Ultrafast Electron, Lattice and Spin Dynamics on Rare-Earth Metal Surfaces

Investigated with Linear and Nonlinear Optical Techniques

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Contents

1 Introduction 1

2 Basics 5
   2.1 Electronic structure and magnetism of gadolinium (Gd) . . . . . . . . . . . . 5
   2.2 Laser-induced electron dynamics . . . . . . . . . . . . . . . . . . . . . . . 10
      2.2.1 Absorption of light in metals . . . . . . . . . . . . . . . . . . . . . . 10
      2.2.2 Optical excitation and relaxation of electrons in metals . . . . . . . 12
   2.3 Electron-magnon scattering . . . . . . . . . . . . . . . . . . . . . . . . . . 17
   2.4 Coherent lattice dynamics . . . . . . . . . . . . . . . . . . . . . . . . . . . 19
      2.4.1 Coherent phonon generation and detection . . . . . . . . . . . . . . . 19
      2.4.2 Coherent phonon relaxation . . . . . . . . . . . . . . . . . . . . . . . 23
   2.5 Ultrafast magnetization dynamics . . . . . . . . . . . . . . . . . . . . . . . . 25
      2.5.1 Earlier work . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 25
      2.5.2 Laser-induced demagnetization . . . . . . . . . . . . . . . . . . . . . . 28

3 Nonlinear magneto-optics - theoretical aspects 33
   3.1 Nonlinear optics . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 33
   3.2 Second Harmonic Generation (SHG) . . . . . . . . . . . . . . . . . . . . . . 35
      3.2.1 SHG - microscopic formalism . . . . . . . . . . . . . . . . . . . . . . 35
      3.2.2 SHG - symmetry considerations . . . . . . . . . . . . . . . . . . . . . 36
      3.2.3 SHG radiation depth . . . . . . . . . . . . . . . . . . . . . . . . . . . 41
      3.2.4 SHG - macroscopic formalism . . . . . . . . . . . . . . . . . . . . . . 42
   3.3 Magneto-Optics . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 44
      3.3.1 Linear magneto-optics . . . . . . . . . . . . . . . . . . . . . . . . . . 44
      3.3.2 Magnetization-induced second-harmonic generation . . . . . . . . . . . 46

4 Experimental details 53
   4.1 UHV chamber . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 53
      4.1.1 Sample preparation . . . . . . . . . . . . . . . . . . . . . . . . . . . . 55
      4.1.2 Sample holder . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 58
   4.2 Laser system . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 60
      4.2.1 Ultrashort laser pulse generation . . . . . . . . . . . . . . . . . . . . . 61
      4.2.2 Cavity-dumped Titanium:Sapphire oscillator . . . . . . . . . . . . . . 64
   4.3 Pump-probe scheme for TR measurements . . . . . . . . . . . . . . . . . . . . 66
   4.4 Measurement description . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 70
## Contents

### 5 Electron, lattice and spin dynamics on Gd(0001)/W(110)

5.1 MSHG on Gd(0001): static properties ........................................... 73
5.1.1 Polarization dependent MSHG response ........................................ 73
5.1.2 Phase-sensitive MSHG measurements .......................................... 79
5.1.3 Conclusions ............................................................................ 88
5.2 Laser-induced magnetization dynamics on Gd(0001) .......................... 89
5.2.1 Femtosecond demagnetization dynamics ...................................... 89
5.2.2 Remagnetization dynamics on Gd(0001) ....................................... 98
5.2.3 Conclusions ............................................................................ 101
5.3 Coherent optical phonons and magnons on Gd(0001) surface .............. 101
5.3.1 Phonon-magnon coupling in equilibrium ..................................... 101
5.3.2 Coherent lattice and spin excitations ......................................... 102
5.3.3 Conclusions ............................................................................ 112
5.4 Coherent surface and bulk lattice vibrations on Gd(0001) .................. 113
5.4.1 Results .................................................................................. 113
5.4.2 Discussion ............................................................................ 117
5.4.3 Conclusions ............................................................................ 120
5.5 Coupled coherent phonon-magnon mode: excitation and relaxation ..... 121
5.5.1 Spectral dependence ............................................................... 121
5.5.2 Temperature dependence ......................................................... 128
5.5.3 Conclusions ............................................................................ 140
5.6 Coupled coherent phonon-magnon mode: the effect of film thickness and
morphology changes ........................................................................ 140
5.6.1 Film thickness effects ............................................................. 141
5.6.2 Morphology effects ............................................................... 148
5.6.3 Conclusions ............................................................................ 155
5.7 Conclusions and outlook ............................................................... 156

### 6 Acoustic phonons on Y(0001)/W(110)

6.1 Introduction .................................................................................. 159
6.2 Thermoelastic model ................................................................. 162
6.2.1 Acoustic pulse generation and propagation .................................. 162
6.2.2 Acoustic pulse detection .......................................................... 166
6.3 Acoustic phonons in yttrium ......................................................... 167
6.4 Influence of the laser wavelength and temperature ......................... 175
6.5 Conclusions and outlook ............................................................... 180

### 7 Summary

7.1 Introduction .................................................................................. 183

### 8 Zusammenfassung

8.1 Introduction .................................................................................. 187

### A Sum-frequency generation from CO on the Ni/Cu(100) system

A.1 Introduction .................................................................................. 191

### B Fitting procedure

B.1 Introduction .................................................................................. 203

### Bibliography

Bibliraphy .......................................................................................... 207
1 Introduction

The continuous and increased demand for a higher density data storage and a faster data access (read/write) in the computer industry triggered a tremendous development of the field of magnetization dynamics over the past decade [1, 2]. In magnetic recording the digital information is stored in the form of small magnetized regions or "bits", whose opposite magnetization or spin orientations correspond to "1" and "0" values. In order to write a bit an external magnetic field can be applied reversing the magnetization of the magnetic bit. Thus, the fundamental questions which the scientific community and the industry have to face and to address are: how one can switch the magnetization of a certain specimen and how fast one can do it.

In this context it is not surprising that "smaller and faster" is the logo that drives the actual development in magnetically-based computer industry. Regarding the "smaller" term, the areal density of nowadays magnetic devices is approaching fast the fundamental limit of superparamagnetism where the thermal energy $k_B T$ is large enough to produce fluctuations of the overall spin orientation of the magnetic nanoparticle used to store a bit of information i.e. leading to a loss of information. For the "faster" term there is still place for improvement since the actual switching speed of the state-of-the-art devices lies in the low limit of GHz range i.e. it takes about several ns (1 ns = $10^{-9}$ seconds).

The manipulation of magnetization in direction and magnitude can be achieved mainly by employing stroboscopic or pump-probe techniques. Here the pump pulse, that perturbs the magnetization ground state, can be either a pulsed magnetic field or a femtosecond (1 fs = $10^{-15}$ seconds) laser pulse whereas a weaker, time-delayed, laser beam can be used as a probe to detect the subsequent transient magnetization dynamics.

Using pulsed magnetic fields, the magnetization can be reversed from "0" to "1" (or viceversa) state due to the torque exerted by the effective magnetic field $B_{\text{eff}}$, which leads to a precession of the magnetization vector along $B_{\text{eff}}$ during the reversal event. With this method the magnetization orientation is reversed with no change in its magnitude at switching rates in the GHz frequency range [3, 4]. However, precessional switching driven by pulsed magnetic fields exhibits the fundamental limit of half a precession period i.e. on a time scale of few hundred of picoseconds [2]. Using femtosecond laser pulses higher frequency spin waves could be obtained (up to 140 GHz) by excitation of transient magnetic anisotropy fields [5, 6] exploiting the dependence of magnetic anisotropy on the laser-induced temperature rise. Only very recently Kimel et al. [7] have been shown that employing the photo-magnetic inverse Faraday effect a coherent magnetization dynamics up to a frequency of 400 GHz could be achieved. Nevertheless, these time scales are orders of magnitude slower than the femtosecond laser pulses which could be used, in an ideal case, for data writing.

\footnote{In the same study a non-thermal excitation of the magnetic system has been observed within the laser pulse duration of 200 fs.}
1 Introduction

In addition to coherent magnetization dynamics, the utilization of femtosecond laser pulses determine the decrease in magnitude or even quenching of magnetization on a sub-picosecond time scale [8, 9] due to laser-induced excitations. A new and exciting research field is emerging namely magnetism on the femtosecond time range: the femtomagnetism. In short, upon absorption of a femtosecond laser pulse the photoexcitation energy resides in the electronic system that leads to an increase of its temperature $T_e$. Subsequently, the energy is redistributed to another degrees of freedom of the system namely to the lattice and spin subsystems. Depending on the characteristics of the system the demagnetization occurs by a direct electron-spin coupling or via electron-lattice-spin interaction. As can be already noticed, in order to understand the laser-induced demagnetization it is crucial to identify the elementary processes (electron-lattice, electron-spin, lattice-spin interactions) that lead to demagnetization of the system, the time-scales on which they evolve and their relative weight with respect to the demagnetization process.

This thesis reports about laser-induced coherent spin dynamics at a frequency of several THz, that is at least one order of magnitude faster than previously reported, as well as ultrafast demagnetization dynamics on a femtosecond time scale ($< 100$ fs). The system under study is the rare-earth gadolinium (Gd) metal, that is considered [10] as a prototype of a Heisenberg ferromagnet due to the localization of the electrons responsible for the ferromagnetic ordering. The coherent and incoherent magnetization dynamics are investigated in the present work by means of a time-resolved nonlinear magneto-optical technique i.e. magnetization-induced second-harmonic generation (MSHG). The MSHG is the tool of choice in this work since is very reliable in investigating magnetization dynamics owing to its high sensitivity to magnetization effects at surfaces and interfaces of centrosymmetric media [11], where the inversion symmetry is broken.

The usual approach in studying ultrafast magnetization dynamics was to investigate 3$d$ ferromagnetic materials i.e. Fe, Co, Ni. In these materials the magnetism is governed by the delocalized or itinerant 3$d$ electrons and one can have a direct access to the magnetic moments by means of a ultrafast laser with photon energies in the visible range. Employing various time-resolved experimental techniques such as magneto-optical Kerr effect (MOKE) [8], magnetization-induced second-harmonic generation (MSHG) [9] and two-photon photoemission (2PPE) [12] the early stages of magnetization dynamics have been accessed. The conclusion was that laser-induced demagnetization evolves on a sub-picosecond time scale ($< 500$ fs) but the elementary processes which are responsible are still not unambiguously identified. In this respect, a crucial point is the conservation of angular momentum during the demagnetization process on the ultrafast time scale. Hence, in spite of the improved level of understanding gained from the manifold of performed investigations, there still exists a "terra incognita" at the early times in the photoinduced spin dynamics.

