means, the wave vector of the incident light gets a "kick" by the wave vector of the grating, and thus can cross the polariton dispersion.

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Figure 1.12: Illustration of the successful excitation of SPhPs in the Otto configuration, where the Reststrahlen band together with the dispersion of SPhPs (eq. 1.44) is shown. The red dispersion (eq. 1.12) corresponds to a photon in material A, i.e. vacuum in this case. No coupling can occur to the SPhP because the light line has no crossing point with the SPhP dispersion. The purple lines correspond to dispersions for the x-component of light travelling in a third material (data for ZnSe) depending on the angle of incidence. Parameters for vacuum and SiC as in fig. 1.3.

In the case of a small grating amplitude h compared to the wavelength ($h \ll \lambda$), the critical coupling condition reads as follows [38]

$$k_x = q_x - n\frac{2\pi}{p},\tag{1.54}$$

where p is the periodicity of the grating and $n \in \mathbb{N}$. For the study of the properties of polaritons on surfaces, however, it is favourable to avoid roughness on the sample, since a smooth surface is much easier to handle theoretically.

In order to couple to polaritons on a smooth surface, in 1968 Otto proposed a coupling method via ATR [14], which uses a prism P in front of material B, leaving a small gap of material A. This setup is illustrated in fig. 1.13 and will be implemented in this work. An alternative configuration was proposed by Kretschmann and Raether [46], where the polariton active medium is a thin film attached to a prism and the SPP propagates at the backside interface between film and air.

One experimental advantage of the Otto configuration is the adjustability of the thickness of the interlayer A, which is not available in the Kretschmann configuration. On the other hand, the precise control of the gap size is quite challenging. For SPhPs, the necessary size lies in the range of μm and is thus achievable, whereas SPPs need gap sizes in the range of 10 - 100 nm. Since this study focusses on the excitation of SPhPs, employing the Otto geometry with variable gap size is a reasonable choice.



Figure 1.13: Illustration of the Otto geometry for prism coupling to SPhPs. A dielectric material A separates by distance d the prism P from the polariton active medium B. The evanescent wave from total internal reflection E_{evan} can excite the SPhP when the critical values incident angle θ , incident wavelength and distance d are matched.

As stated in section 1.1.2, the evanescent wave which emerges at total internal reflection can be accessed when bringing an absorbing medium close enough to the interface. If the attenuating material exhibits a resonance, e.g. a polariton, it can couple to the evanescent wave. When measuring the reflectivity as a function of the incoming wavelength, this resonance manifests as a dip in the reflectivity in the Reststrahlen region at the energy of the polariton, where otherwise unity reflectivity would be measured. The reflectivity spectra will be discussed in detail in section 2.1.1.

As it was stated by Otto [14], the evanescent wave will be resonant with the polariton in the case of matching phase velocities, or, equivalently, when their in plane component of the wave vectors are the same, i.e.

$$q_x = k_x. \tag{1.55}$$

The *x*-component q_x of the incoming light is a function of the incident angle θ and the dielectric function of the prism ϵ_P :

$$q_x = \frac{\omega}{c} \sqrt{\epsilon_P} \,\sin\theta. \tag{1.56}$$

By this means, the incident angle serves as a tuning parameter of the slope of the dispersion line of the incoming light, and hence allows the dispersions to cross, as depicted in fig. 1.12. As a result, for each angle θ (in the region of total internal reflection), there exists a specific light energy $\hbar \omega$, at which the dispersion of light crosses the curve of the SPhP, and hence allows coupling. The wave vector at resonance shall be called k_x^0 . The case of incident angle $\theta = 90^\circ$ defines a natural upper limit, which means that coupling is just possible up to an energy slightly below ω_s , as it becomes clear from fig. 1.12.

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Up to this point, the SPhP was just considered at an interface of two semi-infinite media. In the Otto geometry, however, a third medium is present (the prism), which influences the nature of the SPhP in a non-negligible manner. As a starting point for the understanding of this system, a qualitative description will be given.

For large gap sizes ($d \gg d_{SPhP}$ and $d \gg d_{evan}$, i.e. penetration depths of SPhP and evanescent wave, respectively), the SPhP does not "see" the prism, and hence is not disturbed in its two-layer nature. As the gap between prism and polariton active medium decreases, however, the amount of SPhP leaking into the gap which reaches the prism grows, which enables a radiative loss into the prism. This also results in a change of the value of the resonance wave vector k_x^0 and broadening of the resonance. This difference is, generally, a complex value, where the real part describes a shift of the resonance position, and the imaginary part represents the radiative loss into the prism [39].

For large distances, the exponentially decaying evanescent wave cannot excite the SPhP effectively. This regime will be referred to as the *under-coupled* region. At some point, the evanescent wave and the SPhP overlap such that optimal coupling conditions are reached. At this critical distance d_{crit} , the reflectivity reaches its minimum and will be even zero for resonant wave vector matching, i.e. the incoming light is fully absorbed by the SPhP. When coming even closer, the radiative loss gains the upper hand and the coupling effectiveness decreases. This regime will be referred to as the *over-coupled* region.

In sections 2.1 and 2.2, this rather qualitative picture shall be enriched by a quantitative description of the reflectivity of a smooth, parallel multilayer system. The solutions for three layers will then lead to an accurate prediction of the coupling behaviour in the Otto geometry, as discussed above.

Furthermore, the transmittance in such a three- or multilayer system will be calculated, which provides the field enhancement in the polariton-active medium. This field enhancement turns out to be a good qualitative estimate for the non-linear signal arising from SPhPs, which is one of the main goals of this work. Hence, the following section will briefly introduce and discuss the effect of SHG.

1.3 Second Harmonic Generation

One aim of this work is the investigation of the non-linear response of SPhPs. This section is therefore dedicated to give a brief introduction to second-order non-linear effects, and to discuss the first non-linear effect ever observed [47], i.e. Second Harmonic Generation (SHG).

As stated at the beginning, the response in a material \vec{P} to an applied electric field \vec{E} is approximately linear, as long as the incident intensity is weak enough (eq. 1.7). For stronger incident fields, however, every material exhibits a non-linear response, which is the driving principle of non-linear optics. The electric polarization \vec{P} is then a complicated function of \vec{E} , and cannot be written down analytically any more. This is the origin of many optical non-linear effects like SHG, Sum Frequency Generation, Difference Frequency Generation, or Electro-Optical Rectification - which are all second-order effects and many others of higher order.

In the special case of plane waves and in the electric dipole approximation, the electric polarization \vec{P} can be expanded in a power series of \vec{E} , where the *n*th coefficient is a tensor $\chi^{(n)}$ of rank (n + 1) [48]:

$$\vec{P}(\omega) = \chi^{(1)}(\omega) \cdot \vec{E}(\omega) + \chi^{(2)}(\omega_3 = \pm \omega_1 \pm \omega_2) : \vec{E}(\omega_1)\vec{E}(\omega_2) + \dots .$$
(1.57)

Analogous to the dielectric function ϵ , the susceptibility χ describes all optical properties of a material, and the exact knowledge of all $\chi^{(n)}$ terms would, in principle, allow the prediction of any *n*th order non-linear effect. In practice, however, an exact solution is not feasible even for the most simple nonlinear systems. A thorough experimental investigation of the occurring non-linear effects is therefore of essential importance. Most recently, the Reststrahlen band of a hexagonal polytype of SiC has been studied by means of SHG-spectroscopy [17]. The promising results of this study suggests a similar approach concerning SPhPs, which is demonstrated in the results in chapter 4 and 5.

In a very simple picture, the effect of SHG can be understood in terms of an energy diagram as a threelevel process, which is depicted in fig. 1.14. Two incident photons at energy $\hbar\omega_{FEL}$ from the incident light source, in this experiment an FEL, are needed in order to excite a system from the ground state $|0\rangle$ to the state $|2\rangle$, through the intermediate state $|1\rangle$, which lies at half the energy difference between $|0\rangle$ and $|2\rangle$. The energy from $|2\rangle$ is then emitted as a photon at double frequency $\omega_{SHG} = 2\omega_{FEL}$, constituting the SHG signal. The measured SHG intensity I_{SHG} is then, most generally, given by

$$I_{SHG} \propto |\chi^{(2)}(2\omega = \omega + \omega)\vec{E}(\omega)^2|^2, \qquad (1.58)$$

where $\chi^{(2)}$ is the second-order susceptibility tensor, which has in total 27 coefficients, and \vec{E}^2 is a symmetric tensor. Therefore, the resulting SHG signal can exhibit enhancements of two types, one originating from a $\chi^{(2)}$ resonance, and the other being a resonance in the local fields at the sample site. For the case of SPhPs, the local fields exhibit a strong enhancement, which is the source of SHG coming from SPhPs. This field enhancement can be described by the Fresnel transmission coefficient, i.e. the ratio of field strength where the source is located to the incoming beam, which will be discussed in



Figure 1.14: Energy diagram with three states, visualizing the process of Second Harmonic Generation, where two incident photons at same frequency ω_{FEL} are converted into the second harmonic photon with double frequency ω_{SHG} . Within the electric dipole approximation, this process occurs only in materials with broken inversion symmetry. In general, $|1\rangle$ and $|2\rangle$ can be virtual energy levels. If the material exhibits a resonance at incident frequency, however, these states are real, and the process is called resonant SHG.

further detail in section 2.3. The $\chi^{(2)}$ dispersion, on the other hand, exhibits no features in the spectral range of the SPhP, see section 2.3.

Regarding the SHG signal from the bulk, the $\chi^{(2)}$ coefficients depend on the crystal symmetry, and for the case of centrosymmetric materials, they vanish completely (in the electric dipole approximation). Tables for the non-vanishing coefficients can be found in several text books [48, 49]. At the surface of a crystal, inversion symmetry is broken. Hence, even though a material does not exhibit SHG from the bulk, it will produce a surface SHG signal, which can be employed as a very surface-sensitive probing method [50, 51]. In a material with broken inversion symmetry, on the other hand, the surface signal is usually negligible [51].

When the incident frequency ω_{FEL} coincides with a resonance in the probed material, resonant SHG can be observed [17, 50], accounting for a strong enhancement. In principle, this allows the direct measurement of resonances of the studied sample, which is an advantage compared to reflectivity measurements, where resonant features are mainly only accessible via differentiation. This work aims at applying this approach to the SHG arising from SPhPs. While resonant enhancement of SHG from the bulk in non-centrosymmetric materials [17, 52, 53] as well as surface SHG from inversion symmetric media [50, 54, 55] has been studied intensively, the process of resonant SHG arising from SPhPs has been unclear. In this master's thesis, the measurement of such resonant SHG from SPhPs on non-centrosymmetric materials is performed and analysed, as will be discussed in terms of simulations in chapter 2 and experimental results in chapter 4 and 5.

The last section of this chapter is dedicated to describe the basic operation principle of an FEL. Thereafter, the following chapter will focus on the reflection and transmittance in an isotropic and anisotropic multilayer system. With the understanding given in this section, the field enhancement in the polariton-active medium will be discussed in section 2.2 as a crucial driving force of the expected SHG signal from SPhPs.



Figure 1.15: Typical setup of an oscillator FEL with an undulator constructed out of two sequences of permanent magnets with alternating, opposite poles. Picture taken from [58].

1.4 Operation Principle of a Free Electron Laser

A *laser*, as the name already suggests (*l*ight *a*mplification by stimulated *e*mission of *r*adiation), is a coherent, small-band light source based on the stimulated emission from an atomic or molecular system with population inversion. Compared to this emission process in a conventional laser, the FEL functions rather differently. Nevertheless, the generated radiation, the oscillation cavity as well as several device parameters are similar, and it even turns out that the underlying processes of light amplification in an FEL occur very similarly to stimulated emission and absorption in atoms and molecules. Hence, the wording free electron 'laser' seems again appropriate.

The origin of the light generated in an FEL is the Bremsstrahlung emerging from high energy electrons. Firstly, the electrons are produced in an electron gun and then accelerated up to relativistic velocities, before they enter the gap between two opposing sequences of permanent magnets with alternating poles, the so called undulator. Being forced on a sinusoidal path, the electrons emit coherent synchrotron radiation, which can be amplified in a resonator consisting of two mirrors. In order to operate in this manner, the radiation emitted in each curve of the electron path has to interfere constructively. This condition will be discussed in the following section.

After passing through the undulator, the electrons are finally led into an electron dump. A sketch of a typical setup is shown in fig. 1.15. The content of this section is mainly based on [56, 57].

1.4.1 Amplified Synchrotron Radiation in an Undulator

An undulator as depicted in fig. 1.15 which is oriented lengthwise and crosswise into the z and y direction, respectively, generates a magnetic field B_y of the magnitude

$$B_y = B_0 \cos\left(\frac{2\pi}{\lambda_u}z\right),\tag{1.59}$$

where B_0 denotes the field amplitude and λ_u the period length of the undulator as well as the field wavelength. In fig. 1.16 (a), this magnetic field is depicted. An electron travelling into the *z*-direction will be subjected to the Lorentz force and hence being deflected perpendicular to the *B*-field and the direction of movement, i.e. into the *x*-direction. The resulting movement is illustrated in fig. 1.16 (b).



Figure 1.16: Electron motion in the undulator of an FEL. In (a), the magnetic field B_y produced by an undulator with poles as indicated is illustrated. This field will force an electron travelling into the *z*-direction onto a sinusoidal curve in the *x*-*z*-plane, as depicted in (b). The synchrotron radiation emerges at an angle α with respect to the travelling direction.

In principle, in each curve that the electron follows, synchrotron radiation is emitted at an arbitrary angle α with respect to the travelling direction z. This process is analogous to the spontaneous emission occurring in a conventional laser. In order to achieve constructive interference for the radiation emerging from different points, the wavelength of the radiation λ has to fulfil the condition

$$n\lambda = c\frac{\lambda_u}{\bar{v}_z} - \lambda_u \cos\alpha, \tag{1.60}$$

where n = 1 stands for the fundamental wavelength and n > 1 for higher orders, with n being an integer, and \bar{v}_z denotes the average longitudinal velocity of the electron into the *z*-direction. By calculating the undulating velocity v_x , subsequently, an expression can be found for \bar{v}_z [57]

$$\bar{v}_z = c \left[1 - \frac{1}{2\gamma^2} \left(1 + \frac{K^2}{2} \right) \right],\tag{1.61}$$

with $\gamma = 1/\sqrt{1-\beta^2}$ being the relativistic factor and $\beta = v/c$ the reduced velocity for the treatment of high-energy relativistic particles, and $K = (eB_0\lambda_u)/(2\pi m_0c)$. In the approximation $\gamma \gg 1$ (ultrarelativistic limit) and $\alpha \ll 1$, the radiation wavelength in terms of the period length λ_u becomes

$$\lambda = \frac{\lambda_u}{2\gamma^2} \left[1 + \frac{K^2}{2} + (\gamma\alpha)^2 \right]. \tag{1.62}$$

Considering a bunch of electrons passing through the undulator, the radiation they produce will again interact with the same electrons. By this means, the kinetic energy which is lost into the synchrotron radiation, can be gained again by absorbing energy from the electric field. Exactly at the resonance energy given by eq. 1.60, this happens periodically within the periodic length of the undulator, where in one half of a wavelength the electrons get accelerated, and in the other half decelerated. For a

uniformly spread electron bunch, this results in the grouping of small electron bunches, which is called microbunching.

At the resonance, the processes of energy loss and gain cancel out and the net energy of the electrons is constant. Hence, in order to produce radiation, the electron energy must be slightly different from the resonant case. Denoting the average kinetic energy of an electron by T and describing the relative position of the electron to the electric field of the radiation by the phase ϕ , the following relation holds [57]

$$\frac{dT}{dt} = -\frac{e^2 B_0 E_0 \lambda_u}{4\pi\gamma m_0} \cos\phi.$$
(1.63)

For the resonance case, where $\cos \phi = 0$, this means for the average kinetic energy to be zero. For electron energies slightly below the resonance, i.e. $\cos \phi < 0$, the change in kinetic energy is dT/dt > 0, which means that the electrons retrieve energy from the electromagnetic field. This is analogous to the process of stimulated absorption in an atom or molecule. On the other hand, for energies slightly above the resonance, $\cos \phi > 0$ and therefore dT/dt < 0, i.e. the electrons lose energy into the radiation. This corresponds to stimulated emission in a conventional laser. Hence, the laser emission occurs at wavelengths slightly above the resonant wavelength given by eq. 1.60.
2 Simulations

By taking a look at the history of plasmonics, it quickly becomes clear that reflectivity measurements have always been the tool number one for the study of surface polaritons [14, 15, 44, 46]. Therefore it is quite worthwhile to thoroughly study the theoretical predictions for the reflectivity, ultimately given by the Maxwell equations. In this context, the transmittance into the substrate can be obtained too, which allows to calculate the electromagnetic field enhancement arising from SPhPs.

This chapter is separated into three parts, where the first two develop and apply two theoretical approaches in order to simulate SPhP resonances observable in the reflectivity and transmittance of polariton-active media in the Otto geometry. The first approach assumes only isotropic materials, and will lead to a profound understanding of a SPhP excited in a three-layer Otto system. The second approach includes full anisotropy (section 2.2), and will be used to simulate the reflectivity for a 6H-SiC and a AlN / 6H-SiC sample. In the last section (2.3), the field enhancement in the same systems is discussed.

2.1 Reflectivity of Isotropic Media

In this section, the reflectivity of a multilayer system consisting of isotropic materials will be derived, and then analysed in the case of a three-layer system. The latter is of special interest in this work, since it models adequately the dielectric crystal studied in the Otto geometry. Even though the isotropic reflectivity presented here is a special case of the anisotropic formalism derived later on, it is included in this work, because it leads to formulas which are generally known and widely used, and furthermore features much more simplicity than the elaborate 4×4 - matrix formalism.

2.1.1 Reflectivity of an Isotropic Multilayer System

Starting from Maxwell's equations, an expression can be obtained for the reflectivity of a plane electromagnetic wave impinging on a flat, parallel multilayer system, as it was first derived by Parratt in 1954 [59]. The result is a recursion formula, which can be applied to any number of layers, each of those described by a complex dielectric function. The situation for two interfaces, i.e. a three-layer system as described previously for the Otto geometry, is depicted in fig. 2.1 with the occurring multiple reflections.

A crucial disadvantage of this approach is its applicability restricted to isotropic materials only, which precludes the access to the exact description of several anisotropic materials of interest for the study of SPhPs, such as GaN, AlN, quartz, and all non-cubic polytypes of SiC. The corrections which arise from the anisotropic 4×4 - matrix formalism, as derived in appendix A, in comparison to the Parratt solution, however, are not very large, given that the anisotropy of the considered material is small. Therefore, this section assumes isotropic materials, and by this means benefits from a less complicated formalism.



Figure 2.1: Multiple reflection and transmission in a three-layer system with incident *p*-polarized+radiation at angle θ , with \vec{H} (green) in y-direction and \vec{E} (orange) in the x-z-plane. The blue arrow indicates the wave vector \vec{k} . For the calculation of the reflectivity of the complete system, the Parratt recursion formula starts at layer j = N + 1 and ends at j = 0, with N being the number of interlayers. Each layer is described by a complex dielectric function ϵ and is assumed to be isotropic.