In the present thesis a different approach in accessing ultrafast magnetization dynamics has been followed:

- The femtosecond laser-induced demagnetization dynamics of the localized magnetic moment ferromagnet gadolinium, has been investigated. In gadolinium the ferromagnetic ordering is determined by an indirect exchange interaction (RKKY) among the localized 4$f$ magnetic moments mediated by the 5$d$6$s$ conduction electrons, with
the former ones providing ≈90% of the total magnetic moment of Gd. Due to their binding energies (9 eV below Fermi level) the 4f electrons cannot be accessed by lasers with photon energies in the visible range. The optical excitation and detection of magnetization dynamics evolve via the 5d6s conduction electrons. In the view of these facts there are a few questions that arise. Does the localization and indirect coupling of the 4f electrons slow down the laser-induced demagnetization? What are the spin-scattering elementary processes responsible for demagnetization? What are their characteristic time scales? How does this compare with the photoinduced magnetization dynamics on the itinerant ferromagnets?

- The optical-induced magnetization behavior is addressed by a systematic approach involving the MSHG tool that measures the spin polarization in the surface region. An independent 2PPE measurement performed in our lab by M. Lisowski and P. Loukakos under similar conditions on the same system provide us with information regarding the transient behavior of the exchange-split electronic structure. Based on the information acquired from both investigations we can propose a demagnetization mechanism [13] that challenges the common believe in the community regarding laser-induced magnetization dynamics, which settles the limits at around 0.3 ps [14]. The suggested mechanism is based on the spin-flip scattering of hot electrons with emission/absorption of magnons, a process that is acting within the first 100 fs after excitation and is mediated by a strong electron-magnon coupling present in Gd. The picture of the proposed demagnetization scenario can well be extended on the time scale of non-equilibrium electrons i.e. before electronic thermalization and therefore this thesis is the one of the first reports that shed some light on the femtomagnetism "terra incognita".

Beside the induced electron and spin dynamics, the excitation of a solid with femtosecond laser pulses can trigger also coherent lattice dynamics. These coherent optical phonons, with typical frequencies in the range of a few THz, have been extensively studied on semimetals, semiconductors and high-temperature superconductors employing time-resolved optical techniques [15, 16]. Such coherent optical phonons were not expected to occur in metals due to the effective screening of the spatial electron redistribution, that takes place on a time scale equal with the inverse of the plasma frequency (attoseconds time scale). This thesis represents the first study that reports the observation of coherent optical phonons on a metal surface. The coherent lattice vibration is triggered by the excitation of the exchange-split surface state components on Gd(0001) surface, and is quasi-instantaneously (within our time resolution of 50 fs) coupled to a coherent spin excitation, both oscillating at a common frequency of 3 THz [17]. Here the time-resolved linear and nonlinear optical techniques are employed, that, according to their sensitivity, allow us to disentangle between surface and bulk dynamics. The coupled phonon-magnon quasiparticle is remarkable since it brings to light a novel phonon-magnon coupling mechanism that is based not on the usual spin-orbit coupling, but on the modulation of the exchange interaction strength J by lattice vibration. Moreover, the coupled phonon-magnon mode constitutes itself as a model system for studying the excitation and subsequent relaxation of quasiparticles in ferromagnetic Gd. By varying several experimental parameters like
temperature, laser wavelength and sample morphology a wealth of information could be retrieved regarding the excitation, interaction and the lifetime of the involved quasiparticles: electrons, phonons and magnons.

In addition to the above presented investigations, the physics of propagating acoustic phonons at GHz frequencies is addressed in the second investigated system in this work namely epitaxial yttrium films on a tungsten substrate Y(0001)/W(110). The concept of travelling acoustic phonons, the so-called phonon echo, is very useful in investigation and diagnostics of materials e.g. presence of defects since it has a non-contact, noninvasive and nondestructive character. Also a precise evaluation of thickness and sound velocity can be performed using the laser ultrasonics technique. The laser ultrasonics denote the pump-probe technique which monitors the modulations in the refractive index of the system produced by the sudden distortion of the lattice upon absorption of a laser pulse, that travels as a GHz frequency acoustic pulse. Upon strong laser excitation the presence of a long lived coherent acoustic phonon mode bouncing back and forth in the Y film is revealed. This is ascribed to the high optical absorption of the film, to the high acoustic impedance of the Y/W interface and to the smoothness in the interface region. An accurate estimation of sound velocity in the epitaxial Y thin films prepared under ultra-high vacuum (UHV) conditions could be done.

The present thesis is structured as follows. In chapter 2, the electronic structure and magnetism of Gd as well as the general features of laser-induced phenomena such as electron, lattice and spin dynamics are introduced. In chapter 3 the basics of nonlinear optics are introduced emphasizing the role of nonlinear magneto-optics and in particular of magnetization-induced second harmonic generation that is the tool of choice in this work. The experimental details concerning the ultra-high vacuum system used to grow epitaxial rare-earth thin films as well as the femtosecond laser system that is the light source for ultrafast spectroscopy, are described in chapter 4. Chapter 5 presents the laser-induced phenomena on Gd(0001)/W(110) system comprising incoherent and coherent magnetization dynamics as well as coherent electron and lattice dynamics. Coherent lattice dynamics in GHz regime on Y(0001)/W(110) are detailed in chapter 6. The conclusions and outlook of the present work are given in chapter 7.
2 Basics

In this introductory chapter, the physical background necessary for understanding the laser-induced phenomena encountered on the Gd(0001)/W(110) system is presented. After a description of the ferromagnetic Gd metal and the relationship between magnetism and electronic structure specific to this material, a brief introduction of the laser-induced electron dynamics is given. Furthermore, coherent lattice dynamics and the typical excitation mechanisms are reviewed. Ending this chapter, the optically induced magnetization dynamics together with the possible demagnetization pathways and the responsible elementary excitations involved, will be introduced.

2.1 Electronic structure and magnetism of gadolinium (Gd)

Gadolinium (Gd) belongs to the rare-earth elements that comprise the group of lanthanides metals from lanthanum (La) to lutetium (Lu). The common feature exhibited by the lanthanides is the successive filling of the 4f\(^n\) electron shell along the series: from \(n=0\) for La to \(n=14\) in Lu case. Under the rare-earth element term one usually includes also scandium (Sc) and yttrium (Y) [18, 19] although they have a different electronic configuration. The similarity with the rare-earth elements relies on the valence electronic structure. If the outer electronic shell occupancy is considered, one observes the analogy in electronic configuration between the lanthanides (5d\(^6\)s\(^3\)) and Y (4d\(^5\)s\(^3\)) and Sc (3d\(^4\)s\(^3\)) namely all are trivalent metals\(^1\). Since the conduction electrons are responsible for chemical bonding in the condensed matter phase one can consider [18, 19] these elements as being similar and thus can be included under rare-earth element notion.

Gadolinium is regarded [10] as the prototype of the localized magnetic moment ferromagnet due to its large magnetic moment confined at the core level. With its half-filled 4f shell Gd possess a magnetic moment of 7.63 \(\mu_B\) per atom\(^2\) [20] in solid state phase with the major contribution coming from the spin magnetic moment. Applying the Hund’s rules to the 4f shell one obtains the maximum spin moment of \(S=7/2\) and no orbital moment \(L=0\). Since the 4f wave functions are strongly localized at the core level having a small overlap with the corresponding wave functions in neighboring atoms, there is a weak direct interaction among the 4f moments. Therefore, magnetic ordering on Gd and in general for lanthanides, is governed by the indirect exchange interaction or RKKY interaction\(^3\) [21, 22, 23]. According to RKKY interaction, magnetic coupling of the 4f moments is mediated by the conduction electrons (5d\(6s\))^3 and has an oscillatory spatial dependence. Thus, magnetically polarized conduction electrons contribute with the rest of 0.63 \(\mu_B\) to

\(^1\)In the case of lanthanides there are two exceptions: Eu and Yb that are divalent metals.

\(^2\)The Bohr magneton \(\mu_B\) is defined as \(\mu_B = \frac{e\hbar}{2m_e} = 9.274 \times 10^{-24}\) Am\(^2\)

\(^3\)The acronym comes from the name of the authors Ruderman, Kittel, Kasuya, Yosida.
Figure 2.1: Left: the hexagonal closed-packed (hcp) unit cell for gadolinium together with the respective lattice parameters. The size of the atoms is arbitrary. Right: the corresponding bulk and surface Brillouin zones of the hexagonal lattice showing the high symmetry directions and points.

the total magnetic moment of Gd, this contribution having an itinerant character. As a remark, in general for the rare earth metals, the 4f magnetic moments retain their atomic value also in the solid state phase. This is such because the orbital momentum contribution to the total magnetic moment is not quenched by the crystal field (which is the case for 3d ferromagnets Ni, Fe, Co) due to the ”screening” realized by the closed shells electrons $5s^25p^6$.

The localized-moment magnetism picture is well described in the framework of the Heisenberg model by the hamiltonian operator having the following form:

$$H = - \sum_{i,j} J_{ij} (r_{ij}) S_i S_j$$

(2.1)

where $S_i$ and $S_j$ are the spin moments positioned on two neighbor atomic sites at a distance $r_{ij}$ that are coupled together by the exchange interaction constant $J_{ij}$. Classically, the above expression can be understood in terms of a effective magnetic field $B_{\text{eff}} \sim J_{ij} S_i$ i.e. the exchange field, created by the spin moment $S_i$ that is exerted on the neighbor spin $S_j$. Therefore, depending on the sign of the $J_{ij}$ either a parallel or antiparallel spin alignment take place, which means a ferromagnetic or antiferromagnetic ordering is favored, respectively.

In the lanthanides serie Gd has the highest magnetic ordering temperature of $T_c = 293$K and is the only element that exhibits a simple ferromagnetic to paramagnetic phase transition without an intermediate antiferromagnetic ordering. This is the reason why Gd together with the transition metals ferromagnets (Ni, Fe, Co) is considered as a ”classical” ferromagnet.
2.1 Electronic structure and magnetism of gadolinium (Gd)

Figure 2.2: Calculated spin-resolved band structure for ferromagnetic Gd(0001) surface within local density approximation (LDA) theory. The surface state components are depicted by the thick lines in the band gaps of the majority and minority band structure. Note, that the energetic position of the minority surface state is not coinciding with the experiment. From [26].

Gadolinium crystallizes in a hexagonally closed-packed structure (hcp), a structural symmetry that it is retained also for epitaxially grown thin films on W(110) substrate [24]. The hcp unit cell together with the corresponding bulk and surface Brillouin zones showing the high symmetry points and directions are depicted in the figure 2.1. The lattice parameters for Gd are $a=3.629\,\text{Å}$ and $c=5.796\,\text{Å}$ [25] ($c/2=2.89\,\text{Å}$ defines one monolayer (ML) of gadolinium).