Derivation The multilayer system will be described by N interlayers of thickness d_j , j = 1, ...N, where j = 0 denotes the semi-infinite medium in which incidence and reflectance take place, and j = N + 1 describes the semi-infinite substrate. The incidence medium is taken to be non-absorbing. The surface normal points in the z-direction, and each layer thickness d_j is described by the z-coordinate in the following way

$$d_j = z_j - z_{j-1}.$$
 (2.1)

For mathematical reasons, the thicknesses of both semi-infinite media are set to be $d_0 = d_{N+1} = 0$. As stated earlier (eq. 1.21), the reflectivity R is defined as the ratio of reflected $|\vec{E}'|^2$ to the incident $|\vec{E}|^2$ field intensities, equally valid for \vec{H}

$$R = \frac{|\vec{E}'|^2}{|\vec{E}|^2} = \frac{|\vec{H}'|^2}{|\vec{H}|^2}.$$
(2.2)

For *p*-polarized light incident in the *x*-*z*-plane, the only non-vanishing \vec{H} component is $H \coloneqq H_y$. Employing eq. 1.14, the forward and backward moving waves with \vec{E} components parallel to the *x*-*y*-plane in layer *j* can be written as

$$E_{\parallel}^{j} = E_{x}^{j} = \frac{q_{z}^{j}}{\omega\epsilon_{0}\epsilon^{j}}H^{j}, \qquad E_{\parallel}^{\prime j} = E_{x}^{\prime j} = -\frac{q_{z}^{j}}{\omega\epsilon_{0}\epsilon^{j}}H^{\prime j}.$$

$$(2.3)$$

These components are of particular interest, since they have to fulfil Maxwell's boundary conditions $\vec{E}'_{\parallel} = \vec{E}_{\parallel}$. Furthermore, the boundary conditions imply for the component of the wave vector parallel to the *x*-*y*-plane to be continuous, in which case $q_x^j = q'_x^j = q_x^{j+1} = q'_x^{j+1}$. For each layer *j*, this means

$$\vec{E}_x^j e^{iq_z^j z_j} + \vec{E}_x^{\prime j} e^{-iq_z^j z_j} = \vec{E}_x^{j+1} e^{iq_z^{j+1} z_j} + \vec{E}_x^{\prime j+1} e^{-iq_z^{j+1} z_j}$$
(2.4)

$$\vec{H}^{j}e^{iq_{z}^{j}z_{j}} + \vec{H}^{\prime j}e^{-iq_{z}^{j}z_{j}} = \vec{H}^{j+1}e^{iq_{z}^{j+1}z_{j}} + \vec{H}^{\prime j+1}e^{-iq_{z}^{j+1}z_{j}}.$$
(2.5)

By plugging eq. 2.3 into those equations, the following relations are obtained

$$f_{j}H^{j}e^{iq_{z}^{j}z_{j}}(1-\frac{R_{j}}{a_{j}}) = f_{j+1}H^{j+1}e^{iq_{z}^{j+1}z_{j}}(1-R_{j+1})$$

$$H^{j}e^{iq_{z}^{j}z_{j}}(1+\frac{R_{j}}{a_{j}}) = H^{j+1}e^{q_{z}^{j+1}z_{j}}(1+R_{j+1}),$$
(2.6)

where f_j , a_j and R_j are defined to be

$$f_j = \frac{q_z^j}{\epsilon^j} \tag{2.7}$$

$$a_j = e^{2iq_z^j d_j} \tag{2.8}$$

$$R_{j} = a_{j}e^{2iq_{z}^{j}z_{j}}\frac{H'^{j}}{H^{j}}.$$
(2.9)

The system of equations 2.6 can be solved for R_j by eliminating the exponential functions, which yields the Parratt recursion formula [59]

$$R_j = a_j \frac{r_j + R_{j+1}}{1 + r_j R_{j+1}},$$
(2.10)

with r_j being

$$r_j = \frac{f_j - f_{j+1}}{f_j + f_{j+1}}.$$
(2.11)

Since no reflection will emerge from the last medium (j = N + 1), it is defined that $R_{N+1} = 0$. By calculating the absolute value squared of eq. 2.10 given in the incident medium j = 0, the reflectivity R of the complete system is obtained:

$$R = |R_0|^2. (2.12)$$

Finally, an expression for the z-component of the wave vector in each layer k_z^j remains to be determined. For this means, it is reminded that the (parallel) x-component of the wave vector is conserved in each layer, being

$$q_x = -\frac{\omega}{c}\sqrt{\epsilon^0}\sin\theta.$$
(2.13)

For *p*-polarized light incident onto the *x*-*y*-plane, the wave vector reads $\vec{q} = (q_x, 0, q_z)$ and with the dispersion from eq. 1.12, the *z*-component becomes

$$q_z^j = \sqrt{\frac{\omega^2}{c^2}} \epsilon^j - q_x^2 = \frac{\omega}{c} \sqrt{\epsilon^j - \epsilon^0 \sin^2 \theta}.$$
(2.14)

For the sake of completeness, the reflectivity for *s*-polarized light is given by the same formulas, where the only difference lies in the calculation of f_j :

$$f_j = q_z^j. (2.15)$$

As a side remark, it must be noted that in the derivation presented here, the time dependence of the plane electromagnetic wave was considered to be $e^{i\omega t}$, as originally employed by Parratt. Even though the ongoing physics is not affected, this differs from the sign convention used in the previous sections. In order to achieve consistency, the only necessary follow-up sign change appears in the imaginary part of the dielectric function.



Figure 2.2: Visualization of the reflection and transmission in a three-layer Otto geometry (prism P, gap A, sample B) for p-polarized incident light. \vec{B}_{∞} is added in order to describe the process as a scattering event in terms of the scattering matrix S.

Discussion Considering a single interface (N = 0, j = 0, 1) consisting of material A and B, it can be immediately verified that the reflection coefficient becomes

$$r_{A,B}^{p} \coloneqq R_{0} = F_{0} = \frac{f_{0} - f_{1}}{f_{0} + f_{1}} = \frac{\frac{q_{z}^{A}}{\epsilon^{A}} - \frac{q_{z}^{B}}{\epsilon^{B}}}{\frac{q_{z}^{A}}{\epsilon^{A}} + \frac{q_{z}^{B}}{\epsilon^{B}}},$$
(2.16)

which corresponds to the Fresnel reflection coefficient for *p*-polarized light in terms of wave vectors, as it is usually formulated.

For the case of three layers (N = 1, j = 0, 1, 2) as visualized in fig. 2.1, the Parratt recursion formula yields

$$r_{123} \coloneqq R_0 = \frac{r_0 + r_1 e^{2iq_z^1 d_1}}{1 + r_0 r_1 e^{2iq_z^1 d_1}},\tag{2.17}$$

which resembles exactly the reflectivity of a three-layer system derived by Raether, McIntyre and others [39, 60]. For (almost) isotropic materials, this equation describes adequately the expected reflectivity measured in an ATR experiment in the Otto geometry, which is why it will be discussed in detail in section 2.1.3.

2.1.2 Scattering Matrix Formulation

Recently in 2013, the inventor of the Otto geometry, A. Otto, published a paper concerning the excitation of SPPs by ATR, where the theoretical description was tackled in terms of the scattering matrix S [61]. This approach will not be treated in detail here, but nevertheless suits nicely to give a complementary view on the subject.

The scattering matrix S, as it is known in electronics and quantum mechanics, connects the initial and final state of a particle which is scattered off a target. For p-polarized light, it is convenient to employ a

 2×2 matrix connecting the B-field amplitudes of the incident beams from both sides of the system, B_i and B_{∞} , with the reflected and transmitted beams, B_r and B_t , respectively:

$$\begin{pmatrix} B_t \\ B_r \end{pmatrix} = S \begin{pmatrix} B_i \\ B_\infty \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} B_i \\ B_\infty \end{pmatrix}.$$
(2.18)

Even though in this study, the only incident field is B_i and therefore $B_{\infty} = 0$, the total *S*-matrix is shown for completeness. Following [61], it reads

$$S = \begin{pmatrix} t_{123} & r'_{123} \\ r_{123} & t'_{123} \end{pmatrix} = \begin{pmatrix} \frac{(1+r_0)(1+r_1)}{1+r_0r_1e^{2iq_z^Ad}}e^{i(q_z^A - q_z^B)d} & \frac{-r_1 - r_0e^{2iq_z^Ad}}{1+r_0r_1e^{2iq_z^Ad}}e^{-2iq_z^Bd} \\ \frac{r_0 + r_1e^{2iq_z^Ad}}{1+r_0r_1e^{2iq_z^Ad}} & \frac{(1-r_0)(1-r_1)}{1+r_0r_1e^{2iq_z^Ad}}e^{i(q_z^A - q_z^B)d} \end{pmatrix},$$
(2.19)

where t_{123} and r_{123} denote the transmission and reflection coefficients for the incident field B_i , t'_{123} and r'_{123} for B_{∞} . The three layers are labelled P (prism), A (gap) and B (sample), as in the previous sections and the z-components of the wave vector q_z^j as well as the single interface reflection coefficients r_j (with $r_0 = r_{P,A}$, $r_1 = r_{A,B}$) are given in the previous section by eq. 2.14 and 2.16, respectively.

If a resonance is present in the target, in our case a surface polariton, it will show up as poles in the elements of the S-matrix. This means for their common denominator to be zero, which yields

$$1 + r_0 r_1 e^{2iq_z^A d} = 0. (2.20)$$

The physical meaning of this equation is nothing else than the dispersion relation of surface polaritons in a three-layer system of isotropic materials. Furthermore, it allows to calculate the optimal distance d_{opt} (i.e. the distance between prism and sample, where the SPhP most efficiently absorbs the incoming light, see section 1.2.3), for a given set of incident angle θ and incident frequency ω as follows:

$$d_{opt}(\omega,\theta) = \frac{1}{2iq_z^A(\omega,\theta)} \ln\left(-\frac{1}{r_0(\omega,\theta) r_1(\omega,\theta)}\right).$$
(2.21)

2.1.3 SPhP Resonance in Isotropic SiC in the Otto Geometry

In order to get a deeper understanding of the critical coupling conditions for the excitation of SPhPs in the Otto geometry, the following section focusses on the discussion of the huge information content of eq. 2.17. This is most easily accessible by considering and analysing a specific example. The chosen media are ZnSe for the prism (*P*) with a dispersive dielectric function given by an empiric formula for the mid-infrared spectral region [62], vacuum (*A*), and isotropic SiC (*B*) with dielectric function described by eq. 1.27 ($\omega_{TO} = 796 \text{ cm}^{-1}$, $\omega_{LO} = 972 \text{ cm}^{-1}$, $\gamma = 3.75 \text{ cm}^{-1}$, $\epsilon_{\infty} = 6.5$).

Spectra of the reflectivity R are plotted in fig. 2.3, on the left in (a), (b), and (c) as a function of incident frequency ω for various incidence angles θ and at three different distances d, and on the right in (d), (e), and (f) as a function of θ for various ω , also at three different distances. In the frequency spectra, the Reststrahlen band is clearly visible for angles close to the critical angle of total internal reflection θ_{crit} . For larger angles, the evanescent wave reaches less far into the gap and hence "sees" less of the underlying SiC sample (which is the origin of the Reststrahlen band).

For each graph, a set of parameters (θ, ω, d) can be found, for which the resonance conditions are met, i.e. the SPhP dip in the reflectivity reaches zero. It becomes clear that for increasing distance d, the



Figure 2.3: Calculated three-layer reflectivity (eq. 2.17) for three different gap sizes in the Otto geometry (ZnSe / vacuum / SiC). On the left in (a), (b), and (c), frequency spectra for various θ are shown, and on the right in (d), (e), and (f), the reflectivity as a function of θ for various frequencies is plotted. The resonance position of the SPhP shifts as a function of all three parameters.



Figure 2.4: 2d spectra of the reflectivity (eq. 2.17) of the ZnSe / vacuum / SiC Otto configuration for all combinations of the three parameters frequency ω , incident angle θ , and gap size d, each for 5 different fixed values of the respective third parameter. The reflectivity is encoded from 0 (white) to 1 (green). In all maps, the SPhP resonance appears as a branch of low reflectivity.



Figure 2.5: 3d parametric curve of parameter sets consisting of incident angle θ , frequency ω , and gap size d at critical coupling conditions in the Otto geometry, i.e. where the reflectivity reaches zero due to excitation of a SPhP.

resonance position shifts to lower ω and to smaller θ . This is in perfect agreement with the observations made concerning the penetration depths of evanescent wave and SPhP in sections 1.1.2 and 1.2.1. For larger distances, both have to reach further into the gap, which is achieved for angles closer to θ_{crit} for the evanescent wave, and for frequencies closer to ω_{TO} for the SPhP. A further conclusion which can be extracted is that for smaller angles, the width of the resonance in the frequency is larger whereas for larger frequencies, the angular width increases. This is easy to understand qualitatively by looking at the dispersion of a SPhP as shown in fig. 1.12, since the gradient of the dispersion is close to that of light at ω_{TO} , whereas close to ω_S , a large angle range is covered by a small section of frequency.

In fig. 2.4, 2*d* reflectivity maps are shown for five different *d* as a function of θ and ω (a), for five different ω as a function of *d* and θ (b), and for five different θ as a function of *d* and ω (c). White and red areas denote low reflectivity, which corresponds to the excitation of a SPhP inside the Reststrahlen band. These curved stripes have each a point of zero reflectivity, where the ideal coupling conditions between photon and SPhP are reached. As discussed above, the edges of the Reststrahlen band (columns a and c) are visible for small angles as well as for small distances.

In the 2*d* reflectivity maps, the trace in the θ - ω -*d*-parameter space of optimal coupling conditions is already visible, e.g. in the right column, where the resonance dip moves from ω_{TO} for angles close to θ_{crit} towards ω_S for larger angles. Nevertheless, as an additional visualization, in fig. 2.5 the parametric 3*d* curve of optimal coupling parameters (θ , ω , *d*) is shown. It is interesting to note, that the maximal resonance frequency (the plot reaches up to 940 cm⁻¹) lies well below the actual surface dipole excitation cut-off frequency $\omega_S = 950.4 \text{ cm}^{-1}$. Furthermore, for incidence angles larger than 60°, the resonance position shifts back again to smaller frequencies. This is contradictory to the picture of the crossing dispersion curves as discussed in section 1.2.3 (see fig. 1.12), where the frequency increased monotonically with increasing θ , having a natural upper limit at 90°. This discrepancy is explained by the two different systems under consideration, being a two-layer and a three-layer system. The prism crucially alters the dispersion curve of the SPhP in a two-layer system, having the largest impact at very small gap sizes (the turning back of the zero reflectivity curve in fig. 2.5 happens at $d < 1 \mu$ m).



Figure 2.6: Optimal coupling distance d_{opt} as a function of (a) ω and (b) θ , for various θ and ω , respectively, calculated with eq. 2.21. The dashed, purple line corresponds to the values for which the reflectivity vanishes completely. Interestingly, the maxima of the respective curves lie approximately on the purple lines, therefore being the critical coupling distance d_{crit} .

Finally, in fig. 2.6, the optimal coupling distance d_{opt} from eq. 2.21 is plotted as a function of ω for various θ (a), and vice versa (b). Again, the critical distance increases for larger frequencies as well as larger incident angles. In purple, the numerically calculated parameter (using eq. 2.17) for vanishing reflectivity (R = 0) are plotted. At each (first) crossing point with one of the d_{opt} curves, the three parameter for zero reflectivity can be read out. The general trend seems obvious, i.e. the maxima of d_{opt} correspond approximately to a critical parameter set, even though it must be noted that no absolute agreement is achieved. Therefore, this trend should not be understood as more than a rough guidance for estimation of the critical coupling conditions via d_{opt} .

With this section at hand, the interpretation of data collected measuring the reflectivity in the Otto geometry can now be performed. Since this work employs the Otto geometry, the figures were plotted for a ZnSe / vacuum / SiC system. Nevertheless, the formula for the three-layer reflectivity (eq. 2.17) is equally valid for any kind of isotropic media, and therefore can also be used to model e.g. the corresponding Kretschmann configuration (ZnSe / SiC / vacuum), or a system with any other kind of dielectrics.

Another note should be taken on the parameters ω_{TO} , ω_{LO} , ϵ_{∞} , and γ . All of them are material specific, and therefore, their choice influences the resulting calculated reflectivity. ω_{TO} , ω_{LO} , and ϵ_{∞} , however, only change the frequency range in which SPhPs can exist, i.e. the size of the Reststrahlen band. Hence, these parameter do not influence the shape of all figures shown in this section in any other way than compressing or shifting the ω axis.

The damping γ , on the other hand, has quite a crucial influence on the SPhP coupling properties. In order to visualize this, fig. 2.7 shows the reflectivity spectrum at for different angles θ , each with several different damping constants γ . As it can be seen, it turns out that for each angle, a different γ can be found in order to achieve zero reflectivity. This makes γ a fourth critical parameter for the successful coupling, and hence, it should be considered in the evaluation of measured reflectivity data. Naturally, it is sufficient to determine γ once for each sample. However, the chosen values in fig. 2.7 are quite extreme. Taking SiC as an example, the damping at the most varies by less than 10% around $3.75 \,\mathrm{cm}^{-1}$. Hence, its influence on the critical coupling can be considered rather small.



Figure 2.7: Illustration of the influence of phonon damping on the SPhP resonance in the Otto geometry. Reflectivity spectra are shown for four different incident angles θ , each with seven different damping constants γ . All spectra were plotted at a distance of $d = 7.3 \ \mu m$. For different θ , the critical resonance R = 0 can be obtained by varying γ .

2.2 Reflectivity and Transmittance of Anisotropic Media

As mentioned in the previous section, a purely isotropic calculus can suffice for weakly anisotropic materials, but definitely fails when materials with considerable anisotropy are studied. Hence, a formalism which is capable of handling fully anisotropic dielectric tensors must be developed. This has been proposed by various authors in terms of 4×4 - transfer matrices, emphasizing the work of Berreman, Yeh, and Xu *et al.* [63, 64, 65]. However, each of those approaches lacks either generality or numerical stability, and therefore none on its own is suitable for the purpose of this work.

A possible solution to this problem is to combine several approaches, as it is performed in this thesis, and shown in appendix A. The result provides a formalism capable of calculating the reflectivity and transmission coefficients for any combination of polarization of incident and reflected or transmitted waves in a multilayer medium consisting of any number of layers, each with an isotropic or arbitrarily anisotropic dielectric tensor.

In this section, firstly, the differences to the isotropic three-layer case are studied, when a small anisotropy of the third medium is assumed, which is the case for the first experiment in this work. Secondly in section 2.2.2, the reflectivity is calculated for a 6H-SiC substrate with a nano-meter thick AlN layer on top, which is the system studied in the Otto geometry in the second experiment of this work. In section 2.2.3, the knowledge achieved from the reflectivity without prism coupling is then used to simulate and interpret the spectra obtained in prism coupling experiments. With the same matrix formalism applied here, in the subsequent section 2.3, the field enhancement will be calculated and discussed for both systems.

2.2.1 Reflectivity of 6H-SiC

Even though isotropic materials are much easier to calculate and to understand, they lack the variety of phenomena which occur owing to anisotropy in the dielectric tensor. Furthermore, many polar crystals are anisotropic and can exhibit a much larger anisotropy splitting of the optical phonon modes than SiC, e.g. Quartz, which inevitably requires an anisotropic model for proper description.

In fig. 2.8, the calculated reflectivity of p-polarized light in the Otto geometry for anisotropic 6H-SiC (c-cut, i.e. with the extraordinary c-axis parallel to the sample normal) is compared to the case of isotropic 3C-SiC, where the utilized parameters are given in table 2.1. In colors, the reflectivity of 6H-SiC is shown, whereas the gray dashed lines correspond to 3C-SiC. The first difference to note is the right hand edge of the Reststrahlen band, which exhibits a small yet noticeable shift. This can be attributed to the different LO frequencies for both polytypes.

The large SPhP dip is basically identical in both descriptions. For 6H-SiC, however, three additional features are observed, where the first two lie at 883.2 cm^{-1} and 888.8 cm^{-1} , and the third at 967.4 cm^{-1} . The latter is an expected and well-known feature of uniaxial crystals, arising due to the anisotropy splitting of the *LO* frequencies [43], and hence shall not be further discussed.

The first two features are the so called weak modes, which arise in the non-cubic polytypes of SiC such as 6H-SiC, and can be explained by its crystal structure. The unit cell consists of Si-C layers with ABCACB-stacking, with the *c*-axis pointing in the stacking direction, as illustrated in fig. 2.9 on the left [43, 66]. Due to this superlattice, the Brilloin zone in the *c*-direction is folded and reduced to a sixth of the original width. By this means, the number of phonon modes at the Brillouin zone center increases



Figure 2.8: Effect of anisotropy on the reflectivity comparing 3C-SiC and 6H-SiC. The calculated reflectivity of the three-layer Otto configuration ZnSe / vacuum / SiC is plotted for four different gap sizes d and various incident angles. In color, the anisotropic reflectivity for 6H-SiC is shown, whereas in dashed gray, the corresponding reflectivity for the isotropic SiC sample is plotted. Three features appear additionally in 6H-SiC, as explained in the text.

by a factor of four, as it is shown in fig. 2.9 (b). One of the three folded LO modes is IR-active, splits up at the Γ -point and therefore appears as a double resonance inside the Reststrahlen band.