Particular for the Gd electronic structure at the (0001) surface is the presence of Tamm-like surface state in the band-gap of the projected bulk band structure. It arises from the 5d bulk bands and spatially it is strongly localized in all three directions. This can be seen from the calculated band structure for ferromagnetic gadolinium in figure 2.2 where the surface state exhibits almost no dispersion along $k_\parallel$ direction. The $d_{z^2}$-like orbital symmetry of the surface state depicted in figure 2.3, presents a charge distribution that is positioned at the atomic site having 89% of the charge confined in the topmost layer of Gd surface [27]. Energetically, the surface state resides around the Fermi level with an occupied component having majority spin character and an unoccupied one with minority spin orientation\(^4\) (at T=0 K) [29, 30]. The energetic separation between surface state components, is denoted as exchange splitting ($\Delta_{ex}$) and reflects the degree of magnetic ordering of the system. It was shown that in the case of magnetically ordered lanthanides the zero-temperature (or very low temperature exchange $T=10$ K) splitting scales with the magnitude of the 4f moment [31, 30].

The electronic structure of Gd and in particular the surface state received a lot of attention from both theory and experiment in order to clarify what is the mechanism that governs the magnetic ordering at elevated temperatures. This was a controversial issue over the past years. Various investigation techniques were involved like photoemission, inverse photoemission that access the occupied and unoccupied electronic structure,

\(^4\)The surface state components have a pure majority or minority spin character at T=0 K, for higher temperatures the states being spin-mixed [28].
Figure 2.3: Charge density map of the majority surface state electrons of ferromagnetic gadolinium along [0001] direction. The low density areas are depicted in blue whereas the high density regions are showed in red. The map shows a section through five atomic layers with the atoms sites depicted by the empty circles. The location of the surface plane is indicated by the arrow. Note the $d_{z^2}$ orbital symmetry of the surface state and the distribution of charge that is mostly localized in the first atomic layer. Adapted from [26]

respectively, and scanning tunnelling spectroscopy (STS) that probes both parts in the vicinity of Fermi level. A number of studies reported a decrease of the exchange splitting with increasing temperature and a collapse at the Curie point [32] while others showed a similar temperature dependence in the ferromagnetic phase but a non-zero $\Delta_{ex}$ at $T_C$ and above [33, 34]. Also the existence of an enhanced surface Curie temperature determined by the presence of the surface state and/or the lower atomic coordination number in the surface layer was a matter of debate. This latter issue was settled by the group of Pappas [35] by demonstrating an identical $T_C$ of Gd surface with the bulk. Regarding the exchange-split electronic states, now the common believe is that for both the surface state and the 5$d$ bulk states the exchange splitting remains finite and constant at $T_C$ while the spin polarization is lost [33, 36]. More detailed, the exchange splitting of the surface state varies with temperature from 0.7 eV at 10 K to a constant value of 0.4 eV at Curie point and above [33] (up to the highest investigated temperature of 360 K). These observations are also confirmed by the measurements reported in this thesis (see chapter 5), in which we could probe the spin polarization and the exchange splitting of the surface state by employing magnetization-induced second harmonic generation (MSHG) and two-photon photoemission (2PPE) techniques\(^5\).

\(^5\)The MSHG and 2PPE techniques are described in chapter 3 and chapter 5, respectively.
2.1 Electronic structure and magnetism of gadolinium (Gd)

![Figure 2.4:](image)

**Figure 2.4:** Qualitative illustration of the temperature-dependent scenario of the 5d states on Gd(0001) that includes spin-mixing and Stoner-like behavior. The spin orientation is indicated by the arrows. At $T=0$ the exchange splitting is finite and there are no spin-mixed states. Increasing the temperature the $\Delta_{ex}$ decreases while the amount of spin-mixing increases. At $T_C$ the spin polarization of the states is zero whereas the exchange splitting does not vanish, denoted by the last two instances in the figure, respectively. From [36].

respectively. A similar temperature-dependent behavior was recently reported also for the delocalized 5d bulk bands [36] with the distinction that at low temperature the exchange splitting is slightly larger than at the surface with $\approx 0.8$ eV.

**Magnetism on Gd at finite temperatures: Stoner versus spin-mixing behavior**

On a microscopic level, the ferromagnetic order in solids at finite temperatures is explained in the framework of two different models, Stoner [37] and spin-mixing [10] model, which predict the mutual relationship of magnetism and electronic structure. These models are idealized pictures that treat the origin of magnetic ordering according to the degree of localization of the electrons that carry the magnetic moments. On one side is the Stoner model that describes the itinerant electron systems like Ni, Fe, Co and on the other side is the spin-mixing model based on the Heisenberg model that accounts for the magnetism of the localized electrons. In the Stoner picture the exchange splitting varies with temperature in ferromagnetic phase and collapses to zero in paramagnetic phase reflecting the $M(T)$ behavior, whereas for the spin-mixing model $\Delta_{ex}$ is temperature independent with the magnetization decrease explained by fluctuation and excitation of the localized magnetic moments.

As was shown above, for the localized surface state and the delocalized 5d bands, the exchange splitting varies with temperature exhibiting no collapse at the critical temperature
and higher, although the long-range magnetic order is lost. These results are surprising since one might think that the delocalized states are sensitive to the long-range magnetic ordering, i.e. average magnetization of the sample, which is lost in the paramagnetic phase. On the other hand, the surface state due to its localization is sensitive to the local magnetic ordering i.e. on-site magnetic moment whose magnitude is conserved with regard to temperature variations. Hence, one could expect that the delocalized states to resemble a Stoner-like behavior while the localized ones to behave according to the spin-mixing scenario.

Therefore, it was concluded that neither the Stoner model nor the spin-mixing picture is suitable to describe the magnetic properties of Gd at finite temperatures. Although initially unexpected, the dependence of $\Delta_{ex}$ on temperature is rather a complex interplay between Stoner-like (delocalized) behavior and the spin-mixing (localized) behavior. Such a scenario, which can be considered as the closest picture to the reality, is illustrated in the figure 2.4 where temperature evolution of the exchange-split $5d$ bulk states is presented. At $T=0$ K the majority and minority sub-bands have a well defined exchange splitting and show no spin mixed states. Increasing the temperature the exchange splitting is reduced and a significant amount of spin mixing (also referred to as spectral weight transfer) is taking place. At the Curie point the spin polarization becomes zero while the separation in energy of the spin up and spin down states is still observable i.e. a non-vanishing exchange splitting remains at $T_C$.

### 2.2 Laser-induced electron dynamics

In this section the general features of the laser-induced electron dynamics in metals are described in order to provide a knowledge base for understanding the encountered ultrafast phenomena on Gd(0001) and Y(0001) presented in chapter 5 and 6, respectively.

#### 2.2.1 Absorption of light in metals

Assuming average incident intensities, the absorption of light in solid materials is governed by the Lambert-Beer’s law

$$I(d) = I_0 \exp[-\alpha(\omega) d]$$  \hspace{1cm} (2.2)

which gives an exponential spatial profile of the intensity within the material\(^6\). The optical properties of the material enter in the above equation through the absorption coefficient $\alpha$ (sometimes is called also extinction coefficient). This renders the spatial extent over which the light is absorbed namely the *optical penetration depth* or the *skin depth* $\delta$ \(^7\) which is defined as follows:

$$\delta = \frac{\lambda}{4\pi k} = \alpha^{-1}$$  \hspace{1cm} (2.3)

where $\lambda$ is the light wavelength and $k$ is the imaginary part of the complex refractive index $\tilde{n} = n + ik$. In the case of metals, the optical penetration depth for laser wavelengths in the

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\(^6\)Equation 2.2 is correct in the assumption that multiple reflections and scattering within the material are neglected.

\(^7\)The penetration depth for the electric field amplitude is $\delta = \frac{\lambda}{2\pi k}$
visible spectral range varies between 10 – 30 nm. As a remark, the exponential spatial profile of the absorbed intensity within material leads to an inhomogeneous excitation profile. The gradient in the absorbed energy density determines the transport of the photo-injected energy out of the detection region by ballistic or/and diffusive transport by non-equilibrium or/and thermalized electron population, respectively. These transport effects are detailed in the next section.

In a quantum mechanical approach the absorption coefficient $\alpha$ is given by the transition rate $W_{i\rightarrow f}$ of exciting an electron between initial $\Psi_i$ and final $\Psi_f$ quantum state upon absorption of a photon:

$$W_{i\rightarrow f} = \frac{2\pi}{\hbar} |M_{if}|^2 \delta(E_f - E_i - h\nu) = \frac{2\pi}{\hbar} |\langle f | H | i \rangle|^2 \delta(E_f - E_i - h\nu)$$  \hspace{1cm} (2.4)

where $M_{if} = |\langle f | H | i \rangle| = \int \Psi_f(r) H(r) \Psi_i(r) d^3r$ represents the transition matrix elements involving the perturbation hamiltonian $H(r)$ that describes the interaction of the optical wave with the electron of coordinate $r$. Within electric dipole approximation the perturbation hamiltonian reads $H(r) = \frac{e}{2m_e c} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A})$ with $\mathbf{p}$ and $\mathbf{A}$ being the momentum operator and the vector potential of the incident electromagnetic wave, respectively. The $\delta$-Dirac function determines the energy conservation. The latter quantity is available for transition between discrete energetic levels e.g. for atoms or molecules. For solids this should be replaced by the joint density of states $g(h\nu)$ given by the convolution of the initial and final states of the optical transition. The momentum conservation condition reads:

$$\hbar k_f - \hbar k_i = \hbar k$$  \hspace{1cm} (2.5)

Since the photon wavevector $|\mathbf{k}| = \frac{2\pi}{\lambda}$ for optical frequencies is negligibly small compared to the electron wavevectors that have characteristic size of the Brillouin zone $\pi/a$, where $a$ is the lattice constant, one can write eq 2.5 as:

$$\mathbf{k}_f = \mathbf{k}_i$$  \hspace{1cm} (2.6)

The latter equation shows why an optical transition is represented by a vertical arrow in the $E(k)$ diagram, as can be seen in the figure 2.5.
2 Basics

2.2.2 Optical excitation and relaxation of electrons in metals

Collective electron dynamics

Initially, the absorption of a femtosecond laser pulse of energy $h\nu$ takes place into the limit of the optical penetration depth $\delta$ and produces a coherent collective polarization of the electron population. This induced electronic polarization has an oscillatory behavior and preserves the optical phase memory of the exciting laser pulse. Subsequently (on a $< 10$ fs time scale after excitation\(^8\)), the collective electron motion decays via phase destructive events like electron-electron, electron-thermal phonons or electron-defect scattering. These processes have an elastic character i.e. the electrons retain their kinetic energy but the phase coherence is lost, which means the momentum is randomized. Therefore the initially deposited energy into the system is dissipated by creating an highly excited ensemble of incoherent electron-hole pairs which do not obey the Fermi-Dirac statistics. The resulting non-Fermi distribution is depicted in the top part of the figure 2.6, which sketches its rectangular shape whose dimensions are determined by the energy of the exciting laser pulse $h\nu$ and the absorbed energy density.

Electronic thermalization

Subsequent to the dephasing of excited electron-hole plasma, within the electron system, that is still in a highly non-equilibrated state, a redistribution of the excess energy carried by the optically excited conduction electrons occurs. This process known as the electronic thermalization proceeds through inelastic electron-electron scattering.

Depending on the excitation density one can distinguish two regimes for the photoexcited electron dynamics:

• the low excitation density ($< 10^{-3}$e$^{-}$/atom) determines a single-electron dynamics where the single excited electron interact with the "cold" electrons situated at and below the Fermi level.

• the high excitation density ($> 10^{-3}$e$^{-}$/atom) where one encounters an excited electronic ensemble that will be internally equilibrated by scattering of the excited electrons among themselves.

For the low excitation density regime the scattering rate and thus the lifetime of the excited single-electrons can be deduces within the framework of Landau’s Fermi-liquid theory (FLT) [38, 39, 40] which predicts (for a three-dimensional free electron gas at $T=0$ K):

$$\tau_{e-e} = \tau_0 \frac{1}{(E - E_F)^2}$$  \hspace{1cm} (2.7)

$$\text{with} \quad \tau_0 = \text{const} \cdot n_e^{5\over 2}$$  \hspace{1cm} (2.8)

From here we notice that the electronic lifetime $\tau_{e-e}$ depends on the excess energy of the excited electron with respect to Fermi level and on the density of the electron gas.

\(^8\)One way to investigate this nascent electron dynamics is to employ nonlinear autocorrelation techniques involving ultra-short laser pulses.
2.2 Laser-induced electron dynamics

Figure 2.6: The laser excitation and the subsequent transient electron dynamics. **Top:** At $t=0$ the pump pulse excite the electron gas that exhibits a non-Fermi rectangular distribution given by the absorbed energy density and the photon energy $h\nu$. Before excitation the system is characterized by a temperature $T_{eq}$. **Middle:** The highly excited non-equilibrium electrons thermalize within a typical time $\tau_{th}$ around a few 100 fs, through $e-e$ scattering to a Fermi-Dirac distribution of hot electrons characterized by temperature $T_e$. **Bottom:** Through $e-p$ scattering the energy is transferred from electron to the phonon bath and eventually their temperatures equalize $T_e = T_l$.

$n$. In other words the lifetime of excited electrons depends on the available *phase space* to scatter *i.e.* the number of scattering partners and the available amount of final states for scattering. On one hand, higher the excess energy interval higher is the number of achievable final states that increase the scattering probability and the electronic lifetime becomes smaller. On the other hand, a higher electron density $n$ increases the phase space for scattering but in the same time the Coulomb interaction is reduced due to the reduced screening length and thus reducing the scattering probability and increasing the electronic lifetime. Thus there is the competition between these two effects that gives the final lifetime of the excited electrons.

A relatively good agreement between FLT and experiment was found for electronic lifetimes measured on silver and tantalum [40, 41]. However, a consistent deviation for transition metals Fe, Co, Ni [42, 41] was measured. The authors ascribed this behavior to
larger phase space to scatter in the case of transition metals determined by the unoccupied \( d \) states. For Ag the \( d \) states are completely filled and localized well below \( E_F \) and therefore just the \( s-p \) states play a role in the relaxation of excited electrons. This explains its behavior as a free-electron metal (\textit{i.e.} one of the basic assumptions of the FLT) and the concordance with FLT prediction.

For finite temperatures the accurate description of the electronic lifetime is given by \cite{39}:

\[
\tau_{e-e}^{-1} = 2\beta [(\pi k_B T)^2 + (E - E_F)^2]
\]

(2.9)

where \( \beta \) denotes the probability of \( e-e \) scattering and thus reflecting also the screened Coulomb interaction. However, the temperature-dependent term in eq. 2.9 is usually neglected since at low temperature has a small value while at higher temperatures the contribution from \( e-p \) scattering is dominant. However, on the ultrafast time scales when the electron temperature reaches a few 1000 K (see fig. 2.7), while the lattice is relatively cold, the \( e-e \) lifetime has a \( T^2 \) dependence given by the first term in the above equation.

For the high excitation density regime the electron-electron scattering among the optically excited electrons results in a Fermi distribution of “hot” electrons characterized by an electronic temperature \( T_e \). The electron-electron collisions produce cascades of secondary electrons with energies close to Fermi level\(^9\). Electronic temperatures \( T_e \) in order of a few 1000 K can be achieved before a significant energy transfer due to coupling to phonons can occur. These high electronic temperatures are developed due to small heat capacity of the electronic system compared to phonons.

The inhomogeneous excitation within the absorption profile of the laser pulse results in a spatial energy gradient which is the source of efficient transport effects that dissipate the energy out of the excited region. The transport effects are competing with \( e-e \) and \( e-p \) scattering events that redistribute the photo-injected energy within the excited region. On the time scale of non-equilibrium electrons (<100 fs), there is the so-called \textit{ballistic transport}, that evolves at Fermi velocity \cite{43} \textit{i.e.} \( v \approx 10^6 \text{m/s} \), the energy can by rapidly distributed over large distances \( \text{e.g.} \ 100\text{nm for Au} \ [44] \) to deeper, unexcited regions of the sample.

\textbf{Electron-phonon scattering and the two-temperature model}

After the thermalization of the electron bath, there still exists a thermal non-equilibrium between the electrons and the lattice. In the following few picoseconds (the typical time scale for metals), the electrons excite phonons and therefore an energy exchange with the lattice is taking place until the temperature of the electron system and the lattice equalize. The hot electrons loose their energy to the phonon bath by electron-phonon coupling, the strength of the coupling between those baths governing the time interval on which the energy transfer evolves.

In a simple picture, the electron-phonon interaction can be seen as the local distortion of the lattice produced by a phonon that affects in turn the local electronic structure.

\(^9\)Secondary electrons are low energy electrons produced in cascade and Auger-like events. During these processes, the optically excited electrons release their energy to the electrons situated initially below \( E_F \) that are promoted on higher unoccupied energy states in the vicinity of \( E_F \).
2.2 Laser-induced electron dynamics

Figure 2.7: The calculated temperature transients according to 2TM model [45] of the electron $T_e$ (dashed line) and phonon $T_l$ (solid line) bath for a 20 nm gadolinium thin film upon laser excitation at a fluence of 0.5 mJ/cm$^2$. The initial static temperature of the system was 100 K. Note the relatively high electronic temperature of $\approx 1200$ K and the equilibration with the lattice in 1 ps time scale. The used parameters are displayed in table 2.1.

or vice-versa as a travelling electron that polarizes the local environment and produce a distortion of the lattice (polaron picture). The effect of the electron-phonon interaction is reflected by a modified electron effective mass.

Microscopically, the essence of the e-p interaction resides in the fact that a phonon of energy $\hbar \Omega$ might be created or annihilated during the interaction. The evaluation of the electron-phonon scattering rate and implicitly the lifetime can be done within the Debye model according to the equation [46]:

$$\tau_{e-p}^{-1} = \frac{2\pi \lambda k_B T}{\hbar}$$

(2.10)

where $\lambda$ is the electron-phonon mass enhancement factor and $k_B$ is Boltzmann constant. $\lambda$ gives the strength of the coupling between the electron and phonon bath, which contributes (besides interaction with other quasiparticle e.g. magnons) to the electron mass renormalization as $m_{eff} = m(1+\lambda)$. Here $m$ is the mass of a non-interacting electron. The validity of the above equation has been shown to hold [47, 48] for temperatures $T > \Theta_D/3$ where $\Theta_D$ is the Debye temperature of the system. The linearity between the electron-phonon scattering rate and temperature is determined by the number of the thermally excited phonons that increase linear with temperature, and thus the resulting e-p scattering rate exhibiting the same behavior with respect to T dependence. As a remark, the
### Table 2.1: The physical properties used in the 2TM simulation for Gd at a temperature of 100 K and incident laser pulse of 50 fs duration.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>e-p coupling ((g)) ([W/m^3K]) [50]</td>
<td>2.5 (\times) 10^{17}</td>
</tr>
<tr>
<td>electron heat capacity ((\gamma)) ([J/m^3K^2]) [51]</td>
<td>225</td>
</tr>
<tr>
<td>electronic heat conductivity ((K_e)) ([W/mK]) [52]</td>
<td>11</td>
</tr>
<tr>
<td>penetration depth ([\text{nm}]) (at 800 nm)</td>
<td>20</td>
</tr>
<tr>
<td>Debye temperature ((\Theta_D)) ([K]) [53]</td>
<td>163</td>
</tr>
</tbody>
</table>

\(e-e\) scattering prevails over \(e-ph\) scattering in the low temperature range and vice-versa for higher temperatures. This point is important in the view of investigating the possible decay channels of elementary excitations on ferromagnetic Gd, as will be presented in chapter 5.

At this stage, there is an additional mechanism of energy redistribution of the hot electron bath namely the \textit{electron diffusion} process. This is determined by the temperature gradient in the sample and its efficiency is governed by the electron-phonon coupling.

Both relaxation mechanisms are included in a model that describes the energy transient in time and space between electron and the phonon baths: the \textit{two temperature model} (2TM). Proposed for the first time by Anisimov [49], the model assumes that the electrons and lattice are in a local thermal equilibrium, and the energy transfer is determined by a set of coupled differential equations having the following form:

\[
C_e(T_e) \cdot \frac{\partial T_e}{\partial t} = \frac{\partial}{\partial z} \left( K_e \frac{\partial T_e}{\partial z} \right) - g \cdot (T_e - T_l) + S(z, t) \\
C_l \cdot \frac{\partial T_l}{\partial t} = g \cdot (T_e - T_l)
\]  

(2.11)

Here \(C_e = \gamma T_e\) (\(\gamma\) is a constant related with the density of states at the \(E_F\)) and \(C_l\) denote the electronic and lattice heat capacities, \(K_e\) is the electronic thermal conductivity and common term \(g\) is the electron-phonon coupling constant that gives the energy transfer rate per unit volume between electrons and phonons. The source term \(S(z, t)\) is dependent on the optical properties of the system through the optical skin depth and gives the initial excitation depth profile.

\[
S(z, t) = (1 - R - T) I_0 \alpha e^{-2\alpha z} e^{-\left(\frac{t}{\tau}\right)^2}
\]

(2.12)

where \(R\) and \(T\) represent the reflected and transmitted parts from the incident intensity \(I_0\), respectively, and \(\tau\) is the laser pulse duration.