In order to model the zone folding and the resulting weak modes, a sum approach for the extraordinary dielectric function ϵ_{\parallel} can be used [67], which then enters the dielectric tensor $\bar{\epsilon}$ as an input parameter in the calculus described in appendix A:

$$\bar{\epsilon} = \begin{pmatrix} \epsilon_{\perp} & 0 & 0\\ 0 & \epsilon_{\perp} & 0\\ 0 & 0 & \epsilon_{\parallel} \end{pmatrix}, \qquad (2.22)$$

with the usual coordinate system where z points normal to the sample surface. Employing the sum approach, ϵ_{\parallel} takes the following form:

$$\epsilon_{\parallel} = \epsilon_{\infty}^{\parallel} \left(1 + \sum_{j=0}^{2} \frac{(\omega_{LO}^{\parallel})_{j}^{2} - (\omega_{TO}^{\parallel})_{j}^{2}}{(\omega_{TO}^{\parallel})_{j}^{2} - \omega^{2} - i\omega\gamma_{j}} \right),$$

$$(2.23)$$



Figure 2.9: Explanatory figures regarding the phonon weak modes in hexagonal 6H-SiC, owing to the Brilloin zone folding due to the superlattice in the *c*-direction. Figures taken from [43] (a) and [66] (b). In (c), experimental reflectivity data of the weak mode resonances measured by Bluet *et al.* is shown [67].

where j = 0 corresponds to the strong extraordinary phonon, i.e. the one, which defines the Reststrahlen band, and j = 1, 2 describe the two weak phonon modes, which are denoted as zone folded (*zf*). The ordinary dielectric function ϵ_{\perp} is given by eq. 1.27, and all used parameters are listed in table 2.1.

Table 2.1: Parameters of isotropic 3C-SiC and anisotropic 6H-SiC used for the calculations. The weak mode frequencies have been chosen based on earlier experiments, even though a good agreement with the frequencies found by Bluet *et al.* can be observed [67], see fig. 2.9.

3C-SiC [15]	6H-SiC [43]
$\overline{\omega_{TO} = 796 \mathrm{cm}^{-1}}$	$\omega_{TO}^{\parallel} = 788 \mathrm{cm}^{-1}$
	$\omega_{TO}^{\perp} = 797 \mathrm{cm}^{-1}$
$\omega_{LO} = 972 \mathrm{cm}^{-1}$	$\omega_{LO}^{\parallel} = 964 \mathrm{cm}^{-1}$
	$\omega_{LO}^{\perp} = 970 \mathrm{cm}^{-1}$
$\gamma = 3.75\mathrm{cm}^{-1}$	$\gamma=3.75\mathrm{cm}^{-1}$
$\epsilon_{\infty} = 6.5$	$\epsilon_{\infty}^{\parallel} = 6.78$
	$\epsilon_{\infty}^{\perp} = 6.56$
	$\omega_{rec}^{zf1} = 883.2 \mathrm{cm}^{-1}$
	$\omega_{TO} = 600.2 \mathrm{cm}^2$ $\omega_{LO}^{zf1} = 883.4 \mathrm{cm}^{-1}$
	$\omega_{TO}^{zf2} = 888.8 \mathrm{cm}^{-1}$
	$\omega_{LO}^{zf2} = 888.93 \mathrm{cm}^{-1}$
	$\gamma^{zf}=1.3{\rm cm}^{-1}$

By looking at the weak mode resonances in fig. 2.8, it becomes clear that their resonance strength depends strongly on the SPhP. For sharp SPhP dips lying at different frequency positions than the weak modes, they disappear. For an overlapping SPhP resonance, on the other hand, the weak modes are strongly enhanced, even if the SPhP is extremely broad and does not even exhibit a feature, as it is the case for $d = 1 \,\mu\text{m}$ and $\theta = 26 \,^{\circ}$. This SPhP driven weak mode enhancement occurs due to the unique \vec{E} field distribution of the SPhP, exhibiting unusually large *z*-components. This enhancement effect has been observed similarly in subdiffractional nanostructures supporting localized SPhP [68, 69]. Otherwise, in a reflectivity measurement on a plain *c*-cut crystal, the weak modes would be hardly observable. On the other hand, by using an *a*-cut sample, i.e. where the extraordinary *c*-axis points in the surface plane, the weak mode resonances are accessible without SPhP coupling [24]. On the basis of experimental data, this topic is discussed in further detail in the chapters 4 and 5.

2.2.2 Reflectivity of AlN on 6H-SiC

By stacking two or more nano-meter thick layers of different polariton-active media, a novel kind of material can be created, which supports coupled hybrid polaritons with promising characteristics [16]. For instance, in a monolayer graphene / multilayer hexagonal Boron Nitride (hBN) heterostructure, a coupled plasmon-phonon polariton arises, combining the advantages of both quasi particles, i.e. the wide tuning range of SPPs with the long lifetime of SPhPs [70, 71, 72].

Another possible approach is to combine two polar crystals, resulting in a hybrid material with modified phonon frequencies and thus fundamentally different optical properties, which cannot be described by simply summing the dielectric functions of the constituents. This new material class is referred to as Crystalline Hybrids (XHs), and is proposed to offer a large variety of applications, like user-control of phonon frequencies, crystal anisotropy, thermal conductivity, and even the tunability of electronic and mechanical properties [16, 73, 74, 75].

The physics of XHs is still rather unexplored, which is why this work aims at studying the very fundamental question, how a single nano-scale top layer of AlN on SiC influences the SPhP modes allowed in the structure. With this knowledge at hand, in future studies, this formalism can be extended to XHs composed of stratified layers of AlN and GaN on top of a SiC substrate. In fact, SHG spectroscopy studies on such XH samples have been performed in this thesis, but results and analysis are still following. In brief, in such a system a hybrid AlN-GaN phonon mode arises, which is not covered by classical electrodynamics but can be described by an atomistic model. However, focussing rather on the new phenomena arising by a single AlN layer on top of SiC in the Otto geometry, the transfer matrix calculus already implemented in this work is sufficient.

AlN crystallises in the Wurtzite structure, and is, as well as the hexagonal polytypes of SiC, uniaxial, and therefore anisotropic. For SiC, the parameters of 6H-SiC listed in table 2.1 are used, whereas the parameters of AlN can be found in table 2.2, and the AlN layer thickness is set to 120 nm in most of the calculations (being the nominal thickness of the sample used in the experiments for this work) and to 1000 nm for comparison. The AlN layer is grown epitaxially on top of the *c*-cut 6H-SiC substrate, and therefore, due to a *c*-axes alignment, will naturally also be *c*-cut.

Before discussing the spectra resulting in the Otto geometry in the following section, it is very instructive to take a look at the reflectivity without the prism, i.e. in a three-layer system (vacuum / AlN / SiC). This is plotted in fig. 2.10 for various incident angles and for two AlN layer thicknesses $d_{AlN} = 120 \text{ nm}$

in (a) and 1000 nm in (b). In the subplots (c) and (d), the same spectra in the LO frequency region are shown assuming that both AlN and SiC are isotropic.

Table 2.2: Parameters of uniaxial AIN used for the calculations. The damping constant found in the given literature is exceptionally small compared to other sources [76, 77, 78, 79, 80, 81], and furthermore, a single value is assumed for all four modes, even though their damping constants differ significantly. For the purpose of the theoretical calculations in this section, however, the difference in the spectra arising due to higher and anisotropic damping is insignificant, and hence shall not be discussed further.

uniaxial AlN [82]
$\omega_{TO}^{\parallel} = 611 \mathrm{cm}^{-1}$
$\omega_{TO}^{\perp} = 670.8 \mathrm{cm}^{-1}$
$\omega_{LO}^{\parallel} = 890 \mathrm{cm}^{-1}$
$\omega_{LO}^{\perp} = 912 \mathrm{cm}^{-1}$
$\gamma = 2.2\mathrm{cm}^{-1}$
$\epsilon_{\infty}^{\parallel} = 4.35$
$\epsilon_{\infty}^{\perp} = 4.16$

The Reststrahlen band of the SiC substrate is clearly visible, and some TO and LO frequencies of both materials mark distinct features in the spectrum. For the TO modes, only the ordinary frequency is relevant, whereas for the LO modes, rather the extraordinary frequencies dominate the physics. The upper Reststrahlen edge of SiC exhibits a kink due to the SiC anisotropy splitting, and at the $\omega_{LO\perp}^{AlN}$ frequency, a rather strong feature inside the SiC Reststrahlen band can be observed. Furthermore, the upper SiC Reststrahlen band features a general incident angle dependence, which is known from previous studies [83, 84]. Comparing the two different AlN layer thicknesses in (a) and (b), for $d_{AlN} = 120$ nm, the $\omega_{TO\perp}^{AlN}$ and the $\omega_{LO\parallel}^{AlN}$ generate features, but the overall spectrum has a SiC-like character. For $d_{AlN} = 1000$ nm, on the other hand, the AlN Reststrahlen band starts to form, starting at $\omega_{TO\perp}^{AlN}$ and ending at $\omega_{LO\parallel}^{AlN}$, while the SiC Reststrahlen band is still recognizable. For even larger d_{AlN} , this behaviour continues and the SiC Reststrahlen band disappears.

The strong feature at $\omega_{LO\parallel}^{AlN}$ has been reported elsewhere [85, 86], but a detailed characterization has not yet been performed. Goullet *et al.* describe this feature as a combined coupling into the ordinary SiC TOmode $\omega_{TO\perp}^{SiC}$ and the extraordinary AlN LO mode $\omega_{LO\parallel}^{AlN}$, resulting in a strong energy loss at the $\omega_{LO\parallel}^{AlN}$ frequency. This picture, however, assumes a single anisotropic crystal with a large anisotropy splitting. The situation depicted here is different, because the modes originate from two distinct materials, which do not even have to be anisotropic. This is illustrated in the subfigures (c) and (d) in fig. 2.10, where AlN and SiC are assumed to be isotropic, resulting in the exact same resonance at ω_{LO}^{AlN} with the same dispersive behaviour.

In order to better understand the nature of this feature, its dispersion for $d_{AlN} = 1000$ nm can be compared to the upper Reststrahlen edge of SiC. The frequency shift of the dip minimum from 20 ° to 80 ° incident angle is of about 20 cm⁻¹, and a certain resonant behaviour can be observed resulting in zero reflectivity at angles between 50 to 70 °. The upper Reststrahlen edge of SiC exhibits the same behaviour with the same shift of about 20 cm⁻¹, which indicates that the AlN *LO* dip is correlated to the same physics. However, additionally, this mode and its dispersion characteristics depend on the AlN thickness and only appears due to the underlying substrate, therefore probably featuring a coupled nature.



Figure 2.10: Calculated reflectivity by means of the transfer matrix method of a vacuum / AlN / 6H-SiC system for two AlN layer thicknesses (a) $d_{AlN} = 120 \text{ nm}$ and (b) 1000 nm. The spectra are plotted for various incident angles θ . The feature at the AlN *LO* frequencies and the upper Reststrahlen edge of SiC get blue shifted for increasing incident angle. In the subfigures (c) and (d), the same spectra as in (a) and (b) are plotted in the *LO* frequencies range, but assuming that both AlN and SiC are isotropic. The feature at ω_{LO}^{AlN} appears as well in the isotropic case, which can be understood in terms of a pseudo-anisotropy arising due to the mixing of two distinct materials. On a pure AlN sample, this feature cannot be observed.



Figure 2.11: Calculated reflectivity by means of the transfer matrix method of a vacuum / AlN / SiC system. The spectra are plotted for various AlN layer thicknesses d_{AlN} at an incident angle of 60°. (a) shows the full spectral range calculated for anisotropic AlN and 6H-SiC, while in (b), the *LO* frequency range is shown assuming both materials to be isotropic. The AlN *LO*-like mode appears in both cases, featuring a strong d_{AlN} dependence. For increasing thickness (> 5000 nm), the coupling to the SiC substrate decreases and the mode begins to disappear.

In fig. 2.11, the reflectivity at 60 ° incident angle is shown for various AlN layer thicknesses, again plotted for anisotropic materials in (a), and for isotropic AlN and SiC in (b). Here, the transformation from a SiC-like to an AlN-like spectrum is clearly traceable. Already at $d_{AlN} = 500$ nm, the absorption in the AlN layer so large that the AlN *LO* mode leads to zero reflectivity, while the SiC Reststrahlen edges are still present. For even larger d_{AlN} , the lower SiC Reststrahlen edge disappears rapidly due to the high reflectivity in the AlN Reststrahlen band, and the rest of the SiC Reststrahlen band above $\omega_{LO\parallel}^{AlN}$ slowly weakens in height. At 5000 nm, the anisotropy kink of the AlN *LO* modes already appears, which indicates that the observed feature is not only a small dip arising from the anisotropy splitting of AlN, but rather a new kind of mode. This is further supported by the fact that for isotropic materials, the same feature appears, as plotted in (b). For even larger d_{AlN} , the SiC features disappear completely and the full AlN Reststrahlen band is recovered.

In a nutshell, the observed feature is an angle dependent AlN *LO*-like mode with intrinsic dispersion, which is coupled to the substrate. The fact that the materials do not have to be anisotropic for the mode to exist, can be understood in terms of a pseudo-anisotropy arising due to the nano-scale mixing of two distinct materials. The AlN *LO* frequency necessarily has to lie inside the Reststrahlen band of the substrate. With increasing AlN layer thickness, the SiC Reststrahlen band disappears, together with the AlN *LO* mode. By including anisotropy of the AlN, the extraordinary *LO* mode can be identified as the component which couples to the SiC substrate.

The pseudo-anisotropic LO-like mode described here turns out to be decisive for the nature of the



Figure 2.12: Four-layer Otto geometry structure for the study of the influence of AlN on the SPhP modes existing in this structure. In the reflection simulations of this section, the thickness of the AlN layer is set to 120 nm, and the vacuum gap size d is variable.

appearing SPhPs in such a multilayer structure, which will be disucssed in the following section by examining the reflectivity of the 120 nm AlN / 6H-SiC system in the Otto geometry.

2.2.3 SPhPs in a AIN / 6H-SiC System in the Otto Geometry

In fig. 2.13, calculated reflectivity spectra for the four-layer system ZnSe / vacuum / 120 nm AlN / 6H-SiC (see fig. 2.12) are shown, evaluated at five different vacuum gaps d. Outside the SiC Reststrahlen band, the same AlN ω_{TO}^{\perp} resonance as in the vacuum / AlN / SiC reflectivity appears. Inside the SiC Reststrahlen band, however, two resonances can be distinguished, which depend strongly on the incident angle and on the distance d. Similar to the SPhP of bare SiC, the dips reach zero reflectivity for certain angle-distance-frequency sets.

In analogy, we here assume the two resonant features in the reflectivity of AlN / SiC in the Otto geometry to be two distinct SPhP modes. However, both modes do not behave simply like the SiC SPhP. Exemplary, this can be seen in the upper SPhP-like feature, where two dip minima appear at certain incident angles, especially recognizable at $d = 1 \,\mu$ m. This modified behaviour can be understood as a coupled nature of the mode between a SPhP and the pseudo-anisotropic AlN *LO*-like mode, which has been discussed in the previous section.

In fig. 2.13, the $\omega_{LO\parallel}^{AlN}$ frequency is marked with a blue dotted line, which constitutes the lower limit of the ALN LO-like mode, compare fig. 2.10. At the frequency of the AlN LO-like feature, the Reststrahlen band is split into two parts, allowing the two coupled SPhP-like resonances to exist simultaneously.

By means of the reflectivity spectra presented here, however, the true nature of the mode coupling between SPhP and AlN *LO*-like mode cannot be identified. Therefore, in order to better understand the observed behaviour, the following section reconstructs and discusses the dispersion relations of both arising polariton modes.



Figure 2.13: Calculated reflectivity by means of the transfer matrix method of a ZnSe / vacuum / 120 nm AlN / SiC Otto geometry system, at four different gap sizes. Inside the Reststrahlen region of SiC, two distinct phonon polariton resonances can be observed, which are separated by the pseudo-anisotropic AlN *LO*-like feature discussed in the previous section 2.2.2. Both modes are only existent in this specific multi-layer structure, and hence cannot be allocated to a specific material or subsystem.

2.2.4 Strong Coupling of SPhPs and AlN LO-like Mode in AlN / SiC: Avoided Crossing of the Split SPhP Branch

In order to see the dispersive behaviour of SPhPs in the Otto geometry, the calculated reflectivity can be plotted in a 2d map as a function of wavelength and incident angle, as has been shown earlier (e.g. see fig. 2.4). The incident in-plane wave vector component k_x , see eq. 1.56, is a function of the incident angle θ . Hence, in order to reconstruct the SPhP dispersion relation out of the reflectivity maps, the θ axis can be transformed to a k_x axis by means of the following inverse function

$$\theta = \arcsin\left(\frac{c \, k_x}{\omega\sqrt{\epsilon_{inc}}}\right),\tag{2.24}$$

where $\epsilon_{inc} = \epsilon_{ZnSe}$ [62]. Additionally, θ depends on the frequency, and therefore the axis transformation has to be carried out two-dimensionally and will affect both the frequency and the k_x axis.

By performing this transformation, 2d maps containing the dispersion information of the existing SPhPs are obtained. The result is plotted in fig. 2.14 (a), (b), and (c), for three different AlN layer thicknesses, being 7.5, 120, and 500 nm, respectively. The light line in vacuum splits the map into two regions. On

the left hand side, the incoming light is refracted at the prism backside and then reflected at the sample surface. This is a similar case to the reflectivity without prism, as discussed in section 2.2.2, and indeed, the SiC Reststrahlen band with high reflectivity (green means 1) can be recognized, and in the middle as a red stripe, the AlN *LO*-like feature appears.

On the right hand side of the light line, the region of total internal reflection extends. Here, the reflectivity is almost 1 in the entire parameter space, except for two red lines, where the reflectivity reaches zero. These are the two SPhP-like modes, which are here critically coupled throughout the complete k-axis. This was achieved by calculating the distance d_{crit} of critical coupling for each angle by means of numerically finding the reflectivity minimum of the SPhP in the ZnSe / vacuum / SiC structure. In the inset of fig. 2.14 (a), d_{crit} is shown as a function of θ .

The two SPhP-like features exhibit a strong dependence on the AlN layer thickness d_{AlN} . For the smallest thickness of 7.5 nm, see fig. 2.14 (a), it almost seems that only one strong curve exists, which lies on top of the extraordinary dispersion $k_{SPhP}^{e^1}$ of a SPhP in a two-layer configuration on a *c*-cut 6H-SiC, see eq. 1.52, plotted in blue. At the frequency of the AlN *LO*-like mode, only a faint dip in reflectivity extends throughout the complete *k*-range. This is close to the extreme case of no AlN layer, where only a single SiC SPhP exists. Nonetheless, the thin AlN layer already starts to split the SPhP dispersion at the AlN *LO*-like mode into two individual branches, exhibiting an avoided crossing between $k_{SPhP}^{e^1}$ and the AlN *LO*-like mode.

For larger d_{AlN} , see (b) and (c), the splitting gets unambiguous, and the avoided crossing clearly emerges. At 120 nm AlN layer thickness, in (b), the both branches exhibit comparable intensity, while for 500 nm, the lower branch is much stronger, shifting towards lower frequencies. This corresponds to the merging into a pure AlN SPhP, since for larger d_{AlN} , the SiC substrate becomes less important. The situation of $d_{AlN} = 120$ nm, on the other hand, is perfectly suited to study the coupling behaviour between the SPhP and the AlN *LO*-like mode. This has been observed experimentally, as demonstrated in chapter 5.

In fig. 2.14 (d), the dispersion curves of both branches are plotted for various AlN layer thicknesses. This was achieved by extracting the spectral position of minimum reflectivity for both modes at all in-plane momenta. In this picture, the avoided crossing between the horizontally lying AlN LO-like mode and the curved $k_{SPhP}^{e^1}$ dispersion becomes distinctive. For small d_{AlN} , the splitting is rather small, while for increasing layer thickness, the two dispersion curves gradually drift apart. In the inset in fig. 2.14 (d), the coupling strength between SPhP and AlN LO-like mode as a function of d_{AlN} is plotted, following the curvature of a root function.

The effect of avoided crossing is an interaction principle with wide impact in physics. Most generally, when two energy levels of two distinct states exhibit a crossing point along some coordinate, the energy levels do not become degenerate but will follow a hyperbolic shape, with the energy separation at the crossing point appearing in the off-diagonal terms of the corresponding Hamiltonian.

Similar to the avoided crossing observed here between the SiC SPhP and the AlN *LO*-like mode, earlier in this thesis, an analogous behaviour appeared for the two bulk phonon polariton branches discussed in section 1.1.3, plotted again in fig. 2.14 (e). Here, also an avoided crossing can be observed, where the two coupling features are the bulk phonon modes, splitted up by the Reststrahlen region.

Finally, the last section of this chapter will present calculations of the squared field enhancement, being the principle source of strong SPhP-driven SHG output, for the two systems 6H-SiC and AlN / 6H-SiC in the Otto geometry.



reflectivity maps of a AIN / 6H-SiC system in the Otto geometry are shown for three different AIN layer thicknesses d_{AIN}, nicely illustrating distance between both modes. In (e), the two bulk phonon polaritons in a two-layer system consisting of vacuum and SiC are shown in blue, Figure 2.14: Illustration of the avoided crossing of the SiC SPhP and the AIN LO-like mode. In the subfigures (a), (b), and (c), the transformed he effective dispersion relations of both coupled SPhP - AIN LO-like mode branches. The avoided crossing which occurs between those two for various d_{AlN} . The inset shows the coupling strength as a function of d_{AlN} , which was calculated by extracting the minimum of the spectral modes can be even better understood in subfigure (d), where the reflectivity minima are extracted in order to obtain the dispersion curves, plotted eaturing an analogous avoided crossing as observed in the AIN / SiC heterostructure.



Figure 2.15: Dispersion of non-vanishing $\chi^{(2)}$ components of (a) 3C-SiC and (b) *a*-cut 4H-SiC. The weak modes of 6H-SiC lie at different frequencies. They are the only $\chi^{(2)}$ resonances producing an enhanced SHG output in the frequency region of the SPhP. Therefore, for the simulation of the SHG coming from SPhPs, only the squared field enhancement is considered. Figures are adapted from [24].

2.3 Field Enhancement

One key subject of interest in this work is the SHG resulting from SPhPs. As stated in section 1.3, in general, the SHG intensity can be calculated by the product of the second order susceptibility tensor $\chi^{(2)}$ and the of the local \vec{E} fields, see eq. 1.58. The $\chi^{(2)}$ tensor can be modelled considering the first three orders of the TO phonon frequencies, as it has been proposed by Flytzanis [87] and applied elsewhere, e.g. especially for the description of SPhP resonances [17, 88]. In fig. 2.15, the non-vanishing $\chi^{(2)}$ components of 3C-SiC and 4H-SiC are plotted [24]. As can be seen there, except for the weak mode resonance of 4H-SiC, the $\chi^{(2)}$ curves are flat in the region where the SPhP can be excited. Therefore, in this work, this contribution to the SHG signal will not be included, since it does not constitute the source of the resonant SHG signal coming from SPhPs.

The second factor of the SHG intensity, i.e. the transmitted local electric field at the surface of the sample, can be accurately described by means of the transfer matrix formalism developed here. The SPhP resonance in the material exhibits a strong field localization at the surface, leading to a huge enhancement of the x-component of the local electric fields. This readily provides a good qualitative estimate of the expected SHG signal, which scales with the squared intensity enhancement ($\propto E_x^4$). In this section, first the three-layer geometry will be considered, and secondly, the squared field enhancement E_x^2 in the SiC substrate with the AlN layer on top is discussed.

In fig. 2.16, the reflectivity and squared field enhancement for 6H-SiC in the Otto geometry is plotted at four different gap sizes. The reflectivity is the same as in fig. 2.4 for isotropic SiC, but additionally exhibits the anisotropy features of 6H-SiC discussed in section 2.2.1. The resulting squared field enhancement is plotted on the right hand side and reaches a maximum of 200 for the smallest gap of $1 \,\mu\text{m}$ at an incident angle of almost 90°. For increasing gap size, the maximum of the squared field enhancement, which here is found to coincide with the minimum in the reflectivity and hence the most effective excitation of



Figure 2.16: 2*d* spectra of the reflectivity (left) and the squared field enhancement (right) of 6H-SiC in the Otto geometry at four different and gap sizes *d*. The squared field enhancement reaches maxima up to 200, which lie at the same frequency and incident angle of the reflectivity minimum, hence clearly arising from the SPhP.

the SPhP, shifts to lower frequencies and gets smaller. The latter might be simply explained by the fact that for increasing gap size, the evanescent field from the prism reaching the sample is diminished.

Nevertheless, the predicted squared field enhancement from the SPhP is large compared to e.g. the squared field enhancement arising from the LO resonance at normal incidence, as can be seen in the squared field enhancement plot at 8 μ m in fig. 2.16. Since even the LO phonon features sizeable SHG signals [17], quite a large SHG can be expected from the SPhPs. It should be noted that for the simulations presented here, only the E_x component was considered, because it constitutes the source of the SPhP field enhancement. By including the E_z component, additionally, a weak field enhancement is obtained at the $\omega_{LO||}^{SiC}$ frequency and at the upper SiC Reststrahlen edge.

In fig. 2.17, the reflectivity and squared field enhancement for the four-layer system, i.e. a 120 nm AlN / 6H-SiC sample in the Otto geometry is shown. The reflectivity features the same behaviour as discussed in the sections 2.2.3 and 2.2.4, but here, both cases of reflectivity without prism (below the critical angle of internal reflection θ_{crit}) and the prism coupling situation (above the critical angle) are combined in a single plot. In fact, the upper SPhP resonance seems to smoothly merge with the AlN *LO*-like mode across the critical angle (at about 25 ° for ZnSe, clearly marked by the sudden rise of reflectivity outside the Reststrahlen band and at large gap sizes). The lower SPhP resonance, on the other hand, exhibits no continuation at angles below θ_{crit} inside the SiC Reststrahlen band, but rather seems to merge with the edge of total internal reflection at frequencies below the Reststrahlen region.

Concerning the squared field enhancement in this configuration, mainly two features can be noted. Firstly, for the upper SPhP-like mode, the maximum is smaller by a factor of about 4 compared to the pure 6H-SiC sample. Hence, the thin AlN layer seems to gently suppress the electric field reaching the 6H-SiC. Secondly, the squared field enhancement of the lower SPhP also nicely coincides with the spectral position of the reflectivity dip, but has much smaller peak values compared to the upper SPhP. The latter can be attributed to the fact that the squared field enhancement in SiC is calculated, neglecting any strong sources in the AlN layer. If the fields of the lower SPhP rather exhibit their maximum intensities somewhere inside the AlN layer, the resulting SHG signal of this system is not well described by solely calculating the squared field enhancement in the SiC substrate, and a larger SHG signal can be expected from this SPhP in the experiments. Furthermore, AlN has a negative dielectric function in the region of the lower SPhP, therefore strongly suppressing the fields reaching the SiC substrate. Finally, the $\chi^{(2)}$ dispersion exhibits a declining slope for increasing energy, and hence also influences the relative amplitudes of both SPhP peaks in an experimentally measured SHG signal.

In order to fully understand the SHG sources, the field distribution throughout the complete layer system has to be calculated. In principle, this is feasible by means of the matrix formalism described in appendix A, but exceeds the content of this work. In order to get a quantitative simulation for the SHG signal, finally, the $\chi^{(2)}$ components have to be included in the calculations. However, at this point, the squared field enhancement presented here, i.e. E_x^2 , should rather give the qualitative insight that the huge field enhancement of SPhPs constitutes the main source of an experimentally detectable SHG signal.



Figure 2.17: 2d spectra of the reflectivity (left) and the squared field enhancement (right) of 120 nm AlN / 6H-SiC in the Otto geometry at four different and gap sizes d. Both phonon polaritons exhibit a large squared field enhancement, where the upper SPhP is smaller compared to the pure 6H-SiC sample, while the lower SPhP seems extremely weak. This, however, is due to the fact that the squared field enhancement is calculated in SiC, neglecting the actual field distribution throughout the multilayer system.

3 Experimental Setup

In this section, the experimental setup of the performed measurements is described. As a high intensity, MIR light source, this work employs the FEL at the FHI in Berlin, which will be characterized in the following section. Afterwards in section 3.2, the designed and constructed experimental setup for the reflectivity and SHG measurements in the Otto geometry is pictured. Finally in section 3.3, the procedure of parallel alignment of prism and sample is described.

3.1 The FHI Free Electron Laser

The FHI FEL is a MIR oscillator FEL which has been installed in 2011 on the campus of the Fritz Haber Insitute (FHI) and started operating in 2013 [89]. The setup is illustrated in fig. 3.1.

After generation in a thermionic gridded electron gun, two linear accelerators (linacs) speed up the electrons to energies in the range of 15 MeV to 50 MeV. While the first linac operates at a nominal electron energy of 20 MeV, the second can be tuned to boost or lessen the electron energy in the mentioned range. The electron gun generates pulsed electron bunches of about 200 pC at a repetition rate of 1 GHz. Before entering the linacs, these electron micro pulses pass through a 1 GHz buncher, which reduces the micro pulse length to 1 ps to 5 ps. Each bunch can then be effectively accelerated in the linacs, which create a macro pulse structure of pulse lengths of $1 \mu \text{s}$ to $15 \mu \text{s}$ with a repetition rate of 10 Hz. In table 3.1, the most important properties of the accelerator system are listed.

	Parameter	Value
Electr	on energy	$15-50\mathrm{MeV}$
Bur	ich charge	$200\mathrm{pC}$
Micro pı	ılse length	$1-5\mathrm{ps}$
Micro pulse repe	tition rate	$1\mathrm{GHz}$
Macro pı	ılse length	$1-15\mu s$
Macro pulse repe	tition rate	$10\mathrm{Hz}$

Table 3.1: Specifications of the electron accelerator of the FHI FEL [89].

After guidance through a 90 ° curve by means of isochronous bends, the electron beam enters the MIR wedged-pole undulator which has a total length of 2 m and is composed of 50 periods with a period length of $\lambda_u = 40$ mm. The tunable undulator gap has a nominal minimum size of 16.5 mm and features the generation of radiation in the range of 3 μ m to 50 μ m. At the moment, the MIR undulator is the only operating FEL arm. The construction of the longer, far-IR undulator depicted in fig. 3.1 is still in a planning phase. This second undulator is designed to cover the wavelength range of 40 μ m to 500 μ m.

The undulator is enclosed by two gold-plated copper mirrors, forming the laser cavity of $L_0 = 5.4 \text{ m}$ length. Both mirrors are of concave spherical shape, with radii of curvature of 2.65 m and 3.51 m of the end mirror and the outcoupling mirror, respectively. Since hole outcoupling is employed, five mirrors with different hole diameters (0.75, 1, 1.5, 2.5, and 3.5 mm) are available in order to optimize the lasing performance at all wavelengths. The end mirror is mounted on top of a precision translation stage,



Figure 3.1: Sketch of the FHI FEL showing the electron acceleration segment and the two FEL systems with different undulator length. In two linear accelerators Linac 1 and Linac 2, the electrons are speed up to energies up to 50 MeV, and then are conducted into one of the FEL cavities, where the IR laser pulses are generated. Picture taken from [89].

which can be used for a wavelength dependent cavity length tuning. This adjusts the cavity length to a value of $L_0 - \Delta \lambda$, where $\Delta \lambda = q \lambda$ is the wavelength synchronized cavity detuning. In practice, the factor q is usually set to 0 < q < 5. By this means, the accessible wavelength range at a specific electron energy, i.e. in a single wavelength scan, can be significantly increased. Furthermore and more importantly, the emission bandwidth decreases with increasing q, which enables a practical method of enhancing the spectral resolution. In table 3.2, the most important properties of the MIR FEL are listed.

Table 3.2: Specifications of the MIR FEL [89].

Parameter	Value
Undulator length	2 m
period length λ_u	$40\mathrm{mm}$
number of periods	50
Cavity length L_0	$5.4\mathrm{m}$



Figure 3.2: Pulse structure of the FEL. Each macro pulse (with $\sim 100 \,\mathrm{ms}$ time spacing) exhibits a bunch of micro pulses, separated by $1 \,\mathrm{ns}$ with a duration of $1 - 10 \,\mathrm{ps}$.

The pulse structure of the FEL output radiation is dominated by the input electron pulse structure, exhibiting macro pulses at ~ 10 Hz repetition rate, each consisting of a bunch of micro pulses at 1 GHz repetition rate. The resulting intensity distribution is sketched in fig. 3.2.



Figure 3.3: Setup of the reflectivity and SHG measurements employing the Otto geometry. Different incident angles θ can be measured by rotating the Otto assembly and moving and rotating the pickup mirror to the position, where the detection beam path is met again. Motorized actuators allow the adjustment of the gap size between prism and sample. At the bottom, the optical geometry for a cylindrical and a triangular prism is shown.

3.2 The Otto Geometry Setup

As discussed in the theoretical chapters, SPhPs can be extensively studied by means of the Otto geometry (fig. 1.13) due to the tunability of the gap size. The experimental realisation together with the spectroscopic setup is illustrated in fig. 3.3. The collimated incident FEL beam is focussed by an off-axis mirror (f = 646 mm) onto the prism. After passing through the Otto geometry being totally reflected at the prism backside, the light is separated by a dichroic beam splitter (longwave pass at $\lambda = 7 \mu \text{m}$) in order to measure the reflectivity and the generated SHG signal separately. For the first measurements performed with the cylindrical prism, the complete detection setup was mounted on a movable breadboard, in order to allow measurements at different incident angles. For the subsequent measurements (which are the only measurements analysed in the results chapters), a triangular Thallium Bromo-Iodide (KRS-5) prism (refractive index taken from [90]) was employed and the detection scheme was altered such as it is shown in fig. 3.3, in order to improve the reproducibility and accuracy of the detection for varying incident angles.

The Otto geometry consists of the sample and the prism with a small gap in between. The gap size can be adjusted by means of three *Newport* motorized actuators with a minimum incremental motion of $0.1 \,\mu\text{m}$, which are arranged in a triangular shape. The sample is mounted on top of three *Honeywell* miniature force sensors, which are assembled equally as the actuators, which allows the assignment



Figure 3.4: Home-made and designed 9-axis Otto geometry construction with mounted ZnSe prism. The most important feature are the three motorized actuators, which allow to control the gap size on the sub-micrometer scale.

of each sensor to an actuator when measuring the force. By this means, the nominal parallel gap of size $0 \,\mu\text{m}$ can be found by scanning the force as a function of distance and gradually rearranging the relative positions of the actuators. This assembly is attached to a two-axis mirror mount, which allows the horizontal and vertical matching of the incident and reflected beam. Finally, this is mounted on a rotation stage for measuring at different incident angles θ , and on a x-y-z translation stage for fine adjustment, i.e. altogether being a 9-axis construction.

The constructed Otto geometry structure is shown in fig. 3.4 in a real image, and depicted schematically in detail in fig. 3.5, where (a), (b), and (c) show the top, front, and side view, respectively, while in (d) length indications can be found. For illustration purposes, the prism, the force sensors, the sample and the beam spot are drawn twice as large. The motors (72 mm distance) are much more separated than the sample dimensions (7 × 10 mm) and the beam spot size (~ 1 mm diameter). By this means, considering a perfectly parallel prism backside and sample, a relative motion of one motor of 1 mm will result in a distance change of ~ 14 μ m between sample and prism within the beam spot. Therefore, at least in principle, with a minimum incremental motor motion of 0.1 μ m, the parallelism can be accurately determined. It must also be noted, however, that prism and sample are not necessarily perfectly flat, and furthermore, the contact point of the force sensors is not sharply defined. This is further discussed in section 3.3.

At the bottom of fig. 3.3, the geometrical optics of two different prisms is shown in detail. For a cylindrical prism (inset a, in this work the material is ZnSe), the focus is chosen to lie outside of the prism in such a distance that the refracted ray inside the prism is collimated horizontally (focus distance to prism roughly $d_{focus} = 9 \text{ mm}$ for ZnSe, prism radius R = 0.5'). By this means, the incident angle is homogeneous throughout the light spot and hence the angle spread is reduced. Especially for angles close to the critical angle of total internal reflection, this is quite important, since here even a small angle



Figure 3.5: Sketch of the designed and constructed Otto geometry structure in top, front, and side view illustrated in (a), (b), and (c), respectively. (d) shows the dimensions of the sample (green) and the 3 force sensors (red). The 3 motors (gray) allow the adjustment of the gap size and parallelism between sample and prism (yellow). In order to determine the contact point of zero distance, three force sensors are mounted below the sample in the same triangular shape as the motors.



Figure 3.6: Geometrical beam propagation calculations in a triangular prism. (a) Internal incident angle θ (inside the prism) as a function of the external incident angle φ (normal to the sample) for a triangular prism with $\kappa = 30^{\circ}$, h = 7.22 mm as specified in the inset. (b) Distances *s* and *j* defining the entering point into the prism as a function of φ .

shift leads to completely different coupling conditions. In fact, in a cylindrical prism the horizontal angular spread is so sensitive to the focus position that this constitutes a major drawback in terms of resolution. The vertical spread, on the other hand, is constant due to the focus lying outside of the prism, therefore also contributing to an experimental angular inaccuracy. Furthermore, due to the dispersive refractive index of the prism, an optimized collimated beam is not achievable throughout the spectrum (at least in a static setup).

When employing a triangular prism (inset *b*), care must be taken concerning the incident angle, since the refractive index of the prism is high (around n = 2.4) in order to obtain low critical angles of total internal reflection. The triangular prism used in this work is made of KRS-5, with a basis size of $1' \times 1'$ and side angles of $\kappa = 30^{\circ}$, resulting in a nominal height of h = 7.22 mm. Geometric beam propagation calculations for an incident wavelength $\lambda = 11 \,\mu\text{m}$ are performed in order to convert the incident angle θ inside the prism into the incident angle normal φ to the sample and vice versa. This is plotted in fig. 3.6 (a), where the inset shows a sketch of the prism geometry and the relevant parameters. Furthermore, the entering point of the incident light, at which the center of the prism will be hit (providing a symmetric beam propagation), is calculated in terms of the vertical distance to the center *s* and the height *j*, which is plotted in fig. 3.6 (b). As it becomes clear from the left diagram, the prism geometry was chosen such that incident angle θ can be tuned in a range from still below the critical angle of total internal reflection (for KRS-5 around 25°) up to the maximally possible angle.

Concerning the SHG measurement, it must be noted that ZnSe is known to have a nonzero bulk second order susceptibility and hence is expected to generate a second harmonic signal on its own [91, 92], even without phase matching. This SHG signal was observed in the first experiment, which allowed for a variety of improvements to be implemented. First, in order to be able to detect SHG from the sample, the ZnSe was replaced by a KRS-5 prism, since this material does not produce sizeable SHG. This, secondly, also improved drastically the achieved resolution due to a reduced angular spread. Finally, the tunable pickup mirror setup as shown in fig. 3.3 was put into practice, enhancing the control and reproducibility of the experiment. The results obtained with this improved setup are presented in the following chapter. In the last section of this chapter, the procedure of parallel alignment of prism and sample is explained.



Figure 3.7: Parallel alignment procedure of the Otto geometry. Plotted are the signals of the three force sensors as a function of the relative motor positions in order to determine the point of parallel contact of prism backside and sample. The linear increase in the signals signifies a growing pressure on the force sensors, i.e. prism and sample are in contact.