Since the model treats the electron bath as being already internally equilibrated, does not provide information about the electronic nascent dynamics. This apparent drawback can be circumvented by employing extended variants of the 2TM that account for the non-equilibrated electron distribution [54, 55, 56].
2.3 Electron-magnon scattering

Thermal diffusion

After the temperature equilibration of the electron and phonon baths, the thermal gradient existent in the system determines the cooling of the laser heated regions according to the classic heat diffusion equation:

\[ K \cdot \nabla^2 T + C \cdot \frac{\partial T}{\partial t} = \frac{\partial U}{\partial t} \]  

(2.13)

with \( K \) thermal conductivity, \( U \) the heat per unit volume and \( C \) the heat capacity per unit volume. The thermal gradient is determined partially by the laser absorption profile and the possible energy redistribution through ballistic and diffusive electron transport. Usually the thermal diffusion is ignored in the frame of the 2TM model since it evolves on hundreds of picosecond time scale, which is not of interest for the \( e-p \) temperature equilibration (few picoseconds time scale). The initial temperature of the system, before laser irradiation, will be therefore recovered on a nanosecond to microsecond time scale plus a small increase dependent on the system’s heat capacity and the laser repetition rate.

2.3 Electron-magnon scattering

Beside the above mentioned scattering mechanisms that dissipate the optically injected energy into the system, another decay channel should be considered in the case of ferromagnetic materials. This is the spin-wave or magnon bath which can accommodate some part of the excess energy carried initially by electrons. The energy transfer is driven here by electron-magnon (\( e-m \)) coupling with the efficiency of the energy redistribution depending on the coupling strength.

As for the case of electron-phonon coupling where the electron polarizes the lattice and vice-versa, also the electron-magnon coupling can be viewed as an electron of a certain spin orientation that magnetically polarizes the surrounding electrons with the opposite spin, that compensates its spin. Quantum-mechanically the magnons are excited by spin-flip events which reduce the magnetic moment along the quantization axis of the system.

The \( e-m \) coupling was shown to be comparable or even higher than the electron-phonon coupling in the case of Gd [57, 58]. Therefore it is playing an important role in the overall energy redistribution in the system and consequently in the magnetization dynamics on this material.

In the early measurements performed to determine the heat capacity of ferromagnetic materials, the signature of the electron-magnon interaction was identified from the additional term to the total measured heat capacity of the system which should be accounted for in order to have a good description of the measured data [59, 60]. More recently, photoemission investigation of the surface electronic structure on Gd(0001)/W(110) [28] and on Fe(110)/W(110) [61] systems showed a considerable contribution of \( e-m \) scattering to the decay of photoexcited surface state electrons. Interestingly, a consistent electron-magnon weight to the total decay rate was found mainly for minority (spin down) electrons channel. This last point was also supported by theoretical work of Zhukov et al. [62] for
the case of Fe and Ni, which shows a bigger contribution of spin-flip scattering rate to the decay in the minority channel with respect to the majority one and therefore different lifetimes. The difference in the lifetimes for different spin orientation in 3d metals was ascribed to the restricted phase space for scattering in the spin-up channel with regard to spin-down component i.e. the available density of states (DOS) above $E_F$ (mainly the $d$ band) for minority electrons.

In order to account for the spin dependent lifetimes for the Gd surface, a calculation in the framework of the s-f model was performed [63], which gives the following relation for the lifetime of the minority component:

$$\frac{1}{\tau_{e-m}^\downarrow} = \frac{\sqrt{3}}{4} \frac{p(\uparrow)m^*}{\hbar S} \left( \frac{2JSa}{\hbar} \right)^2$$

(2.14)

where $p(\downarrow)$ is the spin-up relative contribution to the spin-down state written in terms of electronic polarization, $m^*$ is the effective mass in the surface band, $J$ is the exchange interaction, $S$ is the spin moment and $a$ is the lattice constant. The basic decay mechanism invoked in the model is the electron spin-flip scattering with emission or absorption of magnons. From the above relation one can see that the electron-magnon scattering time for a certain spin orientation scales inversely with the number of electrons of opposite spin $p$ and the exchange splitting $2JS$. Thus, the above equation relies also on the phase space related lifetimes since the polarization represents the electronic population and the exchange splitting is giving actually the amount of spin-mixed states where the electrons can scatter. The lifetime of majority electrons can be determined with the same relation 2.14 by including $p(\downarrow) = 1 - p(\uparrow)$.

Since the magnons represent low-energy excitations of the magnetic system, they can couple or even can be excited by the thermal excitations of the lattice that are in the same energy range. Therefore, increasing the temperature of the system the $e-m$ scattering will increase but in the same time also the $e-p$ scattering will grow due to higher magnitude of the thermal background. Hence, for the particular case of Gd, the decay rate of excited electrons, at higher temperatures, will be governed by the sensitive balance between $e-m$ and $e-p$ scattering events, whose strengths are comparable according to literature [57, 58].

Another process that involves the reversal of electron spin is the so-called Stoner excitation [37] that describes an electron-hole pair with opposite spins i.e. the promotion of a spin up (down) electron in the spin-down (up) sub-band leaving behind a hole in the occupied band. Thereby one electron can flip its spin by absorbing or releasing an energy amount equal with the exchange splitting of the corresponding band. For the case of Gd(0001) the exchange splitting of the conduction band amounts to 0.7 eV whereas for the 4f electrons is around 11 eV, which results in a low probability of these processes. Thus, the Stoner excitations provide a direct and fast relaxation channel between the electron and the spin baths and also an energy exchange mechanism between majority and minority sub-bands.

10Spin-flip scattering represents the e-e scattering in which the electrons involved change their spin orientation. Any spin-flip event requires the emission or absorption of a quasiparticle e.g. magnon or phonon in order to conserve momentum.

11The s-f model or Kondo-lattice model describes the interaction of the localized 4f electrons possessing a spin moment $S$ with the itinerant 5d6s conduction electrons via an interband exchange interaction $J$. 
Summarizing, the electron-magnon scattering is one important decay channel in the case of ferromagnetic systems, and depending on its strength may play an essential role in the laser induced demagnetization dynamics, as will be shown in chapter 5.

2.4 Coherent lattice dynamics

In the previous section we have identified different stages in the time evolution of the excitation and relaxation of the electron population in metallic systems upon an ultrashort laser pulse irradiation. The initial deposited energy in the system was redistributed to electron, phonon and magnon baths by inelastic collision events like $e-e$, $e-p$ and $e-m$ scattering resulting in an incoherent dynamics of the involved quasiparticles. Beside these incoherent phenomena, another type of effects might appear upon laser photoexcitation since the equilibrium between the electrons and the lattice is dramatically disturbed. These are lattice vibrations that posses a high degree of spatial and temporal coherence, the so-called coherent phonons. The generation and relaxation of coherent optical phonons will be the topic of the following section, with special attention being devoted to the excitation mechanisms. The physics of the acoustic phonon modes generated by lattice heating following the laser excitation together with a theoretical model that describes their excitation and temporal evolution, will be addressed in chapter 6.

2.4.1 Coherent phonon generation and detection

Coherent lattice vibration in THz frequency range were observed on various materials such as bulk insulators, semiconductors, semi-metals and superconductors being investigated in time domain with linear and nonlinear optical methods and in frequency domain by Raman scattering. Until very recently [17, 64] there was no report about coherent optical phonons measured on metals. This might be related with the ultrafast screening of the excited carriers by the surrounding electron bath, which results in a less effective driving term (eq. 2.17) for the phonon excitation. Actually, the measurements performed on Gd(0001) presented in this thesis, are the first time reported coherent optical phonons on a metallic material. A thoroughly description of this new observed phenomenon is given in chapter 5.

One of the main ingredients of coherent phonon generation is the laser pulse duration, which should be shorter than the period of the excited lattice vibration. This condition is usually fulfilled employing femtosecond laser systems that can deliver pulses down to 10 fs duration, since the eigenfrequencies of the phonon optical modes lie in the range of a few THz i.e. an oscillation period of several hundreds of femtoseconds. The example of the observed coherent phonons on Gd(0001) surface [17] (see figure 5.21) is eloquent here with an oscillation frequency of 3 THz that corresponds to a period of 330 fs.

Historically, there are two types of excitation mechanisms that are considered for the generation of coherent optical phonons: the impulsive stimulated Raman scattering (ISRS) [65] and displacive excitation of coherent phonons (DECP) [15]. The former one is thought to be responsible for lattice vibrations in transparent materials whereas the latter one is employed for absorbing media. As one can readily see from these limitations, the ISRS
mechanism involves the nonlinear process of phonon generation in the electronic ground state by a Raman process while the DECP is related with an excited electron population upon laser pulse absorption. Both excitation mechanisms are sketched in figure 2.8.

In the case of ISRS, the excitation of coherent phonon population is realized via the inelastic Raman scattering process, and produces the ions oscillation in the ground state around the equilibrium nuclear coordinate $Q_0$ (see upper part of the figure 2.8). The energy of the coherent phonon $\hbar\Omega$ is given by the energy difference between the two photons involved in the inelastic Raman process, whom energies $\hbar\nu$ and $\hbar\nu_1$ are covered by the spectral bandwidth of the exciting femtosecond laser pulse. Also phonons with wavevector $q \neq 0$ can be generated according to momentum conservation by choosing different angles of incidence for the two incident photons. This fact constitutes an advantage of this excitation model.

Regarding the DECP mechanism, the excitation of the electronic system will quasi-instantaneous (on the time scale of laser pulse duration) change the electron-ion potential i.e. screening of the Coulomb repulsion of the ions is less effective and therefore a new equilibrium separation is established. Accordingly, the system will evolve on a new potential energy surface with the minimum position $Q^*$ displaced with respect to the initial ground state minimum coordinate $Q_0$ (see lower part of the figure 2.8). This will set an in-phase oscillatory motion of the ions around the new equilibrium position.

One way to distinguish between the excitation mechanisms is to account for the initial phase of the detected oscillations (see figure 2.8): there is a sine-like phase for the ISRS whereas a cosine-like describes the DECP. These criteria arise from the particular way of excitation: (i) in DECP case the photoexcited electron population produces a step-like change in the electron-ion potential configuration which will displace the lattice quasi-instantaneously and therefore the oscillation starts with a maximum; (ii) the ISRS shows a gradual increase of the phonon amplitude starting with $t=0$ which resembles a sines-like oscillatory motion. However, it was shown [66] that both mechanisms can be described in a more general theoretical framework that includes an excitation term based on two Raman tensors that have similar real components but different imaginary parts. The real part is related to the ISRS mechanism while the imaginary part with the displacive mechanism, and therefore DECP can be considered just a particular case of ISRS.