3.3 Parallel Alignment of Prism and Sample

Before starting the reflectivity and SHG measurements in the Otto geometry, it is crucial to assure that the prism backside and the sample are aligned to be parallel. Otherwise, the distance d varies within the sample area and the laser spot, resulting in a highly softened resonance. Furthermore it is necessary to stabilize distances of a few μ m to achieve resonant coupling, which is why the position of zero distance has to be determinable and reproducible.

For this means, the signals of the three force sensors beneath the sample are recorded as a function of the relative motor positions, slowly approaching the prism to the sample. The point zero for each motor is then clearly visible as an abrupt onset in the signal. By changing the relative position of the motors among each other, the onset of all three signals can be shifted to the same point, which then corresponds to a parallel alignment with known zero position.

In fig. 3.7, an exemplary final alignment for subsequently performed measurements is shown, where the three signals were shifted vertically in order to see the onsets separately. The point of contact can be determined within a range of about $4 \,\mu\text{m}$. Within the beam spot, this would yield a variation of 56 nm in the distance d, and hence would not crucially soften the SPhP coupling condition (which varies on the order of μ m).

However, for all measurements, the absolute distance *d* measured by the motor positions turned out to be very different from the actual value, which could be determined by analysing the resulting spectra. In fact, for some measurements, an incremental motor motion resulted in a spectrum with smaller distance *d*. This behaviour can only be explained by an uneven sample surface. For instance, a small protrusion would lead to an effective finite gap, even though the force sensors suggest contact. The situation is further complicated by the fact that the small contact balls of the force sensors are not perfectly fixed, allowing the sample to shake a little before the nominal contact is indicated by the force signal. For this

reasons, the distance d measured by the motors cannot be used as a system parameter. It is, however, still adequate for the parallel alignment and the determination of the desired measuring range.

All measurements presented in the following chapter were realized with the force sensor alignment, and therefore, all spectra had to be fitted in order to retrieve the respective gap size. This is an acceptable approach as long as the investigated system is well understood by a theoretical model, as it is the case for both samples studied here.

For further experiments, where samples with yet theoretically unknown behaviour will be of interest, however, the gap size would remain an unknown parameter. In order to overcome this crucial drawback in future studies, the realization of an interferometric Fabry-Pérot approach is currently in progress. For this means, a broadband visible-IR light source will be collimated and installed such that the light shines perpendicularly through the prism onto the sample (naturally, for this means, the prism needs to be cut at the top). The reflected light is then analysed in a spectrometer, and the interference pattern allows to determine the gap size at any time, and to achieve sufficient parallelism by optimizing the contrast of the interference spectrum.

4 Resonant SHG from SPhPs Excited on 6H-SiC

In this chapter, the results of reflectivity and SHG spectroscopy measurements obtained from a c-cut 6H-SiC sample in the Otto geometry are presented and discussed. In such a system, a SPhP can be resonantly excited in the Reststrahlen band of SiC, with an excitation efficiency as a function of incident laser frequency ω , incident angle θ , and gap size d between prism and sample.

The excitation characteristics in the reflectivity spectra observed here are in perfect agreement with previous studies [14, 15], and are excellently described by the developed theory in this thesis. The SHG spectroscopy measurements on SPhPs have been performed for the first time in this work, and are in a good qualitative agreement with theoretical calculations.

This section is separated into three parts, which address a general spectral analysis of the obtained reflectivity and SHG data, a study of the gap dependence of the SPhP resonances (section 4.2), and finally, a reconstruction of the SPhP dispersion with comparison to the measured spectra (section 4.3).

The measurements on the KRS-5 / air / 6H-SiC system presented here were performed at four nominal incident angles 27° , 29° , 31° , and 35° , and the complete obtained information is shown in appendix B in fig. B.1, B.2, B.3, and B.4, respectively. There, also general experimental details and the fitting procedure applied on the reflectivity spectra are explained.

4.1 Spectral Analysis

In fig. 4.1, the obtained reflectivity (a) and SHG spectroscopy data (b) are shown (plotted as open circles) for a nominal incident angle of 29° and at five different gap sizes d. In both data sets, the strong SPhP resonance is the most pronounced feature, which shall be discussed in the following first for the reflectivity, and then for the SHG signal from SPhPs.

In the reflectivity, the lower and upper SiC Reststrahlen edge can be distinguished, where the lower is defined by the $\omega_{TO\perp}^{SiC}$ frequency, while the upper shifts to higher energies for increasing incident angle [83, 84]. Both edges are most pronounced at the smallest gap size, similarly to the Reststrahlen band in reflectivity measurements without prism coupling (compare with fig. 1.4). For increasing *d*, the edges continuously rise and approach 1, which corresponds to the exponential decrease of the fraction of evanescent wave which reaches the sample, since the spectra are taken at incident angles above the critical angle of total internal reflection.

At about 900 cm^{-1} , a strong dip is observed, which arises due to the phase-matched excitation of the SPhP at the air / SiC interface. For the smallest gap size, the feature is very broad and shallow, which means that the excitation occurs in the over-coupled regime, i.e. the radiative damping of the SPhP back into the prism is large, see section 1.2.3. For increasing *d*, the SPhP dip becomes slimmer and deeper, reaching the critical coupling distance at about 5.8 μ m, where the reflectivity drops to 0.25. Here, most of the incoming light gets absorbed by the SPhP due to resonant excitation. For an even larger gap size, the SPhP dip depth decreases again, which is the regime of under-coupling, where the evanescent wave reaching the sample is not strong enough to efficiently excite the SPhP. As a side remark it should be noted that the measured reflectivity does not reach zero even at critical coupling. This can be attributed to a combined broadening by a finite angular spread $\Delta \theta$ ($\pm 0.39^{\circ}$) and a non-zero bandwidth $\Delta \omega$ of



Figure 4.1: Spectral reflectivity (a) and SHG (b) measurements and simulations in the Reststrahlen region of 6H-SiC in the Otto geometry, exhibiting the expected SPhP resonance. All reflectivity spectra were fitted employing the matrix formalism, nicely reproducing the data. The SHG signal is plotted together with the calculated squared field enhancement at the SiC surface multiplied with the transmittance at double frequency 2ω backwards through the Otto structure. The peak position, width, and amplitude behaviour is well reproduced. The dashed lines mark features in the SHG spectrum, i.e. $\omega_{TO\perp}^{SiC}$, weak modes, $\omega_{LO\parallel}^{SiC}$, and the angle shifted upper Reststrahlen band, reasonably well corresponding to the respective features in the reflectivity.
the exciting FEL laser pulses ($\pm 4 \text{ cm}^{-1}$). Depending on the frequency position in the dispersion curve, either $\Delta \theta$ (close to ω_{TO}) or $\Delta \omega$ (close to ω_S) is dominating the broadening.

Beside the $\omega_{TO\perp}^{SiC}$ and the upper SiC Reststrahlen edge frequency, in fig. 4.1, three more features are marked with dashed lines. Two are the weak modes of 6H-SiC, which arise due to the zone folding of the LO mode onto the Γ point coming from the sixfold stacking of atomic layers in c-direction, see section 2.2.1. These resonances appear as small dips on the background of the SPhP feature, and disappear with increasing gap size. On a c-cut sample, these modes can hardly be measured in a reflectivity measurement without prism coupling. Here, however, the special \vec{E} field distribution of the SPhP with large z-components leads to an effective weak mode enhancement, as long as the SPhP mode overlaps spectrally with the frequency positions of the weak modes. The last dashed line marks the $\omega_{LO||}^{SiC}$ frequency, where slightly above, a small dip in the reflectivity can be observed. Both the weak modes and this small dip arise due to the special, anisotropic nature of 6H-SiC, and are observed in the experiment exactly as has been predicted in the simulations in section 2.2.1.

In fig. 4.1, along with experimental reflectivity data, the fitted reflectivity is plotted with solid lines. A very good agreement is achieved, covering the overall shape as well as all minor features in the spectra. The global fitting procedure is explained in detail in appendix B, where also the fitted gap sizes d are listed in table B.1. Here in table 4.1, on the other hand, the fitted SiC parameters such as the damping and the TO and LO frequencies are shown and compared to values from other sources, being in a good agreement.

Table 4.1: Fitted and fixed global parameters of the reflectivity measurements performed on 6H-SiC in the Otto
geometry, which are shared by all four incident angles. Individual parameters such as gap size d and factor a are
specified in appendix B in the corresponding figures B.1, B.2, B.3, and B.4, and in table B.1. At the bottom, the
nominal and fitted incident angles are listed.

	Parameter	Value	Literature		
Fitted	$\Delta \theta$	0.39°	-		
	$\Delta \omega$	$4.05\mathrm{cm}^{-1}$	-		
	$\omega_{TO\parallel}^{SiC}$	$783.67{\rm cm}^{-1}$	$788.1{ m cm^{-1}}$ [93]		
	$\omega_{TO\perp}^{SiC}$	$794.78{ m cm}^{-1}$	797 cm ⁻¹ [93]		
	$\omega_{LO\parallel}^{SiC}$	$962\mathrm{cm}^{-1}$	$965.3\mathrm{cm}^{-1}$ [93]		
	$\omega_{LO\perp}^{SiC}$	$967.93{\rm cm}^{-1}$	969.9 cm ⁻¹ [93]		
	γ^{SiC}	$3.54\mathrm{cm}^{-1}$	$3.75{ m cm^{-1}}$ [15]		
Fixed	$\epsilon_{\infty\parallel}^{SiC}$	6.78	6.72 [93]		
	$\epsilon_{\infty\perp}^{SiC}$	6.56	6.56 [93]		
	$\omega_{ m zf split}$	$0.2\mathrm{cm}^{-1}$	-		
	ω_{TO}^{zf1}	$881\mathrm{cm}^{-1}$	$884{\rm cm}^{-1}$ [67]		
	ω_{TO}^{zf2}	$886\mathrm{cm}^{-1}$	889 cm ⁻¹ [67]		
	γ^{zf}	$1.3\mathrm{cm}^{-1}$	$\sim 1.7 {\rm cm}^{-1}$ [67]		
$\overline{\theta_{nominal}} = 27^{\circ}$	29 °	31°	35 °		
$\theta_{fitted} = 26.82^\circ$	28.90°	29.92°	34.76 °		

In fig. 4.1 at the bottom, the measured SHG signal (open circles) at 29° is plotted together with a theoretical estimate (solid line). Power dependence confirmed the second-order nature of the signal. A large SHG peak can be observed at the same frequency of the SPhP dip in the reflectivity, which is largest at the smallest gap and reduces in intensity with increasing gap size. In fact, at critical coupling where the reflectivity reaches its minimum, the experimental SHG signal is already decreased to less than 10% of the maximal amplitude.

This seems contradictory to the calculated intensity enhancement in section 2.2, which exhibits maxima at the resonant SPhP excitation. However, this intensity enhancement is calculated in the third layer, i.e. the SiC sample, and does not take into account the transmittance back through the gap and the prism, which ultimately determines the measured far-field signal. First of all, the in-plane momentum of the SHG light lies, as does the exciting beam, far above the light dispersion in vacuum, and hence the SHG signal cannot couple to far-field radiation directly, but decays evanescently into the gap. Furthermore, at double frequency, the penetration depth of the evanescent wave is only half of that for the fundamental (see eq. 1.22, neglecting ϵ dispersion of the prism), and hence, the SHG signal measured in reflection depends strongly on the gap size, leading to a quickly vanishing signal for increasing *d*.

In order to confirm this qualitative argument, in fig. 4.1, the SHG intensity, being proportional to the intensity enhancement squared and multiplied with the transmittance at double frequency is plotted for each spectrum:

$$SHG_{theory} = |t_x(\omega)|^4 (1 - |r_{pp}(2\omega)|^2),$$
(4.1)

where the transmittance is calculated as 1 - R, because notably, there are no spectral features for SiC in the region of 2ω , i.e. in the range of $1500 - 2100 \text{ cm}^{-1}$. Therefore, the absorption only has an effect on the amplitude and not on the shape of the transmitted spectrum, and hence can be neglected. The transmittance is solely calculated by the reflection coefficient of *p*-polarized light r_{pp} , since no *s*-polarized SHG is generated in a *c*-cut crystal for incoming *p*-polarization [24]. The amplitude of the theoretical curve at smallest gap size was normalized to the maximum of the corresponding experimental spectrum, and all other spectra were scaled by the same factor. As has been stated in the simulations in section 2.3, the intensity enhancement is only calculated from the E_x component, being the main source of the SHG signal from the SPhP.

With this description, the relative amplitudes, peak positions and peak widths of the SPhP resonance are quite comparable to the experimental data. Some minor features, on the other hand, cannot be described by this model, but would need the inclusion of the $\chi^{(2)}$ tensor for the calculation of the SHG output, and the E_z field component, which has been neglected here.

Especially in the first spectrum at smallest gap size, where the SiC properties are most pronounced, four additional peaks are observable, which are marked with dashed lines in fig. 4.1. As described above, from left to right, these features are the $\omega_{TO\perp}^{SiC}$, weak modes, and $\omega_{LO\parallel}^{SiC}$ resonances, and at 1000 cm^{-1} for 29°, the upper Reststrahlen edge of SiC. The weak modes appear as a double shoulder in the SHG, but are not as clearly distinguishable as in the reflectivity spectra. On the other hand, the other three features in the SHG signal are known from other measurements on 4H-SiC without prism coupling [17], and hence shall not be discussed in further detail.

It shall be noted, though, that the $\omega_{TO\perp}^{SiC}$ and the weak mode features arise due to resonances in the $\chi^{(2)}$ dispersion, while the $\omega_{LO\parallel}^{SiC}$ and the upper Reststrahlen edge peaks can be attributed to the z component of the intensity enhancement. The next section is dedicated to further analyse the behaviour of the SPhP resonance in the reflectivity as well as the SHG spectra.

4.2 Gap Dependence

In order to achieve a deeper understanding of the SPhP resonance behaviour, the SPhP resonances in the reflectivity and SHG spectra were fitted with a Lorentzian in the range of the Reststrahlen band, i.e. $\sim 800 - 980 \,\mathrm{cm^{-1}}$ (for the reflectivity, 1–Lorentzian is used). The extracted peak positions, peak widths, and peak amplitudes are shown in fig. 4.2. (a) and (b) are the measured reflectivity and SHG spectra at 35 ° as an exemplary data set. The inset here shows the fitted peak width for reflectivity and SHG, highlighting the higher spectral resolution of the SPhP resonance in the SHG signal.

In the subfigures (c)-(h), the peak amplitude, peak width, and peak position as a function of gap size, for both reflectivity and SHG and for all four incident angles is plotted together with simulation results. These were obtained by applying the same Lorentzian analysis on the theoretically calculated spectra, which are simulated using all extracted fitting parameters described in the previous section. The SHG intensity is calculated with eq. 4.1, and concerning the extracted Lorentzian parameters, only the maximal amplitude of the theoretical Lorentzian peaks is normalized to the maximal value of the experimental data.

The agreement of measurements with the simulated data is excellent for both reflectivity and SHG. Regarding the SHG intensity, the high accordance might even surprise, since it was described only by the x-component of the intensity enhancement, neglecting any contributions from the E_z component and the $\chi^{(2)}$ tensor. However, as has been described in the previous section, E_z and $\chi^{(2)}$ only constitute the sources of minor features in the SHG spectra, while E_x is the principle driving force of the SHG intensity from the SPhP.

At the bottom of fig. 4.2, the peak amplitude of both reflectivity and SHG intensity is plotted over the gap size normalized by the critical distance d_{crit} , for the experimental and simulated data as well as theoretical calculations, see (j) and (k), respectively. It can be clearly seen that at critical distance, independent of the incident angle, the SPhP resonance in the reflectivity is largest, being the point of most efficient coupling into the SPhP. Furthermore, the SHG intensity peaks at distances well below d_{crit} , and has almost vanished at the optimal coupling conditions. As stated above, this can be attributed to the very inefficient back-coupling for the SHG signal through the Otto setup.

Since at critical distance, the field enhancement has its maximum, the actually produced SHG signal must be much stronger than the maximally measured values in the current configuration. Furthermore, the SHG light propagates at angles of total internal reflection inside the medium, and at a wavelength with low absorption. This leads to the conclusion, that the sample might be used as an SHG wave guide, and by attaching an out-coupling lens at the back side, this signal should be detectable. In this work, such an approach has not been realized. For future experiments, however, this might be a possible way to fully exploit the SHG arising from SPhPs, and implement a SPhP-driven SHG wave guide.



Figure 4.2: Analysis of the gap dependence of the SPhP resonance in 6H-SiC. (a) and (b) show the measured reflectivity and SHG, respectively, for $\theta = 34.8^{\circ}$, where the SHG is plotted logarithmically. The inset highlights the higher spectral resolution of the SPhP resonance in the SHG compared to the reflectivity. A detailed peak analysis by means of Lorentzian fitting curves for all four angles is shown in (c)-(h), being in very good agreement with simulations. (j) and (k) is the SPhP resonance amplitude in experiment and theory, respectively, for gap sizes normalized to the critical coupling distance d_{crit} . The theoretically calculated SHG signal has been modelled by means of the backward transmittance through the Otto structure of the SHG light produced in the sample at double frequency, see eq. 4.1.

4.3 Dispersion Curve

Finally, the fitted parameter of the measured data were used to simulate reflectivity and SHG signal maps as a function of incident wavelength and incident angle. By means of the same axis transformation discussed in section 2.2.4, these maps are translated into a dispersion plot, thereby reconstructing the SPhP dispersion relation.

The reflectivity and SHG maps are shown in fig. 4.3 in (a) and (c), respectively. In the inset in (a), the numerically extracted function of critical distance $d_{crit}(\theta)$ is shown. Due to the axis transformation, lines of constant incident angle are no longer vertical but rotated to the right, which is illustrated for the four measured incident angles 26.8°, 28.9°, 29.9°, and 34.8°. Analogously to the dispersion plot in fig. 1.12 in the theory section 1.2.3, the light line marks the asymptotic limit of the SPhP dispersion (red stripe), while for varying incident angle, the SPhP dispersion can be crossed at tunable frequency position. Additionally, in the reflectivity map, the anisotropic dispersion from eq. 1.52 for a *c*-cut uniaxial crystal has been plotted in blue. Slight deviations from the reconstructed curve especially at high k_x are not surprising, since the theoretical dispersion describes a two-layer SPhP, and by means of the reflectivity reconstruction, the three-layer dispersion is obtained.

In subfigures (b) and (d) of fig. 4.3, the experimental reflectivity and SHG spectra at critical coupling for each angle are plotted, i.e. the four spectra with deepest SPhP dip are shown. The SHG spectra are individually normalized, because by changing the incident angle, the exact same measurement conditions are lost and hence a comparison of absolute intensities at different angles is not possible. Horizontal, dotted lines connect the spectral position of reflectivity dips and SHG peaks with the reconstructed dispersion, being in excellent agreement with the intersection with the corresponding incident angle (black lines).

As a conclusion, the here presented experiment constitutes the first non-linear study of propagating SPhPs. An experimental setup with tunable incident wavelength, incident angle, and gap size allowed to critically couple light to the SPhP at almost all points in the dispersion, which therefore becomes experimentally determinable. Despite of having a poor out-coupling efficiency, an appreciable non-linear signal has been observed, which arises owing to very efficient non-linear optical conversion due to extreme field enhancements.





5 Strong Coupling Between SPhPs and AlN LO Mode in AlN / 6H-SiC

This section focusses on the experimental reflectivity and SHG spectra obtained in the Otto geometry from the sample consisting of a 110 nm thin AlN layer on top of a 6H-SiC substrate. In appendix B, the general experimental details and the analysis procedure is described in detail for the plain 6H-SiC sample, and therefore, will not be explained again here.

The discussion is divided into three parts. First, the experimental spectra are discussed in general, presenting the successful excitation of two SPhP branches and the detection of a large SHG signal arising from both modes. Secondly, an observed weak mode suppression and the emergence of an unexpected SHG signal in the frequency range of the AlN *LO*-like mode is analysed (section 5.2). Finally, the two SPhP dispersion curves arising due to an avoided crossing with the AlN *LO*-like mode are reconstructed via simulations (section 5.3), exhibiting an excellent agreement with the measured reflectivity and SHG spectra.