A simple way to describe the coherent phonon dynamics is to employ the equation of motion for a damped oscillator with different driving terms according to each excitation mechanism. Thus, one can write:

$$\mu^* \left( \frac{d^2 Q}{dt^2} + \gamma \frac{dQ}{dt} + \omega^2 Q \right) = F(t) \quad (2.15)$$

Here $\mu^*$ is the reduced mass of the system, $Q$ is the coherent phonon amplitude with a frequency $\omega$ and a damping constant $\gamma$. The driving force is $F(t)$ that has the following expression for the stimulated Raman mechanism [16, 66]:

$$F(t) = \sum_{1,2} \chi_R^{(3)} E_1(t) E_2(t) = \sum_{1,2} \frac{\partial \chi^{(1)}}{\partial Q} E_1(t) E_2(t) \quad (2.16)$$

where $\chi_R^{(3)}$ is the Raman tensor given by the variation of susceptibility with the phonon
2.4 Coherent lattice dynamics

Figure 2.8: Comparison between the excitation mechanisms of coherent optical phonons. **Top:** the impulsive stimulated Raman scattering (ISRS). **Bottom:** displacive excitation of coherent phonons (DECP). On the left the excitation mechanisms are depicted in terms of potential energy surfaces (PES): for ISRS the excitation takes place in the ground state by emitting a phonon of energy $\hbar \Omega$ via inelastic Raman process whereas for DECP the laser promotes the system to an excited potential surface with a displaced lattice coordinate $Q^*$ different from the ground state coordinate $Q_0$. The system evolves on the excited PES a time $\tau$ and starts to oscillate. After some time the vibrational potential is relaxed back to the ground state. On the right the corresponding oscillatory behavior for each type of excitation is displayed in the simple picture of the harmonic oscillator with the driving force shown by the arrow. The ISRS exhibits a sine-like oscillatory motion while the DECP a cosine-like one.

Coordinate and $E_1$ with $E_2$ are the electric fields of the two photons involved in the Raman process. For the displacive mechanism, in the case of a semiconductor, the expression for the driving force has been deduced by Kuznetsov et al. [67] in the following form:

$$F(t) = 2\omega \sqrt{\frac{\hbar}{2\omega \rho V}} (C^v - C^c) N(t)$$  \hspace{1cm} (2.17)

where $\rho$ is the reduced mass density and $V$ is the volume, $C^v$ and $C^c$ are the deformational potentials for the valence and conduction bands, respectively, and $N(t)$ is the photoexcited electron population. From here one can see that the "initial kick" that launches the coherent phonon wavepacket is determined by the amount of excited carriers through $N(t)$ and, very important, the change of the electronic structure produced by lattice displacement i.e. electron-ion deformational potential.
Coherent phonon detection

One way to detect coherent phonons is to employ time-resolved optical methods that can resolve the small modulation in the refractive index of the system produced by lattice motion. This can be done in pump-probe measurements by detecting the relative changes in the linear reflectivity and/or transmissivity of the probe pulse, that appear after pump pulse excitation. In a similar manner, one can investigate phonon dynamics with optical second-harmonic generation i.e. a nonlinear optical method that gives information restricted to the surface/interface region due to symmetry considerations (see chapter 3). Thereby, phonon modes located at surfaces and even at buried interfaces can be detected [17, 68, 69]. Hence, employing simultaneously bulk and surface sensitive techniques i.e. linear reflectivity and SHG, respectively, one can distinguish between bulk and surface phonon modes, as was shown in [70].

A more direct way to visualize the coherent lattice dynamics is employing time-resolved x-ray diffraction [71], since this method gives access to phonon dynamics in a spatially and temporally resolved manner. This emerging field is under a continuous development in order to achieve a better temporal resolution [72].

The lattice vibrations at THz frequencies can be sources of electromagnetic radiation with a similar frequency. This has been demonstrated by Dekorsy et al. [73], detecting the terahertz radiation emitted by coherent phonons in Te with time-resolved terahertz spectroscopy. There are a manifold of investigation methods that can not be remotely cited here but it is worth mentioning the multi-photon nonlinear ones, like coherent anti-Stokes Raman scattering (CARS) [74]. By choosing well-defined wavevectors of the involved photons one can produce tailor-made coherent phonons wavepackets with various q wavevectors.

At this point we close the discussion regarding the possible methods of investigation of coherent lattice dynamics and focus on the employed measurements tools in this work: the linear reflectivity and second harmonic generation. The basic questions to be answered are: (i) how to detect the modulation of the dielectric function of the material due to lattice vibration, (ii) what information can be retrieved from the transient signal e.g. in terms of excitation mechanism, (iii) can one get more insight about the available relaxation channels.

Let us start the discussion by looking at the figure 2.9 that shows the transient behavior of the SHG signal on the Gd(0001) surface as a function of pump-probe delay. Here one can immediately observe the well pronounced oscillations that are superimposed on a smoothly varying background. The former feature is ascribed [17] to a coherent optical phonon that oscillate at a frequency of 3 THz and the latter one to the transient relaxation of the excited electronic system via e-e and e-p scattering. Hence, the optical response of the system can be decomposed in different contributions that, in a first approximation, are proportional to the measured SHG signal and can be modelled as follows:

$$\Delta \text{SHG} \propto \chi^{(2)}_0 + \frac{\partial \chi^{(2)}}{\partial T_e} \Delta T_e + \frac{\partial \chi^{(2)}}{\partial T_l} \Delta T_l + \frac{\partial \chi^{(2)}}{\partial Q} \Delta Q$$

(2.18)

with $\chi^{(2)}_0$ is the susceptibility tensor for an unperturbed system and the other terms are the changes induced by the electronic temperature $T_e$, lattice temperature $T_l$ and displaced
2.4 Coherent lattice dynamics

Figure 2.9: Time-resolved second harmonic response from Gd(0001) surface that shows the signature of the coherent optical phonon as the oscillatory component of the signal. This is superimposed on a smoothly varying background that describes the incoherent transient electron dynamics.

A similar approach can be followed in order to retrieve the changes induced by coherent phonons in linear reflectivity of the sample:

$$\Delta R \propto R_0 + \frac{\partial R}{\partial \epsilon} \frac{\partial \epsilon}{\partial T_e} \Delta T_e + \frac{\partial R}{\partial \epsilon} \frac{\partial \epsilon}{\partial T_l} \Delta T_l + \frac{\partial R}{\partial \epsilon} \frac{\partial \epsilon}{\partial Q} \Delta Q$$

(2.19)

where $\epsilon$ is the complex dielectric function of the system. After filtering out the incoherent background from the total signal, one ends-up with the pure oscillatory contribution and thus can identify the phase of the oscillation. In the above presented case of Gd(0001), the phase reveals a cosine-like behavior that points out to a displacive type of excitation.

2.4.2 Coherent phonon relaxation

Generally, the relaxation of a coherent phonon mode evolves via scattering events with the available incoherent population in the system that comprises thermal phonons, defects, electrons etc. In the case of ferromagnetic materials the coherent phonon mode can couple with excitations of the magnetic system i.e. magnons via phonon-magnon interaction. Depending on the involved scattering partners elastic and inelastic scattering events contribute to the relaxation of the coherent mode. Through elastic scattering the phase coherence is lost due to momentum randomization with no energy transfer, as is the case for scattering to defects [75]. Such a scattering process is known as dephasing. Inelastic scattering events involve changes in the momentum and energy among the scattering partners, this process being known as decay/depopulation or energy relaxation.

Thus we can evaluate the relaxation time of a coherent phonon mode according to Matthiessen’s rule as the sum of the scattering rates determined by the total inelastic and
Figure 2.10: The anharmonic decay process in a generic phonon dispersion curves diagram, in which a zone center longitudinal optical (LO) phonon of energy $\hbar \Omega$ decays in two symmetric acoustical ones of energy $\hbar \Omega/2$ with the conservation of energy and momentum.

elastic scattering events that contribute:

$$\Gamma = \Gamma_e + \Gamma_i$$  \hspace{1cm} (2.20)

where $\Gamma = \tau^{-1}$ is inverse proportional with the lifetime time $\tau$. In time-domain measurements one can determine $\tau$ as the characteristic decay time of the oscillatory components of the time-resolved signal.

In general the relaxation of the coherent optical phonons in semiconductors and semimetals [76, 77] is dominated by the inelastic scattering with thermal phonons. This phonon-phonon scattering or the anharmonic decay denotes (in the first approximation) the decay of a coherent optical phonon of energy $\hbar \Omega$ in two acoustical phonons with opposite wavevectors and energy $\hbar \Omega/2$. This process is illustrated in the figure 2.10 where a zone-center optical phonon decays in two symmetric acoustical phonons fulfilling the energy and momentum conservation. Depending on the details of the phonon dispersion curves also higher order anharmonic decay processes are possible that involves more phonons [76]. However, due to the strict momentum conservation condition these processes exhibit a lower probability.

In a first approximation, the phonon dynamics can be described in terms of the harmonic oscillator model. In reality the lattice potential is anharmonic (especially for the non-equilibrium conditions generated by the laser excitation) and higher order terms in lattice displacement should be accounted for. The phonon-phonon interaction or the anharmonic decay is determined by this anharmonicity of the lattice potential. For instance, the cubic anharmonic term gives rise to a three-phonon decay process, the fourth power term to a four-phonon process and so on.

In order to identify and disentangle the various decay channels one can modify some external parameters e.g. temperature, doping concentration (for semiconductors), defects density etc. This approach has been followed in the case of Bi [75], where the dephasing and energy relaxation time were separated by introducing various degrees of disordering produced by controlled ion implantation i.e. varying the dephasing rate.

Also varying the temperature of the system one can get information about the involved decay mechanisms. For example, the above mentioned cubic anharmonic decay gives a linear dependence of the decay rate $\Gamma$ with temperature [76]. This can be quantified from experiment as [76, 64]:

$$\Gamma(T) = \Gamma_0 \cdot \left(1 + \frac{2}{\exp\left(\frac{\hbar \Omega}{k_B T}\right) - 1}\right)$$  \hspace{1cm} (2.21)
where $\Gamma_0$ is the anharmonic constant that gives the decay probability of the optical phonon of energy $\hbar \Omega$ in two acoustic phonons of energy $\hbar \Omega/2$, the latter being described by the Bose-Einstein function. The cubic (three-phonons) anharmonic decay can be also identified from the temperature-dependence of the coherent mode frequency: increasing the temperature a downwards shift in the frequency is expected [77].