5.1 General Discussion of the Experimental Results

In fig. 5.1, the reflectivity and SHG spectra obtained at nominal incident angle of 28° are shown in order to exemplary discuss the main characteristics. The fitted curves are plotted as lines in the reflectivity, being in excellent agreement with the data. Analogously to the spectra of bare 6H-SiC, the SiC Reststrahlen band is clearly visible, and the edges rise with increasing gap size, approaching a reflectivity of 1.

Inside the Reststrahlen band, two phonon polariton dips appear in the reflectivity, with one lying below and the other above the $\omega_{LO\parallel}^{AlN}$ frequency. As it has been discussed in the simulations (see section 2.2.4), the AlN LO frequencies cut the SiC Reststrahlen band into two halves (at small incident angles rather defined by $\omega_{LO\parallel}^{AlN} = 885 \,\mathrm{cm}^{-1}$) and thereby create two SiC-AlN coupled polaritons. However, none of those can exist at the cutting position, constituting an avoided crossing of the two SPhP branches.

By taking a look at the gap dependence of the reflectivity spectra, quite a different resonance behaviour of the two polariton modes can be observed. The lower polariton is broad and relatively shallow at small gap size d. With increasing d, the dip gets slimmer, reaching the critical coupling distance at about 7.3 μ m, and for even larger d, the resonance becomes weaker. This is the same behaviour observed for the SPhP on bare 6H-SiC. The upper polariton, on the other hand, evolves differently with increasing gap size. At the smallest d, already a minimal reflectivity of 0.1 is reached, which is maintained during an increase of 2 μ m of the gap size. It is not until a gap size > 5 μ m, where the resonance depth starts to decrease. This particular behaviour differs from the SPhP on bare 6H-SiC, featuring rather the properties of the AlN *LO*-like resonance in the reflectivity spectra of an AlN / SiC system, see section 2.2.2.

In an intuitive picture, these tendencies of being rather SPhP-like or AlN LO mode-like can be understood by the spectral proximity of the polariton mode to the splitting frequency, i.e. at $\sim \omega_{LO\parallel}^{AlN}$. At an incident angle of 27.6°, as shown in fig. 5.1, the lower polariton branch lies farther away from the AlN LO-like mode, therefore being rather SPhP-like. The upper polariton branch, on the other hand, is spectrally closer to the AlN LO-like mode, and thus predominantly exhibits an AlN LO-like nature.



Figure 5.1: Spectral reflectivity (a) and SHG (b) measurements and simulations in the Reststrahlen region of 6H-SiC of the 110 nm AlN / 6H-SiC sample in the Otto geometry, exhibiting the two expected SPhP resonances. All reflectivity spectra were fitted with the matrix formalism, nicely reproducing the data. The SHG signal is plotted logarithmically in order to be able to distinguish weak resonances. The dashed lines mark features in the SHG spectrum, three of them being $\omega_{TO\perp}^{SiC}$, $\omega_{LO\parallel}^{SiC}$, and the angle shifted upper Reststrahlen band, reasonably well corresponding to the respective features in the reflectivity. The weak mode resonances are also marked, but not clearly visible in the SHG spectra and not at all in the reflectivity. The upper weak mode coincides roughly with the $\omega_{LO\parallel}^{AlN}$ resonance, not showing any feature in the data. The SHG signal above $1020 \,\mathrm{cm}^{-1}$ is artefact.

For an increasing incident angle, i.e. by passing the avoided crossing of the two polariton branches, the situation is reversed. There, the upper mode merges into the SPhP dispersion loosing its AlN LO mode-like nature, while the lower mode, originally being rather SPhP-like, approaches the AlN LO mode and adopts its characteristics. Thus, the critical coupling behaviour appears to be a very interesting parameter to analyse the character of the mode.

The SHG data exhibits two large resonances, coming from the field enhancement of the two polaritons. Exactly as for plain 6H-SiC, their peak amplitudes continuously decrease for increasing gap size, which can be understood again as an effect of inefficient out-coupling of the SHG signal with increasing gap size. When comparing both polariton peaks, however, their relative amplitude shifts from the upper SPhP peak, to the lower SPhP peak being higher. Interestingly, the distance of transition seems to approximately correspond to the distance, where the lower SPhP starts to couple stronger than the upper SPhP (see reflectivity dips).

In order to confirm this theoretically, however, the field enhancement in both SiC substrate and AlN layer must be calculated, but at the moment, only the substrate is accessible. Hence, the lower SPhP peak is drastically underestimated in the current calculations, and no reliable estimate can be made. In principle, the 4×4 - matrix formalism provides the electric field components at any point in the multilayer system, and thus should be capable of shedding light on the spatial origin of the measured SHG signal.

Table 5.1: Fitted and fixed global parameters of the reflectivity measurements performed on $110 \mathrm{nm} \mathrm{AlN}$ / 6H-SiC
in the Otto geometry, which are shared by all four incident angles. Individual parameters such as gap size d and
factor <i>a</i> are specified in appendix C in the corresponding figures C.1, C.2, C.3, and C.4, and in table C.1. At the
bottom, the nominal and fitted incident angles are listed.

	Parameter	Value	Literature			
Fitted	$\Delta \theta$	0.44°	-			
	$\Delta \omega$	$3.85\mathrm{cm}^{-1}$	-			
	d_{AlN}	$110.2\mathrm{nm}$	-			
	$\omega_{LO\parallel}^{AlN}$	$885.17{\rm cm}^{-1}$	$888.9{ m cm^{-1}}$ [94]			
	γ^{AlN}	$8.87\mathrm{cm}^{-1}$	$\gamma_{TO\perp}^{AlN} = 5.2 \mathrm{cm}^{-1}$			
			$\gamma^{AlN}_{LO\perp} = 10.4\mathrm{cm}^{-1}$			
			$\gamma_{TO\parallel}^{AlN} = 6.7 \mathrm{cm}^{-1}$			
			$\gamma_{LO\parallel}^{AlN} = 8.8 \mathrm{cm}^{-1}$ [76]			
Fixed	$\omega_{TO\parallel}^{AlN}$	$608.5\mathrm{cm}^{-1}$	[94]			
	$\omega_{TO\perp}^{AlN}$	$667.2{\rm cm}^{-1}$	[94]			
	$\omega_{LO\perp}^{AlN}$	$909.6\mathrm{cm}^{-1}$	[94]			
	$\epsilon_{\infty\parallel}^{AlN}$	4.35	[94]			
	$\epsilon_{\infty\perp}^{AlN}$	4.16	[94]			
	All 6H-SiC parameters listed in table 4					
$\theta_{nominal} = 26^{\circ}$	28°	30 °	34°			
$\theta_{fitted} = 25.34^\circ$	27.56°	29.29°	33.39°			

Concerning the AlN thickness d_{AlN} , it must be noted that a 120 nm thick layer was expected, which is why in the simulations in chapter 2 the calculations were performed for this size. The fitting of the experimental data, however, yields a thickness of ~ 110 nm, which is why in the results chapter, the sample is referred to as 110 nm AlN / 6H-SiC. A high agreement with the features studied in the simulations for $d_{AlN} = 120$ nm is still met.

The same fitting procedure as for 6H-SiC yields the parameter values listed in table 5.1, where $\Delta\theta$, $\Delta\omega$, the AlN layer thickness d_{AlN} , and the AlN parameters $\omega_{LO\parallel}^{AlN}$ and γ^{AlN} were fitted. A special remark shall be made on the damping γ^{AlN} , which has been assumed to be the same for all modes. In the literature, as shown in table 5.1 and mentioned in table 2.2 in section 2.2.3, however, the ordinary and extraordinary TO and LO modes have quite different values. As a matter of fact, the fitted value is comparable to the average damping of the values given by Kazan *et al.* [76], see table 5.1. In this work, however, the measured reflectivity spectra, which are used to extract the material constants, do not provide sufficient information for the determination and differentiation of all four damping constants, which is why a single average value is appropriate.

The *TO* frequencies of AlN lie below the chosen spectral range, and furthermore, the reflectivity is not sensitive to the $\omega_{LO\perp}^{AlN}$ mode, see section 2.2.3. Therefore, only the $\omega_{LO\parallel}^{AlN}$ frequency was chosen to be a fitting parameter, while the other three frequencies were fixed to literature values [94]. The parameters of the 6H-SiC sample, on the other hand, were fixed to the values obtained in the previous section. The complete measured data of all four angles can be found in appendix C in figures C.1, C.2, C.3, and C.4 for 26°, 28°, 30°, and 34°, respectively.

5.2 Weak Modes and the AIN LO-like Feature

As for the plain 6H-SiC sample, in fig. 5.1, again all features other than the polariton resonances visible in the SHG spectra are marked with dashed lines. Hereby, the weak modes are especially interesting, which are expected at the two lines at 881 and 886 cm^{-1} . In the reflectivity, no evidence of a resonance can be found, and in the SHG signal, barely a vague kink can be distinguished. This is quite different from the plain 6H-SiC sample, where the weak modes are quite noticeable.

The explanation for this suppression is most probably a combination of two effects, the first being the lack of a polariton at the frequency positions of the weak modes, and the second being the high absorption in the AlN layer up to its upper Reststrahlen edge. Coincidentally, the weak modes of 6H-SiC lie very close to $\omega_{LO\parallel}^{AlN}$, i.e. in the range of the avoided crossing, and therefore cannot be enhanced by the polaritons.

In order to determine, which of the two explanations has more impact, an interesting follow-up experiment would be to use a 4H-SiC substrate, which exhibits one weak mode resonance at 838.9 cm^{-1} [67]. At an incident angle of about 26°, the lower SPhP peaks at the same frequency, and therefore, an enhanced weak mode resonance might be observed. If this is the case, the SPhP efficiently counteracts the high absorption of the AlN and still enhances the underlying SiC resonances. Thereby, as a function of AlN thickness d_{AlN} , the weak mode resonance might even grant experimental access to the field distribution of the SPhP in the heterostructure.

A surprising feature can be found in the SHG signal at a nominal incident angle of 34° at $\sim 897 \text{ cm}^{-1}$, which is shown in fig. 5.2 and marked with a dashed, red line. This peak is rather small, appears only for larger incident angles and lies at a frequency, where no feature can be observed in the reflectivity



Figure 5.2: Measured reflectivity (a) and SHG (b) spectra and simulations in the Reststrahlen region of 6H-SiC of the 110 nm AlN / 6H-SiC sample in the Otto geometry, at an incidence angle of 33.4° . Between the two expected polariton peaks in the SHG signal, a small feature can be observed at 897 cm^{-1} . In the reflectivity in the Otto geometry, at this energy no feature appears. For the reflectivity without prism, as shown in the inset, on the other hand, the AlN *LO*-like mode carves a deep feature into the SiC Reststrahlen band, lying at 893 cm^{-1} at an incidence angle of 33.4° . Very likely, this constitutes the origin of the SHG signal, even though further investigations are necessary in order to confirm this statement.

spectrum, being in the region of the AlN LO modes. In the inset in the reflectivity data, the calculated reflectivity of a KRS-5 / 110 nm AlN / 6H-SiC sample is shown for three different incident angles, with the second one being the incident angle of the measurement data, i.e. 33.4° . As discussed in section 2.2.2, the AlN LO dip in the SiC Reststrahlen band can be attributed to a pseudo-anisotropic AlN LO-like mode coupled to the SiC substrate. For the angle of 33.4° , the dip position is marked with a dashed, red line lying at a wavenumber of $893 \,\mathrm{cm}^{-1}$, which is quite comparable to the measured signal at $897 \,\mathrm{cm}^{-1}$.

Assuming that the LO resonance in the AlN layer is accompanied by a field enhancement in the AlN, the data suggests that this SHG signal is exclusively generated in the AlN layer. However, with the current state of knowledge, the measured feature at $897 \,\mathrm{cm}^{-1}$ cannot be securely attributed to the AlN LO-like mode without further studies, which are currently in progress.

5.3 Dispersion Curve

Finally, as it has been described previously in section 2.2.4 in the simulations, calculated reflectivity and SHG maps for the AlN / 6H-SiC sample are axis transformed in order to reconstruct the dispersion relation. The same critical distance as a function of θ has been used as for the plain 6H-SiC sample, which is appropriate for the upper SPhP, and, in terms of spectral resolution, matches sufficiently well the critical distances of the lower polariton branch.

The reflectivity and SHG maps are plotted in fig. 5.3 in (a) and (c), again together with all four light dispersions at measured incident angles, the light line in vacuum, and the uniaxial dispersion curve (blue line) of a SPhP in a two-layer system on 6H-SiC. In the subfigures (b) and (d), the measured reflectivity and SHG spectra, respectively, at all four incident angles at critical coupling distances are shown. The dip and peak positions of both polariton resonances are again connected by horizontal, dashed lines with their corresponding angle dependent in-plane dispersion, being in excellent agreement with the respective polariton branch.

As stated earlier, the SHG has been estimated in the SiC substrate. In the calculated SHG spectra, the lower SPhP is almost invisible, but a large signal is obtained experimentally. This can be explained by the neglected $\chi^{(2)}$ constribution to the SHG intensity, which is much larger close to the TO frequencies of 6H-SiC, see fig. 2.15 in section 2.2.4. Therefore, for the lower SPhP branch, much more SHG is obtained out of less field enhancement than for the upper SPhP.

The uniaxial dispersion curve of a SPhP on 6H-SiC, which is plotted as a blue line, only matches the upper SPhP at high energies. At energies around the AlN LO-like mode, i.e. where the avoided crossing takes place, on the other hand, this SPhP branch deviates from the two-layer dispersion and merges smoothly with the strong AlN LO-like feature at incident angles below θ_{crit} , as discussed in section 2.2.2. At frequencies close to the TO modes of 6H-SiC, finally, the SPhP dispersion on plain 6H-SiC merges into the lower branch. Therefore, a strong coupling behaviour between the SPhP and the AlN LO-like mode can be observed, featuring the avoided crossing discussed in the simulations chapter (section 2.2.4).

As a summary, we here observed strong, resonant coupling of a propagating SiC SPhP with an intrinsic anisotropic resonance in a nm-scale AlN add-layer. This coupling is so efficient that it leads to a splitting of the SPhP into two branches, with a dispersion showing an avoided crossing between them at the AlN *LO* resonance. For studying these phenomena in such multilayer structures, the performed reflectivity





and SHG spectroscopy measurements constitute an excellent experimental approach. By means of the SHG, even sensitivity to the field distribution in the multilayer system is granted. At the moment, new samples with thinner AlN layer thickness are being produced, which will allow to further explore the physics of the coupled SPhP mode, thereby granting insight into the interaction nature of polaritons in polar dielectric heterostructures.

Conclusion

This master's thesis provides a detailed experimental and theoretical study of SPhPs at the surface of a single polar crystal, and at the interfaces of a two-material multilayer structure in the Otto geometry. The undertaken investigation of SHG of SPhPs reveals an enormous field enhancement capable of driving the atomic motion far into the non-linear regime. Furthermore, by studying the optical response of a nm-scale multilayer system, a strong coupling of a SPhP with an AlN *LO* phonon mode has been discovered, granting thereby a first glance at the non-trivial physics emerging from the exploration of polar dielectric heterostructures. The here gained knowledge aims to constitute an essential building block for target-design of artificial SPhP materials with desired properties.

On the experimental side of this work, a gap size and incident angle flexible Otto geometry setup has been designed and successfully implemented. Employing the free electron laser at the FHI as an excitation source, reflectivity and SHG spectroscopy experiments were carried out. Regarding the theoretical side, a 4×4 - matrix formalism for the treatment of multilayer optics was developed. In contrast to various other works [63, 64, 65, 95, 96], the here presented calculus is capable of computing the reflection and transmission coefficients of any polarization and incident angle of a multilayer system with N layers, each being isotropic or anisotropic, described by an arbitrarily anisotropic complex dielectric tensor.

As a proof of concept, SPhP excitation and SHG generation was demonstrated for a simple model system of 6H-SiC. This polar crystal is known to exhibit a SPhP resonance in the Reststrahlen band when measuring the reflectivity [14, 15]. The SHG spectra obtained here, on the other hand, have not been presented elsewhere before. At the SPhP resonance, a strong peak in the second harmonic (SH) signal was observed, which could be determined to be generated by the exceptional field enhancement arising from SPhPs. The findings of this work nicely demonstrate the potential of SPhPs in the development of transient control and manipulation of material phases by means of tunable resonant lattice excitations.

The matrix calculus could perfectly describe the reflectivity data, thereby allowing a precise prediction of the properties of SPhPs. Furthermore, even minor features like the weak modes of 6H-SiC or the anisotropy splitting feature of the LO modes are perfectly reproduced. The SHG spectra could be simulated with a decent qualitative agreement with the experimental data. Deviations from the measurements arise since only the *x*-component of the field enhancement was calculated so far, neglecting the *z*-component and $\chi^{(2)}$ contributions. The *z*-component of the field enhancement, however, is known to only describe resonances at the LO frequencies, and in the frequency region of the SPhP, $\chi^{(2)}$ is featureless. Therefore, the here calculated field enhancement provides an adequate estimate of the SHG signal produced by SPhPs.

The second sample studied here, being a 110 nm thin AlN film on top of a 6H-SiC substrate, was investigated in order to shed light on the unique properties of SPhPs in multilayer structures. Especially notable, the performed simulations of this structure revealed the emergence of two individual SPhP modes, exhibiting a strong avoided crossing in the coupling region to an AlN *LO* mode. Following these theoretical predictions, experiments were carried out, indeed showing that two SPhP modes clearly appear in the SHG and reflectivity spectra, exhibiting a particular SPhP - AlN *LO* mode coupled nature depending on the dispersion position relative to the point of avoided crossing.

The matrix formalism allowed to perfectly describe the reflectivity spectra, while at the moment, the field enhancement simulations deviate from the experimentally observed spectra, since they are calculated only in the substrate. On the basis of the predicted characteristics in the reflectivity simulations, more samples are currently been produced in order to further explore the properties of SPhPs in such multilayers.

The performed reflectivity and SHG measurements feature an excellent experimental approach for studying the properties of SPhPs in multilayer systems. For instance, the employed technique even grants sensitivity to the field distribution in the heterostructure, as has been demonstrated by the observed weak mode suppression in 6H-SiC. Finally, an unexpected SHG resonance was observed at the frequency of the coupled AlN LO mode, which has not been reported before. With the knowledge gained here, a valuable starting point has been established for such multilayer systems, thereby facilitating the development of user-defined SPhP materials.

As a summary, this thesis provides a detailed study of the physics of SPhPs excited with light in polar dielectric structures. By implementing a new experimental and theoretical methodology, novel phenomena of SPhPs in heterostructures and their unique interaction nature has been discovered, being a promising field of research with a variety of possible applications. The approach developed during this thesis, therefore, shows high promise of crucially contributing to the scientific advance in the fields of non-linear phononics and nanophotonics.

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Appendices

A | Reflectivity and Transmittance of an Arbitrarily Anisotropic Multilayer Medium

This section provides a full description of a 4×4 - matrix approach for the calculation of reflectivity and transmission of a one-dimensional multilayer medium consisting of N layers with isotropic or anisotropic dielectric tensors.

In the last decades, many authors have provided different approaches to this particular problem, but either they focus on special cases, thus lacking full generality, or the calculation, when implemented in a computer program, leads to numerical instabilities. So, for instance, the two well-known Berreman and Yeh formalisms [63, 64] as well as the generalized approach by Lin-Chung and Teitler [95] assume solely fully anisotropic tensors, and lead to singularities, if the material is isotropic or even if the three main dielectric components coincide with the laboratory coordinate system. A solution to these singularities is given by Xu [65], which, on the other hand, provides an unstable solution for solving the eigensystem of electric field modes of the multilayer system.

In the approach presented here, the different solutions are combined in such a way that a numerically stable formalism is achieved, which is capable of handling isotropic or anisotropic materials for each layer including the substrate. The incident medium is assumed to be non-absorptive and isotropic. Furthermore, the magnetic permeability μ is taken as a scalar and no optical activity is included in the formalism.

The coordinate system is defined such that the multilayer surfaces lie in the x-y-plane and the z-direction is orthogonal to the surface, pointing from the incident medium towards the substrate and being zero at the first interface between incident medium and layer i = 1. The layers are indexed from i = 1 to i = N, whereas the incident medium is i = 0 and the substrate i = n + 1 = s. Each layer has an individual thickness d_i , and the thickness of the complete multilayer system is $D = \sum_{i=1}^{N} d_i$.

Exactly as defined in section 2.1.1, the incident beam is chosen to lie in the *x*-*z*-plane, resulting in the following wave vector \vec{k}_i in layer *i*:

$$\vec{k}_i = \frac{\omega}{c}(\xi, 0, q_i),\tag{A.1}$$

with $\xi = \sqrt{\epsilon_{inc}} \sin(\theta)$ being the *x*-component which is conserved throughout the complete multilayer system, ϵ_{inc} is the isotropic dielectric constant of the incident medium, θ is the incident angle, and q_i is the unit-free *z*-component of the described wave in layer *i*.

For a given dielectric tensor $\bar{\epsilon}$ with principle dielectric constants ϵ_x , ϵ_y , and ϵ_z , the following transformation allows to rotate the crystal orientation into the lab frame:

$$\bar{\epsilon}' = \Omega \,\bar{\epsilon} \,\Omega^{-1} = \Omega \,\begin{pmatrix} \epsilon_x & 0 & 0\\ 0 & \epsilon_y & 0\\ 0 & 0 & \epsilon_z \end{pmatrix} \Omega^{-1}, \tag{A.2}$$

with the coordinate rotation matrix Ω given by the Euler angles ϑ , φ , and ψ [64]:

$$\Omega = \begin{pmatrix} \cos\psi \cos\varphi - \cos\vartheta \sin\varphi \sin\psi & -\sin\psi \cos\varphi - \cos\vartheta \sin\varphi \cos\psi & \sin\vartheta \sin\varphi \\ \cos\psi \sin\varphi + \cos\vartheta \cos\varphi \sin\psi & -\sin\psi \sin\varphi + \cos\vartheta \cos\varphi \cos\psi & -\sin\vartheta \cos\varphi \\ \sin\vartheta \sin\psi & \sin\vartheta \cos\psi & \cos\vartheta \end{pmatrix}.$$
(A.3)

In general, any material will have exactly four eigenmodes, i.e. four possible solutions for the propagation of an electromagnetic wave. They differ in polarization and propagation direction and have four different *z*-components of the wave vector, which will be called q_{ij} , with j = 1, 2, 3, 4. In order to obtain these four solutions, in the following, the approach by Berreman is sketched [63].

First, the Maxwell equations are written in a 6x6-matrix form, where the time derivative has already been performed, assuming a time dependence of $e^{-i\omega t}$:

$$\mathbf{RG} \coloneqq \begin{pmatrix} 0 & 0 & 0 & 0 & -\frac{\partial}{\partial z} & \frac{\partial}{\partial y} \\ 0 & 0 & 0 & \frac{\partial}{\partial z} & 0 & -\frac{\partial}{\partial x} \\ 0 & 0 & 0 & -\frac{\partial}{\partial y} & \frac{\partial}{\partial x} & 0 \\ 0 & \frac{\partial}{\partial z} & -\frac{\partial}{\partial y} & 0 & 0 & 0 \\ -\frac{\partial}{\partial z} & 0 & \frac{\partial}{\partial x} & 0 & 0 & 0 \\ \frac{\partial}{\partial y} & -\frac{\partial}{\partial x} & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \\ H_x \\ H_y \\ H_z \end{pmatrix} = -i\omega \begin{pmatrix} D_x \\ D_y \\ D_z \\ B_x \\ B_y \\ B_z \end{pmatrix} =: -i\omega \mathbf{C}.$$
(A.4)

If only linear effects are considered, a relation between G and C can be formulated as follows

$$\mathbf{G} = \mathbf{M}\mathbf{C} \eqqcolon \begin{pmatrix} \bar{\epsilon} & \bar{\rho}_1 \\ \bar{\rho}_2 & \bar{\mu} \end{pmatrix} \mathbf{C}, \tag{A.5}$$

where $\bar{\mu}$ is the permeability tensor, and $\bar{\rho}_1$ and $\bar{\rho}_2$ are optical rotation tensors. In the approach described here, the generality of $\bar{\mu}$, $\bar{\rho}_1$, and $\bar{\rho}_2$ is dropped later on in order to achieve stable solutions without singularities for any case of $\bar{\epsilon}$. Therefore, at this point, the following definitions are made:

$$\bar{\mu} = \mu \, \mathbb{1} \tag{A.6}$$

$$\bar{\rho}_1 = \bar{\rho}_2 = 0, \tag{A.7}$$

where $\mathbb{1}$ and $\mathbb{0}$ are the unity matrix and the matrix consisting just of zeros. By combining eq. A.4 and A.5, the following spatial wave equation is obtained, where Γ is the spatial part of **G**:

$$\mathbf{R}\boldsymbol{\Gamma} = -i\omega\mathbf{M}\boldsymbol{\Gamma}.\tag{A.8}$$

As shown explicitly by Berreman, the third and sixth variable of Γ , being $\Gamma_3 = E_z$ and $\Gamma_6 = H_z$, can be solved in terms of the other four parameters, and thus be eliminated. This yields the following equation

$$\frac{\partial}{\partial z}\Psi = i\frac{\omega}{c}\Delta\Psi,\tag{A.9}$$

where

$$\Psi = \begin{pmatrix} E_x \\ H_y \\ E_y \\ -H_x \end{pmatrix}$$
(A.10)

is the reordered field vector. Δ is exactly defined in terms of M as follows:

$$\begin{split} \Delta_{11} &= M_{51} + (M_{53} + \xi)a_{31} + M_{56}a_{61} \\ \Delta_{12} &= M_{55} + (M_{53} + \xi)a_{35} + M_{56}a_{65} \\ \Delta_{13} &= M_{52} + (M_{53} + \xi)a_{32} + M_{56}a_{62} \\ \Delta_{14} &= -M_{54} - (M_{53} + \xi)a_{34} - M_{56}a_{64} \\ \Delta_{21} &= M_{11} + M_{13}a_{31} + M_{16}a_{61} \\ \Delta_{22} &= M_{15} + M_{13}a_{35} + M_{16}a_{65} \\ \Delta_{23} &= M_{12} + M_{13}a_{32} + M_{16}a_{62} \\ \Delta_{24} &= -M_{14} - M_{13}a_{34} - M_{16}a_{64} \\ \Delta_{31} &= -M_{41} - M_{43}a_{31} - M_{46}a_{61} \\ \Delta_{32} &= -M_{45} - M_{43}a_{35} - M_{46}a_{65} \\ \Delta_{33} &= -M_{42} - M_{43}a_{32} - M_{46}a_{62} \\ \Delta_{34} &= M_{44} + M_{43}a_{34} + M_{46}a_{64} \\ \Delta_{41} &= M_{21} + M_{23}a_{31} + (M_{26} - \xi)a_{61} \\ \Delta_{42} &= M_{25} + M_{23}a_{35} + (M_{26} - \xi)a_{65} \\ \Delta_{43} &= M_{22} + M_{23}a_{32} + (M_{26} - \xi)a_{62} \\ \Delta_{44} &= -M_{24} - M_{23}a_{34} - (M_{26} - \xi)a_{64}, \end{split}$$
(A.11)

where the elements of a_{ij} are given by

$$a_{3j} = \begin{pmatrix} (M_{61}M_{36} - M_{31}M_{66})/b \\ ((M_{62} - \xi)M_{36} - M_{32}M_{66})/b \\ 0 \\ (M_{64}M_{36} - M_{34}M_{66})/b \\ (M_{65}M_{36} - (M_{35} + \xi)M_{66})/b \\ 0 \end{pmatrix} \qquad a_{6j} = \begin{pmatrix} (M_{63}M_{31} - M_{33}M_{61})/b \\ (M_{63}M_{32} - M_{33}(M_{62} - \xi))/b \\ 0 \\ (M_{63}M_{34} - M_{33}M_{64})/b \\ (M_{63}(M_{35} + \xi) - M_{33}M_{65})/b \\ 0 \end{pmatrix}, \quad (A.12)$$

and b is defined by

$$b = M_{33}M_{66} - M_{36}M_{63}. \tag{A.13}$$

Note that Δ and a_{ij} , in contrast to the formulas given by Berreman, do not contain the factor $\frac{c}{\omega}$ before each ξ , which is due to a different definition of ξ .

The M-matrix of the corresponding material is assumed to be z-independent. In that case, the four independent solutions q_{ij} are given by the eigenvalues of Δ , and the four eigenvectors Ψ_{ij} resemble the eigenmodes in the material.

At this point, the four solutions have to be ordered in an unambiguous manner in order to avoid unstable solutions and discontinuities, which has not been done by any author mentioned up to now. The solution presented here is based on the work of Li *et al.* [96].

First of all, the modes have to be separated into forward propagating (transmitted) and backward

propagating (reflected) waves, which is done as follows:

$$\begin{array}{cccc} \text{If } q_{ij} \text{ is real:} & q_{ij} \geq 0 & \longrightarrow \text{ transmitted} \\ & q_{ij} < 0 & \longrightarrow \text{ reflected} \\ \text{If } q_{ij} \text{ is imaginary:} & Im(q_{ij}) \geq 0 & \longrightarrow \text{ transmitted} \\ & Im(q_{ij}) < 0 & \longrightarrow \text{ reflected.} \end{array}$$

$$\begin{array}{c} \text{(A.14)} \\ \end{array}$$

This is immediately intuitive considering that real wave vectors point in the propagation direction, and imaginary wave vectors describe an exponentially damped wave. In the latter, the lack of sorting the waves as explained could easily result in exponentially increasing waves.

The transmitting waves will be labelled q_{i1} and q_{i2} , whereas the reflected waves are named q_{i3} and q_{i4} . Each pair, however, has also to be sorted in order to ensure solutions without discontinuities. For this means, the eigenvectors of each eigenvalue have to be computed and evaluated by the following equation:

$$C_p = \frac{|E_x|^2}{|E_x|^2 + |E_y|^2}.$$
(A.15)

Finally, the four eigenvalues are sorted as follows:

$$C_p(q_{i1}) > C_p(q_{i2})$$
 and $C_p(q_{i3}) > C_p(q_{i4}).$ (A.16)

This means for the four solutions, that q_{i1} and q_{i3} describe *p*-polarized, and q_{i2} and q_{i4} *s*-polarized waves, transmitted and reflected, respectively.

As mentioned earlier, various authors assume fully anisotropic dielectric tensors, and their formalisms suffer from singularities for several special cases, i.e. if the material is isotropic, or even if the dielectric tensor has only diagonal components. These cases have in common that the four solutions become degenerate, and this is why an easy workaround can be found, covering all appearing singularities simultaneously. This solution is proposed by Xu *et al.* [65], and will be formulated in the following.

The starting point is slightly different than explained above, and thus shall be mentioned briefly. The Maxwell equations for each component of the electric field can be formulated as follows, assuming a scalar magnetic permeability μ :

$$\begin{pmatrix} \mu_{i}\epsilon_{i11} - q_{i}^{2} & \mu_{i}\epsilon_{i12} & \mu_{i}\epsilon_{i13} + \xi q_{i} \\ \mu_{i}\epsilon_{i21} & \mu_{i}\epsilon_{i22} - \xi^{2} - q_{i}^{2} & \mu_{i}\epsilon_{i23} \\ \mu_{i}\epsilon_{i31} + \xi q_{i} & \mu_{i}\epsilon_{i32} & \mu_{i}\epsilon_{i33} - \xi^{2} \end{pmatrix} \begin{pmatrix} E_{ix} \\ E_{iy} \\ E_{iz} \end{pmatrix} = 0,$$
(A.17)

and the four solutions q_{ij} , in principle, can be obtained by solving the fourth-order polynomial equation resulting from setting the determinant of the matrix in eq. A.17 equal zero. This approach, however, does not permit to properly sort the obtained eigenvalues as described above, and hence unavoidably leads to discontinuities in the solutions.

The electric fields of the four eigenmodes j (obtained and sorted as explained above) in each layer i will be written as follows:

$$\vec{E}_{ij} = E_{ij} \begin{pmatrix} \gamma_{ij1} \\ \gamma_{ij2} \\ \gamma_{ij3} \end{pmatrix}, \qquad (A.18)$$

where E_{ij} are the common factors of the three field components. The rest of the formalism does not depend on those factors. The 12 values of γ_{ijk} are given by the following formula [65]:

$$\begin{split} \gamma_{i11} &= \gamma_{i22} = \gamma_{i42} = -\gamma_{i31} = 1 \\ \gamma_{i12} &= \begin{cases} 0 & \text{if } q_{i1} = q_{i2} \\ \frac{\mu_{i}\epsilon_{i23}(\mu_{i}\epsilon_{i31} + \xi q_{i1}) - \mu_{i}\epsilon_{i22}(\mu_{i}\epsilon_{i33} - \xi^{2})}{(\mu_{i}\epsilon_{i33} - \xi^{2})(\mu_{i}\epsilon_{i22} - \xi^{2} - q_{i1}^{2}) - \mu_{i}^{2}\epsilon_{i23}\epsilon_{i32}} & \text{if } q_{i1} \neq q_{i2} \end{cases} \\ \gamma_{i13} &= \begin{cases} -\frac{\mu_{i}\epsilon_{i31} + \xi q_{i1}}{\mu_{i}\epsilon_{i33} - \xi^{2}} & \text{if } q_{i1} = q_{i2} \\ -\frac{\mu_{i}\epsilon_{i33} + \xi q_{i1}}{\mu_{i}\epsilon_{i33} - \xi^{2}} - \frac{\mu_{i}\epsilon_{i32}}{\mu_{i}\epsilon_{i33} - \xi^{2}} \gamma_{i12} & \text{if } q_{i1} \neq q_{i2} \end{cases} \\ \gamma_{i21} &= \begin{cases} 0 & \text{if } q_{i1} = q_{i2} \\ \frac{\mu_{i}\epsilon_{i32}(\mu_{i}\epsilon_{i13} + \xi q_{i2}) - \mu_{i}\epsilon_{i12}(\mu_{i}\epsilon_{i33} - \xi^{2})}{(\mu_{i}\epsilon_{i13} + \xi q_{i2}) - (\mu_{i}\epsilon_{i13} + \xi q_{i2})} & \text{if } q_{i1} \neq q_{i2} \end{cases} \\ \gamma_{i23} &= \begin{cases} 0 & \text{if } q_{i1} = q_{i2} \\ -\frac{\mu_{i}\epsilon_{i33}}{\mu_{i}\epsilon_{i33} - \xi^{2}} & \text{if } q_{i1} = q_{i2} \\ -\frac{\mu_{i}\epsilon_{i33} - \xi^{2}}{\mu_{i}\epsilon_{i33} - \xi^{2}} & \text{if } q_{i1} = q_{i2} \end{cases} \\ \gamma_{i32} &= \begin{cases} 0 & \text{if } q_{i3} = q_{i4} \\ \frac{\mu_{i}\epsilon_{i33} - \xi^{2}}{\mu_{i}\epsilon_{i33} - \xi^{2}} & \text{if } q_{i3} = q_{i4} \end{cases} \\ \gamma_{i33} &= \begin{cases} \frac{\mu_{i}\epsilon_{i33} + \xi q_{i3}}{\mu_{i}\epsilon_{i33} - \xi^{2}} & \text{if } q_{i3} = q_{i4} \\ \frac{\mu_{i}\epsilon_{i33} - \xi^{2}}{\mu_{i}\epsilon_{i33} - \xi^{2}} + \frac{\mu_{i}\epsilon_{i32}}{\mu_{i}\epsilon_{i33} - \xi^{2}} \gamma_{i32} & \text{if } q_{i3} = q_{i4} \end{cases} \\ \gamma_{i41} &= \begin{cases} 0 & \text{if } q_{i3} = q_{i4} \\ \frac{\mu_{i}\epsilon_{i33} - \xi^{2}}{(\mu_{i}\epsilon_{i33} - \xi^{2})} + \frac{\mu_{i}\epsilon_{i32}}{\mu_{i}\epsilon_{i33} - \xi^{2}} \gamma_{i32} & \text{if } q_{i3} = q_{i4} \end{cases} \\ \gamma_{i43} &= \begin{cases} -\frac{\mu_{i}\epsilon_{i32}}{\mu_{i}\epsilon_{i33} - \xi^{2}} & \text{if } q_{i3} = q_{i4} \\ -\frac{\mu_{i}\epsilon_{i33} - \xi^{2}}{\mu_{i}\epsilon_{i33} - \xi^{2}} & \text{if } q_{i3} = q_{i4} \end{cases} \\ \gamma_{i43} &= \begin{cases} 0 & \text{if } q_{i3} = q_{i4} \\ -\frac{\mu_{i}\epsilon_{i33}}{\mu_{i}\epsilon_{i33} - \xi^{2}}} & \text{if } q_{i3} = q_{i4} \\ -\frac{\mu_{i}\epsilon_{i33} - \xi^{2}}{\mu_{i}\epsilon_{i33} - \xi^{2}} & \text{if } q_{i3} = q_{i4} \end{cases} \end{cases} \\ \gamma_{i43} &= \begin{cases} 0 & \text{if } q_{i3} = q_{i4} \\ -\frac{\mu_{i}\epsilon_{i33} - \xi^{2}}{\mu_{i}\epsilon_{i33} - \xi^{2}}} & \text{if } q_{i3} = q_{i4} \\ -\frac{\mu_{i}\epsilon_{i33} - \xi^{2}}{\mu_{i}\epsilon_{i33} - \xi^{2}} & \text{if } q_{i3} = q_{i4} \end{cases} \end{cases} \end{cases}$$

Now that the solutions of the four eigenmodes \vec{E}_{ij} in layer *i* are found, boundary conditions have to be applied in order to connect the fields of two adjacent layers i - 1 and *i*. Formulated for all four modes simultaneously, the Maxwell boundary conditions for \vec{E} and \vec{H} become [65]:

$$(\vec{E}_{(i-1)1} + \vec{E}_{(i-1)2} + \vec{E}_{(i-1)3} + \vec{E}_{(i-1)4}) \times \vec{n} = \vec{E}_{i1} + \vec{E}_{i2} + \vec{E}_{i3} + \vec{E}_{i4}) \times \vec{n}$$
(A.20)

$$\frac{1}{\mu_{i-1}} (\vec{k}_{(i-1)1} \times \vec{E}_{(i-1)1} + \vec{k}_{(i-1)2} \times \vec{E}_{(i-1)2} + \vec{k}_{(i-1)3} \times \vec{E}_{(i-1)3} + \vec{k}_{(i-1)4} \times \vec{E}_{(i-1)4}) \times \vec{n}
= \frac{1}{\mu_i} (\vec{k}_{i1} \times \vec{E}_{i1} + \vec{k}_{i2} \times \vec{E}_{i2} + \vec{k}_{i3} \times \vec{E}_{i3} + \vec{k}_{i4} \times \vec{E}_{i4}) \times \vec{n},$$
(A.21)

where \vec{n} is the surface normal vector. Equations A.20 and A.21 can be written shortly as follows:

$$\mathbf{A}_{i-1}\vec{E}_{i-1} = \mathbf{A}_i\vec{E}_i,\tag{A.22}$$

where A_i is defined in terms of γ_{ijk} by

$$\mathbf{A}_{i} = \begin{pmatrix} \gamma_{i11} & \gamma_{i21} & \gamma_{i31} & \gamma_{i41} \\ \gamma_{i12} & \gamma_{i22} & \gamma_{i32} & \gamma_{i42} \\ \frac{1}{\mu_{i}}(q_{i1}\gamma_{i11} - \xi\gamma_{i13}) & \frac{1}{\mu_{i}}(q_{i2}\gamma_{i21} - \xi\gamma_{i23}) & \frac{1}{\mu_{i}}(q_{i3}\gamma_{i31} - \xi\gamma_{i33}) & \frac{1}{\mu_{i}}(q_{i4}\gamma_{i41} - \xi\gamma_{i43}) \\ \frac{1}{\mu_{i}}q_{i1}\gamma_{i12} & \frac{1}{\mu_{i}}q_{i2}\gamma_{i22} & \frac{1}{\mu_{i}}q_{i3}\gamma_{i32} & \frac{1}{\mu_{i}}q_{i4}\gamma_{i42} \end{pmatrix}.$$
(A.23)

Finally, by multiplying the inverse A_i^{-1} on both sides of eq. A.22, the following relation is obtained, where the interface matrix L_i is defined implicitly:

$$\vec{E}_{i-1} = \mathbf{A}_{i-1}^{-1} \mathbf{A}_i \vec{E}_i =: \mathbf{L}_i \vec{E}_i.$$
(A.24)

It becomes clear that the columns of the matrix A_i represent the four eigenmodes of the respective layer, and the order of the elements is E_x , E_y , H_x , and H_y . This is different than in eq. A.10, since different approaches from various authors are mixed together, and hence the different order conventions must be adjusted. This will be done conveniently after formulating the transfer matrix of the complete multilayer system.