The temperature behavior of the dephasing rate i.e. elastic scattering given e.g. by scattering with defects (impurity atoms), is considered to be temperature-independent. This is due to the low energy of the thermal phonons (generally a few tens of meV) that cannot excite internal atomic-like states (discrete, high-energy levels) of the impurity atoms.

For the case of metals, owing to the high density of the conduction electrons, the electron-coherent phonon scattering might play a role in the decay of coherent phonons. However, has been shown [64] for the case of Zn and Cd metals that the same phonon-phonon scattering mechanism plays the major role in the coherent phonon decay with a weak influence of the coherent phonon-electron scattering. This is not the case for the coherent phonons on the Gd(0001) metal surface, where the temperature-dependent study reveal an interesting behavior of the decay rate, being dominated by the scattering with electrons. These results are presented in detail in chapter 5.

2.5 Ultrafast magnetization dynamics

In this section we tackle another "hot" topic in the laser induced phenomena namely the femtosecond (de)magnetization dynamics on the ferromagnetic metals. The intention is to give a short overview of the relevant work done in the field and to present the actual understanding regarding the laser induced magnetization dynamics. This is meant to be a base for understanding of the results obtained on ferromagnetic Gd(0001), presented in chapter 5, that give a new approach concerning the ultrashort loss of magnetization following the femtosecond laser pulse excitation.

2.5.1 Earlier work

The first work reporting the demagnetization of a ferromagnetic Ni film after laser irradiation was by Agranat et al. [78]. Using variable laser pulse durations (between 5-20 ps and 40 ns) they concluded that demagnetization proceeds on a nanosecond time scale. Vaterlaus et al. employing time-resolved spin-polarized photoemission could show that spin relaxation time is approaching the picosecond range i.e. hundreds of picoseconds. They measured the magnetization behavior on Gd and Fe films using a 10 ns pump pulse and a probe pulse duration of 60 ps. The result was a spin relaxation time of $100 \pm 80$ps for gadolinium [79] while for iron a time scale ranging between 30 ps and 20 ns was deduced [80]. A theoretical input regarding the Gd results was provided by Huebner et al. [81]. According to their theory a spin relaxation time of 48 ps was computed, which was attributed to spin-lattice relaxation and was in a relatively good agreement with the experiment. These results lead to the conclusion that the demagnetization evolves via spin-lattice interaction and that the typical timescale resides somewhere in the hundreds of picosecond range.
In 1996 the group of Beaurepaire [8] came up with a surprising result for that time, namely a magnetization loss on a picosecond time scale i.e. orders of magnitude quicker as previously observed. They investigated Ni thin films with time resolution of 60 fs by employing pump-probe MOKE (magneto-optical Kerr effect) measurements. The observed drop in the remanent MOKE signal (that is assumed to be proportional to the magnetization of the system) was reaching the lowest value around 2 ps. This important result is depicted in the figure 2.11. In order to explain this result a phenomenological three temperature model has been employed (i.e. electron, spin, and lattice temperatures) with the spin bath dynamics being delayed with respect to electron temperature formation. The observed demagnetization was attributed to an efficient electron-spin scattering process.

The work of Beaurepaire et al. initiated a new development of the field since their results were triggering a lot of interest in the community. Another important result was obtained by Hohlfeld et al. [9] by measuring the time-resolved nonlinear magneto-optical response of bulk Ni with second harmonic generation (SHG). They observed a quasi-instantaneous drop in magnetization within laser pulse duration (150 fs) employing various laser fluences. In this work, was demonstrated that after 280 fs, when the electronic system is thermalized, the transient magnetization depends on the electronic temperature in a classical Bloch’s law dependence $M(T)$ with $T = T_e$. This result is plotted in the figure 2.12. In the same year, the results of Scholl et al. [12] confirm the ultrashort drop in magnetization observed by Hohlfeld et al. They measured ultrathin Ni films (6 Å and 12 Å thickness) with spin-resolved two-photon photoemission (SP-2PPE) and the main observation was that the transient magnetization evolves on two time scales: an initial, sudden magnetization drop on a 100 fs scale and a longer, smoother decrease on 500 ps scale. The former one was ascribed to demagnetization via excitation of Stoner pairs and the latter one to the phonon-magnon coupling. An improved version of the SHG work done by Hohlfeld et al. [9] was reported in [82] with a better time resolution of 40 fs and involving thin Ni and Co films grown under ultra-high vacuum (UHV) conditions [83, 84]. The conclusion was the same: instantaneous drop in magnetization within pulse duration and no delay between electron

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For details regarding the physics of MOKE please see chapter 3.
2.5 Ultrafast magnetization dynamics

Figure 2.12: The magnetization dynamics as a function of electronic temperature measured on bulk Ni by Hohlfeld et al. [9] with time-resolved MSHG. The upper panel displays the values of transient magnetization (as measured by MSHG) at delays >300 fs for various pump fluences, which follow a $M(T_e)$ curve. The lower panel shows the measured data, at 280 fs and 80 fs delay time. For the 280 fs (electronic thermalization time) data the $M(T)$ behavior is reproduced whereas a consistent deviation is observed for the 80 fs delay.

and magnetization dynamics. Moreover, a total demagnetization of the thin ferromagnetic films (7 ML) was observed upon laser heating due to their reduced Curie point.

Some doubts about the quasi-instantaneous magnetization response after laser excitation were raised by Koopmans et al. [85] by ascribing their observed drop in the MOKE signal to artifacts determined by the state-filling or dichroic bleaching effects. In the same trend was the work of Regensburger et al. [86] who suggested that the observed pump-induced changes in the SHG response from Ni(110) surface does not reflect the magnetization dynamics at early times < 500 fs.

More recently [87, 88], from the dynamics of MOKE response measured on the CoPt$_3$ compound the authors concluded that, indeed, the ultrashort loss of MOKE signal on the first 100 fs time scale represents the magnetization behavior. Furthermore, they ascribed the spin dynamics on this compound to the 50 fs range during the thermalization of the electronic system [87].

Further insight in the laser-induced demagnetization dynamics can be obtained by monitoring the transient exchange-split electronic structure after excitation. Such a measurement has been performed by Rhie et al. [89] employing time-resolved photoemission spectroscopy on thin films (7 ML) of Ni/W(110). They reported a collapse of the exchange splitting of the 3$d$ states on a time scale of $\approx$300 fs and a subsequent recovery with a $\approx$3 ps time constant. The invoked mechanism was electron-electron scattering with spin-flip mediated by the spin-orbit coupling for angular momentum conservation. One question that arises here is in how far one can consider the transient variation of the exchange split-
ting as reflecting the magnetization behavior, since Ni does not exhibit a pure Stoner-like behavior [90].

Recently [91] a linear magneto-optical study performed on various ferromagnetic insulator and metallic compounds showed again the existence of two time scales in photoinduced magnetization dynamics: an ultrashort one that has been ascribed to multiple emission of magnetic excitations, and a longer delay time scale that is material dependent and scales to magnetic anisotropy of the respective material.

From theory side an important input was provided by Zhang and Huebner [92, 93] in which they showed an accessible time range of 10 fs for magnetization dynamics on the transition metal Ni. This ultrashort time interval was obtained by taking into account the combined effect of spin-orbit coupling and the optical laser field. However, unrealistic high laser fields have been involved in the computation of these ultrashort time scales for demagnetization dynamics.

Very recently, Koopmans et al. [94, 95] have proposed a microscopic model where, in principle, the electron-phonon scattering with spin flip can be considered as an additional pathway responsible for demagnetization on the sub-picosecond time scale.

Summarizing the above presented works one can formulate a few conclusions that are emerging:

- there are two observed time scales on which magnetization evolves: upon laser excitation an ultrashort one within the first hundreds of fs and a slower one around few 100 ps;
- based on previous work the common agreement is that laser-induced demagnetization evolves on a sub-picosecond time scale (< 500 fs) but the elementary processes which are responsible are not unambiguously identified.
- the major question concerns the mechanism of transfer of angular momentum involved in the demagnetization process
- mostly transition metals and compounds were investigated using time-resolved MOKE, SHG and photoemission techniques;
- there is no systematic study of the same material involving complementary investigation techniques, that can access e.g. the magnetization and electronic structure simultaneously;

### 2.5.2 Laser-induced demagnetization

The demagnetization of a ferromagnetic sample is of fundamental interest for science and also of high relevance for applications in industry. There are several methods to demagnetize a piece of ferromagnetic material but here we will focus on the underlying physics of optically induced (de)magnetization dynamics. The interested reader is referred to the review works [1, 2] where different methods of manipulating magnetization on various time scales are presented.

We have seen earlier in this chapter that the optically injected energy by the laser pump pulse is redistributed and is relaxed mainly by electron-electron and subsequently
2.5 Ultrafast magnetization dynamics

Figure 2.13: Illustration of the possible paths that can lead to demagnetization of a system after laser excitation. The laser pulse transfers the energy to the electron sub-system that can couple to the phonon or spin bath. The way in which the energy transfer take place among the quasiparticles i.e. either directly via electron-spin interaction or via electron-phonon and subsequently phonon-magnon coupling gives the characteristic time scale of demagnetization dynamics. A direct electron-magnon interaction favors a ultrafast loss of magnetization on a 100 fs range while an electron-phonon-magnon interaction sequence renders a 100 ps time interval for the demagnetization process. Note the necessity of angular momentum conservation for the involved interaction among quasiparticles baths.

electron-phonon scattering processes. Their characteristic time scales range from several hundreds of fs to several ps, respectively. On a longer time scale the energy relaxation is governed by thermal diffusion. Since there is an intrinsic relationship between electronic structure and magnetism, the question is to what extent is the latter one affected by the photoexcited electron population. Moreover, the presence of the magnetic ordering introduces another microscopic degree of freedom i.e. the spin bath to which the excited electrons can couple via electron-magnon interaction. Therefore, in order to investigate the ultrafast demagnetization one should account for the scattering events among electron, lattice and spin subsystems as well as for their coupling.