In order to do so, first the propagation matrix P_i , as it was called by Yeh [64], has to be defined. For the here chosen sign convention, it is given by

$$\mathbf{P}_{i} = \begin{pmatrix} e^{-i\frac{\omega}{c}q_{i1}d_{i}} & 0 & 0 & 0\\ 0 & e^{-i\frac{\omega}{c}q_{i2}d_{i}} & 0 & 0\\ 0 & 0 & e^{-i\frac{\omega}{c}q_{i3}d_{i}} & 0\\ 0 & 0 & 0 & e^{-i\frac{\omega}{c}q_{i4}d_{i}} \end{pmatrix}.$$
 (A.25)

With this, the transfer matrix T_i of a single layer *i* can be defined, which is composed of parts from the enclosing interface matrices and the propagation matrix, as follows:

$$\mathbf{T}_i = \mathbf{A}_i \mathbf{P}_i \mathbf{A}_i^{-1},\tag{A.26}$$

and the transfer matrix \mathbf{T}_N of all N layers is then obtained as follows:

$$\mathbf{T}_N = \prod_{n=1}^N \mathbf{T}_n. \tag{A.27}$$

However, \mathbf{T}_N on its own is not sufficient to calculate the reflectivity or transmittance of the multilayer system, since for the first and the last interface, i.e. the interfaces with the incident medium i = 0 and the substrate i = N + 1, only half of the interface matrices \mathbf{L}_1 and \mathbf{L}_{N+1} are included. Therefore, the full transfer matrix $\mathbf{\Gamma}_N$ is obtained as follows, where equivalent notations are shown in order to clarify the equivalence of the various approaches found in the literature [63, 64, 65, 95]:

$$\boldsymbol{\Gamma}_{N} = \mathbf{A}_{0}^{-1} \mathbf{T}_{N} \mathbf{A}_{N+1}$$

$$= \mathbf{A}_{0}^{-1} \mathbf{T}_{1} \mathbf{T}_{2} \dots \mathbf{T}_{N} \mathbf{A}_{N+1}$$

$$= \mathbf{A}_{0}^{-1} \mathbf{A}_{1} \mathbf{P}_{1} \mathbf{A}_{1}^{-1} \mathbf{A}_{2} \mathbf{P}_{2} \mathbf{A}_{2}^{-1} \dots \mathbf{A}_{N} \mathbf{P}_{N} \mathbf{A}_{N}^{-1} \mathbf{A}_{N+1}$$

$$= \mathbf{L}_{1} \mathbf{P}_{1} \mathbf{L}_{2} \mathbf{P}_{2} \dots \mathbf{L}_{N} \mathbf{P}_{N} \mathbf{L}_{N+1}.$$

$$(A.28)$$

The first line is perfectly suited for the implementation in a computer program, and furthermore allows to immediately see how the transfer matrix of a single interface is calculated, i.e. $\Gamma_0 = \mathbf{A}_0^{-1} \mathbf{A}_{N+1}$. The last line, on the other hand, nicely illustrates how systematic the matrix approach solves the propagation of electromagnetic waves in a multilayer medium, simply stringing together interface matrices \mathbf{L}_i and propagation matrices \mathbf{P}_i , for each interface and layer, respectively.

From the full transfer matrix Γ_N , reflection and transmission coefficients for both *s*- and *p*-polarized incident, reflected, and transmitted waves can be calculated, which is provided by Yeh [64]. However, before writing down the equations, the matrix Γ_N has to be transformed such that the order of the field components corresponds to the chosen order of Yeh.

The way in which A_i is formulated (eq. A.23), the interface matrix L_i connects two \vec{E} field vectors with the components

$$\vec{E}_{\text{not sorted}} = \begin{pmatrix} E_{refl}^{p} \\ E_{refl}^{s} \\ E_{trans}^{p} \\ E_{trans}^{s} \end{pmatrix}, \qquad (A.29)$$

but the formulas given by Yeh are formulated for a field vector

$$\vec{E}_{\text{sorted}} = \begin{pmatrix} E_{trans}^{p} \\ E_{refl}^{p} \\ E_{trans}^{s} \\ E_{refl}^{s} \end{pmatrix}, \qquad (A.30)$$

which affects the order of the rows of Γ_N . Furthermore, the eigenvalues q_{ij} were sorted in the order E_{trans}^p , E_{trans}^s , E_{refl}^p , E_{refl}^s , which affects the order of the columns of Γ_N .

Therefore, the following transformations have to be applied to Γ_N , which can be achieved by multiplying the given matrices:

1. swap rows of
$$\Gamma_N$$
 with new order 3142 : $\Lambda_{3142} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}$ (A.31)
2. swap columns of Γ_N with new order 1324 : $\Lambda_{1324} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$, (A.32)

which yields for the transformed full transfer matrix Γ_N^* :

$$\Gamma_N^* = \Lambda_{3142} \Gamma_N \Lambda_{1324}. \tag{A.33}$$

Finally, with this matrix given, the reflection and transmission coefficients for *s*- and *p*-polarized light, i.e. r_{ss} , r_{pp} , t_{ss} , and t_{pp} , and the mode coupling reflection and transmission coefficients r_{sp} , r_{ps} , t_{sp} , and

 t_{ps} can be calculated, where the subscripts refer to incoming and outgoing polarization, respectively. The coefficients are given in terms of the matrix elements of Γ_N^* as follows [64]:

$$r_{pp} = \frac{\Gamma_{21}^* \Gamma_{33}^* - \Gamma_{23}^* \Gamma_{31}^*}{\Gamma_{11}^* \Gamma_{33}^* - \Gamma_{13}^* \Gamma_{31}^*} \qquad \qquad t_{pp} = \frac{\Gamma_{33}^*}{\Gamma_{11}^* \Gamma_{33}^* - \Gamma_{13}^* \Gamma_{31}^*} \qquad (A.34)$$

$$r_{ss} = \frac{\Gamma_{11}^* \Gamma_{43}^* - \Gamma_{41}^* \Gamma_{13}^*}{\Gamma_{11}^* \Gamma_{33}^* - \Gamma_{13}^* \Gamma_{31}^*} \qquad t_{ss} = \frac{-\Gamma_{11}^*}{\Gamma_{11}^* \Gamma_{33}^* - \Gamma_{13}^* \Gamma_{31}^*} \qquad (A.35)$$

$$r_{ps} = \frac{\Gamma_{41}^* \Gamma_{33}^* - \Gamma_{43}^* \Gamma_{31}^*}{\Gamma_{41}^* \Gamma_{33}^* - \Gamma_{13}^* \Gamma_{31}^*} \qquad t_{ps} = \frac{\Gamma_{31}^*}{\Gamma_{41}^* \Gamma_{33}^* - \Gamma_{13}^* \Gamma_{31}^*} \qquad (A.36)$$

and the reflectivity for a certain polarization is obtained, as usually, by calculating the absolute square of the corresponding coefficient.

B | Measurements of 6H-SiC in the Otto Geometry

In this appendix, general experimental details and the fitting procedure are explained, which is valid for both measurement series of the 6H-SiC and the 110 nm AlN / 6H-SiC sample. Furthermore, the complete data set for the reflectivity and SHG measurements performed on 6H-SiC in the Otto geometry are shown. The data for 110 nm AlN / 6H-SiC is presented in appendix C.

B.1 Experimental Details and Fitting Procedure

The reflectivity was measured with a pyroelectric infrared sensor (pyro) as a function of incident wavelength with a range from 13.3 to $9.5 \,\mu\text{m}$, i.e. in wavenumbers ω from 750 to $1050 \,\text{cm}^{-1}$ for all measurements, whereas the SHG was measured with an infrared Mercury Cadmium Telluride (MCT) detector. The position of 30 ° was determined by overlaying the reflection of the alignment laser from prism front with the incoming beam, and the conversion from external to internal angle was performed as shown in fig. 3.6. Both samples were studied at four different incident angles, and at each, several spectra at different distances d were measured, recording simultaneously the reflectivity and the SHG signal.

The reflectivity data was fitted by means of the derived matrix formalism explained in appendix A. In order to do so, however, two more steps had to be done for simulating experimental inaccuracy, which is explained in the following.

Firstly, the fitting curve contains a factor a, which compensates for the error in the normalization of the data. This is done with a reference intensity measurement taken at large distances $d (\sim 40 \,\mu\text{m})$, where no contribution from the sample is expected. However, this reference spectrum does not perfectly normalize the spectra, mainly due to drifts in the FEL and the detection parameter during the measurement of several spectra, each taking about 20 minutes. Therefore, slight deviations from the fitted curve are unavoidable in the current setup. Nonetheless, the agreement of the data with theory is surprisingly good, suggesting a reliable experimental setup as well as a solid theoretical understanding of the underlying physics.

Secondly, the incident angle and the FEL wavelength had to be convolved with a Gaussian function, in order to compensate for an angle and wavelength spread, softening all sharp features such as the Reststrahlen edges, the weak mode and the SPhP resonances. With only $\Delta \theta = 0.39^{\circ}$ (FWHM), the fitted angle spread is rather small. Since the angle scales with the in-plane momentum of the SPhP, a larger influence of the angle spread can be observed for small incident angles, since here the dispersion is steep on the momentum axis. The fitted wavelength spread of $\Delta \omega = 4.05 \text{ cm}^{-1}$, on the other hand, is rather important for larger angles, which is why both spreads have been fitted only in their corresponding angle region of influence. While the wavelength spread is an FEL intrinsic and well known parameter, the angle error might be explained by the divergence of the focussed beam, and by not perfectly flat prism and sample surfaces. Since also the parallelism of prism and sample cannot be perfectly achieved, a certain error from the distance distribution throughout the beam spot influences the spectral resolution. By combining angle and wavelength spread, however, the data seems to be sufficiently well represented.

With this fitting function at hand (three-layer anisotropic reflectivity + factor + angle convolution + wavelength convolution), the reflectivity data sets for each angle were approached with a global fit. Concerning the 6H-SiC sample, the SiC parameters damping γ^{SiC} , the mode frequencies $\omega_{TO\perp}^{SiC}$, $\omega_{TO\parallel}^{SiC}$, $\omega_{LO\perp}^{SiC}$, and $\omega_{LO\parallel}^{SiC}$, the weak mode oscillator strength (described by the *TO-LO* splitting $\omega_{\rm zf \, split}$) and both angle and wavelength spread $\Delta\theta$ and $\Delta\omega$ were global fitting parameters, while the distance *d* of each curve and the factor *a* was adjusted individually. All global parameters which are shared by all four incident angle data sets are listed in section 4.1 in table 4.1 and compared to values found in the literature.

In general, the fitted frequencies seem to be about 3 cm^{-1} smaller than the values found in the given references, which might indicate that the nominal FEL frequency measured by a built-in spectrometer has a shift due to erroneous calibration. The difference, however, still resides within the experimental accuracy, and quite a decent agreement is reached. Concerning the weak mode splitting $\omega_{\text{zf split}} = \omega_{LO} - \omega_{TO}$, which defines the oscillator strength and hence the dip depth of the modes, the second mode is known to be weaker [67]. In order to account for this, the splitting $\omega_{\text{zf split}}$ of the second mode was reduced by a constant factor of 0.667.

In table 4.1 in section 4.1, also the fitted incident angles are listed, while the individual gap sizes d and factors a are specified below in table B.1. Except for nominal 31° , the experimentally chosen angle could be reproduced within a reasonable inaccuracy of the angle alignment ($\pm 0.5^{\circ}$). For 31° , however, the fit of the data indicates that in reality, 30° had been measured. The factors a lie all in a range in the order of 10^{-2} around 1, and hence do not influence significantly the resulting spectrum, but rather compensate almost negligibly the error in the absolute amplitude of the spectra due to the used normalization technique.

The distances d exhibit an average increment of $\sim 1.2\,\mu{\rm m}$ for $27\,^{\circ}$ and $29\,^{\circ}$, and of $\sim 0.6\,\mu{\rm m}$ for $31\,^{\circ}$ and $35\,^{\circ}$. The chosen motor step between each measured spectrum, however, had been chosen to be $2\,\mu{\rm m}$ for $27\,^{\circ}$ and $29\,^{\circ}$, and $1\,\mu{\rm m}$ for $31\,^{\circ}$ and $35\,^{\circ}$. Since the ratio between both steps is the same, a qualitative agreement is met, but the absolute values measured by the motors is significantly different. As discussed in section 3.3, an interferometric Fabry-Pérot approach for the distance measurement will facilitate this particular problem, which arises using the force sensors and motor step approach.

As a summary concerning the reflectivity measurements, the theoretical description by means of the anisotropic matrix formalism leads to a very good agreement with the data, covering all distinct features observable in the spectra. Furthermore, the 6H-SiC material parameters could be extracted and nicely bear comparison with values found in the literature. Concerning the SHG spectra, on the other hand, only a qualitative agreement with the calculated intensity enhancement is met. This is discussed in detail in the results in chapter 4.

B.2 Measurement Data of 6H-SiC

The 6H-SiC sample was measured at nominal incident angles 27° , 29° , 31° , and 35° , and the complete obtained information is shown in fig. B.1, B.2, B.3, and B.4, respectively, where the circles represent the experimental data and the lines are fitted curves. The extracted global fitting parameters shared by all four incident angles are listed in section 4.1 in table 4.1, while the individual fitting parameters gap size d and factor a are shown here in table B.1.

Table B.1: Fitted incident angles θ and individually fitted gap sizes d and factors a of the reflectivity measurements on 6H-SiC. Global parameters shared by all four data sets are listed in table 4.1.

nominal	27°		29°		31°		35°	
fitted	26.82°		28.90°		29.92°		34.76°	
Spectrum #	$d [\mu \mathrm{m}]$	a						
1	2.32	1.03	2.12	1.05	2.23	1.02	1.15	1.02
2	2.54	1.03	3.22	1.03	2.39	1.03	1.68	1.03
3	3.53	1.03	4.56	0.99	2.77	1.03	1.85	1.04
4	4.68	1.03	5.75	1.00	3.33	1.02	2.29	1.04
5	5.79	1.03	7.00	1.00	3.90	1.03	2.79	1.05
6	6.93	1.02	8.16	0.99	4.61	1.02	3.57	1.04
7	9.82	0.99	9.34	0.99	5.29	1.02	4.08	1.04
8	10.73	1.00	10.44	0.99	6.03	1.02	4.67	1.04
9	11.58	1.00			6.56	1.02	5.25	1.04
10	12.55	1.00			7.20	1.01		
11	13.72	1.00			8.33	1.01		
12	14.82	1.00						
Average step	1.25		1.18		0.63		0.57	



Figure B.1: Spectral reflectivity and SHG measurements (open circles) in the Reststrahlen region of 6H-SiC in the Otto geometry at nominal incident angle of 27° , exhibiting a SPhP resonance. All reflectivity spectra were fitted with the anisotropic matrix formalism described in appendix A. Further detail concerning the global fitting parameters see section 4.1.



Figure B.2: Spectral reflectivity and SHG measurements (open circles) in the Reststrahlen region of 6H-SiC in the Otto geometry at nominal incident angle of 29°, exhibiting a SPhP resonance. All reflectivity spectra were fitted with the anisotropic matrix formalism described in appendix A. Further detail concerning the global fitting parameters see section 4.1.



Figure B.3: Spectral reflectivity and SHG measurements (open circles) in the Reststrahlen region of 6H-SiC in the Otto geometry at nominal incident angle of 31° , exhibiting a SPhP resonance. All reflectivity spectra were fitted with the anisotropic matrix formalism described in appendix A. Further detail concerning the global fitting parameters see section 4.1.



Figure B.4: Spectral reflectivity and SHG measurements (open circles) in the Reststrahlen region of 6H-SiC in the Otto geometry at nominal incident angle of 35°, exhibiting a SPhP resonance. All reflectivity spectra were fitted with the anisotropic matrix formalism described in appendix A. Further detail concerning the global fitting parameters see section 4.1.

C | Measurement Data of 110 nm AlN / 6H-SiC in the Otto Geometry

In this appendix, the complete data set for the reflectivity and SHG measurements performed on the 110 nm AlN / 6H-SiC sample in the Otto geometry are shown. The reflectivity was fitted likewise as for 6H-SiC, as described in appendix B. Global fitting parameters shared by all four incident angles are listed in chapter 5 in table 5.1, while the individual fitting parameters gap size d and factor a are shown here in table C.1.

nominal	26°		28 °		30°		34°	
fitted	25.34°		27.56°		29.29°		33.39°	
Spectrum #	$d [\mu \mathrm{m}]$	a						
1	3.96	0.93	3.40	0.97	3.72	1.05	3.24	1.05
2	4.97	0.95	3.85	1.01	3.61	1.04	3.58	1.04
3	6.91	0.97	5.10	1.04	3.91	1.02	3.90	1.00
4	9.28	0.98	7.25	1.02	4.58	0.99	4.45	0.99
5	11.96	0.99	9.08	1.02	5.02	1.01		
6	15.39	0.99	11.46	1.02	5.52	1.02		
7	18.21	0.99			6.04	1.01		
8	20.97	0.99			6.57	1.02		
9					7.75	1.03		
10					8.95	1.01		

Table C.1: Fitted incident angles θ and individually fitted gap sizes d and factors a of the reflectivity measurements on 110 nm AlN / 6H-SiC. Global parameters shared by all four data sets are listed in table 5.1.



Figure C.1: Spectral reflectivity and SHG measurements on 110 nm AlN / 6H-SiC (open circles) in the Reststrahlen region of 6H-SiC in the Otto geometry at nominal incident angle of 26° , exhibiting two SPhP resonances. All reflectivity spectra were fitted with the anisotropic matrix formalism described in appendix A. Further detail concerning the global fitting parameters see section 5.



 $\theta = 27.6^{\circ}$

Figure C.2: Spectral reflectivity and SHG measurements on 110 nm AlN / 6H-SiC (open circles) in the Reststrahlen region of 6H-SiC in the Otto geometry at nominal incident angle of 28° , exhibiting two SPhP resonances. All reflectivity spectra were fitted with the anisotropic matrix formalism described in appendix A. Further detail concerning the global fitting parameters see section 5.



Figure C.3: Spectral reflectivity and SHG measurements on 110 nm AlN / 6H-SiC (open circles) in the Reststrahlen region of 6H-SiC in the Otto geometry at nominal incident angle of 30° , exhibiting two SPhP resonances. All reflectivity spectra were fitted with the anisotropic matrix formalism described in appendix A. Further detail concerning the global fitting parameters see section 5.


 $\theta = 33.4^{\circ}$

Figure C.4: Spectral reflectivity and SHG measurements on 110 nm AlN / 6H-SiC (open circles) in the Reststrahlen region of 6H-SiC in the Otto geometry at nominal incident angle of 34° , exhibiting two SPhP resonances. All reflectivity spectra were fitted with the anisotropic matrix formalism described in appendix A. Further detail concerning the global fitting parameters see section 5.

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