A possible scenario that can lead to demagnetization upon optical excitation of electronic system is presented in figure 2.13. The initially excited electron ensemble can couple directly to the spins (and/or excitation of the spin system i.e. magnons) via e.g. quasi-elastic spin-flip scattering. Alternatively, it might follow an indirect path where the deposited energy is transferred first to the lattice via e-p interaction and afterwards exciting the spin system via phonon-magnon coupling. The first mentioned demagnetization route has a purely electronic character and therefore a characteristic time scale for e-e interaction i.e. several 100 fs. For the latter one the energy flow involves an intermediate
energetic sink, the phonon bath, and therefore this process would take place on a slower picosecond time scale, that is less likely to explain a 100 fs magnetization loss. Thus, for a comprehensive understanding of the laser-induced demagnetization process one has to address several issues such as:

- to identify and disentangle the elementary spin scattering mechanisms and their relevant timescales
- to identify the processes which ensure the conservation of angular momentum on the ultrafast time scale

One of the microscopic mechanisms that can mediate the laser-induced demagnetization is the spin-orbit coupling. Upon laser irradiation the electronic system is excited. Since the light can access just the orbital part of the electronic wavefunction there is no direct light-induced spin-flip. Assuming a strong spin-orbit interaction, there will be a net momentum transfer from orbit to the spins, which disturb the last ones from equilibrium and start to fluctuate. Average spin fluctuations are equivalent to a decrease in magnetization. The spin-orbit strength gives the time scale on which this demagnetization scenario evolves. More accurately, the spin-orbit interaction that can mediate electronic spin-flip scattering events can be express under the following hamiltonian:

\[ H_{so} = \lambda \mathbf{L} \cdot \mathbf{S} = \lambda \left( \mathbf{L}_z \cdot \mathbf{S}_z + \frac{1}{2}(\mathbf{L}^+ \cdot \mathbf{S}^- + \mathbf{L}^- \cdot \mathbf{S}^+) \right) \]  

where \( \mathbf{L} \) and \( \mathbf{S} \) are the the orbital and spin moment operators and \( \lambda \) is the spin-orbit coupling strength. The spin-flip event is given in terms of annihilation and creation spin moment operators. One can see that any change in the spin moment \( \mathbf{S} \) e.g. spin flip is balanced by a corresponding reaction in the orbital moment \( \mathbf{L} \) and vice-versa. The probability of such a process is determined by the strength of the spin-orbit coupling \( \lambda \).

The quantization axis of the system, given by magnetization direction, is along \( z \) direction.

But what is happening in systems with a weak or vanishingly small spin-orbit interaction, like Gd(0001)? Is the demagnetization process slower? Or there is another microscopic mechanism involved? These questions will be addressed in the chapter 5 of this thesis.

Another way of thinking at the photoinduced ultrafast demagnetization process is by starting from the picture of the finite-temperature magnetization in equilibrium conditions. Depending on the type of the ferromagnet, i.e. itinerant or localized moment, there are two opposite models, Stoner and spin-mixing (see section 2.1), that describe the magnetization state under the effect of thermal excitations i.e. temperature. In the spin-mixing picture the magnetization is decreased by excitations (magnons emission) or fluctuations of the localized magnetic moments accompanied by a constant exchange-split electronic structure whereas in the Stoner model the magnetization at elevated temperatures is decreased by spin-flip scattering between bands with opposite spin orientation accompanied by a decreased exchange splitting that vanishes above \( T_C \). Thus, it will be interesting to monitor these two quantities, the magnetization or the local spin polarization and the exchange splitting on an ultrafast timescale upon laser excitation. This approach
has been followed in this work on the localized magnetic moment ferromagnet Gd, using the complementary information given by time-resolved nonlinear magneto-optics and photoemission spectroscopy.

Summarizing this section, it is still unclear which of the above mentioned demagnetization mechanisms governs the nature of photoinduced magnetization dynamics. Whether is the spin-flip scattering, the emission/absorption of quasiparticles like magnons or phonons, the effect of non-equilibrium electron dynamics, the exchange interaction or the interplay between spin-orbit coupling and laser field is still to be investigated. The contribution of the present work relies on laser-induced spin dynamics on the localized-moment ferromagnet Gd and propose a novel demagnetization mechanism on an ultrashort timescale of 100 fs and faster. This "femtomagnetism" behavior will be detailed in chapter 5.
2 Basics
3 Nonlinear magneto-optics - theoretical aspects

The aim of this chapter is to introduce the nonlinear optics in general, and the nonlinear magneto-optical effects, in particular. As a representative of the latter ones is the magnetization-induced second harmonic generation (MSHG), that is the tool of choice employed in the present work. Here, the MSHG is used as a method of investigation of ferromagnetic materials since it has a non-invasive and nondestructive optical character and it exhibits high surface and interface sensitivity. Moreover, due to its symmetry with respect to magnetization reversal, provides simultaneously information about the electron/lattice dynamics as well as spin dynamics.

The chapter is structured as follows: after a brief introduction to nonlinear optics presented in the first section, a more detailed description regarding the second harmonic generation process is developed in the next part. The last two sections focus on the origin of the linear and nonlinear magneto-optical effects and to the description of the MSHG formalism involved in determining the statical and dynamical properties of ferromagnetic metals.

3.1 Nonlinear optics

The field of the nonlinear optics was growing with the laser development. One of the first experiments in which the generation of second harmonic light (in a quartz glass) was demonstrated [96], took place shortly after the discovery of the laser by Maiman in 1960. This fact points out the necessity of having high incident optical intensities involved in order to produce efficient nonlinear processes. Such high electromagnetic field strengths (intensity is the square of electric field) are achievable, for instance, by focussing an ultrashort laser pulse that carries high peak power.

The optical response of a medium to an incident electromagnetic wave \( \mathbf{E}(r,t) \) is described by the induced electrical polarization \( \mathbf{P}(r,t) \). Subsequently, the medium response perturbs the propagation of the optical wave, this mutual dependence giving rise to a richness of optical phenomena like linear and nonlinear optical reflection, linear transmission etc. These are used as investigation tools of optical and electronic properties of materials, just to mention a few potential applications.

Starting from Maxwell equations, one can deduce the optical wave equation for the propagation of the electric field \( \mathbf{E}(r,t) \) through a medium under the following form [97]:

\[
\nabla \times \nabla \times \mathbf{E}(r,t) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{E}(r,t) = -\frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{P}(r,t) \tag{3.1}
\]
The wave equation describes the optical response of a medium being subject to an incoming electromagnetic field. In the right-hand part of eq. 3.1, the time variation of polarization acts as a source term for the emitted waves, which in the classical physics picture is the equivalent of an oscillating dipole that radiates light.

Depending on the strength of the incident field, the polarization consists of two contributions, a linear and a nonlinear one:

\[ P(r, t) = P^L(r, t) + P^{NL}(r, t) \] (3.2)

The linear response of the medium is described by [97]:

\[ P^L(r, t) = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} \varepsilon_0 \chi^{(1)}(r - r_1, t - t_1) E(r_1, t_1) dr_1 \] (3.3)

where \( \varepsilon_0 \) is the dielectric constant in vacuum and the \( \chi^{(1)} \) is the linear susceptibility tensor. Since the medium response is described by a tensor, has not necessarily the same directionality as the incoming electric field i.e. can be optically anisotropic.

For stronger optical fields higher orders terms in polarization expression become non-negligible and should be take into account. Expanding the polarization in power series of electric field, one obtains:

\[ P^{(n)}(r, t) = \int_{0}^{+\infty} dt_1..dt_n \int_{-\infty}^{+\infty} \varepsilon_0 \chi^{(n)}(r - r_1,..,r - r_n, t - t_1,..,t - t_n) E(r_1, t_1)..E(r_n, t_n) dr_1..dr_n \] (3.4)

with the total polarization being:

\[ P(r, t) = \sum_n P^{(n)}(r, t) \] (3.5)

Here, the \( n \)-th order polarization is determined by the \( n \)-th order nonlinear susceptibility tensor and the \( n \)-th power of the incident electric field. We notice that the nonlinear susceptibility tensor \( \chi^{(n)} \) has a nonlocal and a non-instantaneous character. In other words, the induced polarization is not a local (point-like) characteristic and is not produced simultaneously when the incident light reached the medium under consideration. The causality principle is fulfilled since in equations 3.3 and 3.4 one integrates over time between 0 and infinity which means that one takes into account only past values of \( E \) vector but not the future ones i.e. \( t - t_n > 0 \). The non-locality aspect, which is important in the context of bulk contributions to the SHG process, will be addressed later in this section.

If one assumes an incident monochromatic electromagnetic wave and calculates the Fourier transformation of equation 3.5, one ends up with the total polarization in frequency space, which in the dipole approximation reads:

\[ P(\omega) = P^{(1)}(\omega) + P^{(2)}(2\omega = \omega_1 + \omega_2) + P^{(3)}(3\omega = \omega_1 + \omega_2 + \omega_3) + ... \] (3.6)

which is equivalent with:

\[ P = \varepsilon_0 [\chi^{(1)}(\omega) E(\omega) + \chi^{(2)}(\omega = \omega_1 + \omega_2) E(\omega_1) E(\omega_2) + ...] \] (3.7)

The first term in the above equation is the source for linear optical processes like reflection and absorption whereas the next term describes second-order processes as SHG, SFG and so on. Examples of second and higher order nonlinearities described by the eq. 3.7 are given in the table 3.1, all processes being listed with the corresponding nonlinear tensors.
3.2 Second Harmonic Generation (SHG)

As an example for a second order nonlinear optical processes, we take the case of second harmonic generation, being the main tool of investigation in this work. Actually, the SHG is a degenerate case of sum-frequency generation (SFG) i.e. $\omega = \omega_1 + \omega_2$ with both incident photons having the same frequency $\omega_1 = \omega_2 = \omega$. Thus, one can write, within electric-dipole approximation\(^1\), the nonlinear polarization governing the SHG process as :

$$P^{(2)}(2\omega) = \varepsilon_0 \chi^{(2)}(2\omega) E(\omega) E(\omega)$$  \hspace{1cm} (3.8)

In a cartesian coordinate system, the polarization can be express as:

$$P^{(2)}_i(2\omega) = \varepsilon_0 \chi^{(2)}_{ijk}(2\omega) E_j(\omega) E_k(\omega)$$  \hspace{1cm} (3.9)

where the subscripts $i, j, k$ run over the cartesian coordinates $x, y, \text{ and } z$. The above relation shows that the $i$-th component of the second-order polarization is induced by the $j$-th and $k$-th components of the incoming electric field at the fundamental frequency.

### 3.2.1 SHG - microscopic formalism

Microscopically the second-harmonic generation process is described by a nonlinear susceptibility tensor that can be deduced within the density matrix formalism of quantum mechanics and has the following expression \([97]\):

$$\chi_{ijk}(2\omega) = -Ne^3 \int dk \frac{<1, k| r_i|3, k> <3, k| r_j|2, k> <2, k| r_k|1, k>}{2\hbar \omega - E_{31}(k) - i\hbar \Gamma_{31}} \frac{1}{|\hbar \omega - E_{21}(k) - i\hbar \Gamma_{21}|} f_1(k) + \chi^{NR}_i$$  \hspace{1cm} (3.10)

\(^1\)Within electric-dipole approximation one takes into account just the contribution from the oscillating electric dipoles induced by the incident electromagnetic field. The contributions from the magnetic field part of the light wave and from the electric quadrupoles are much weaker and are usually neglected.

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Table 3.1: Examples of second-, third- and higher-order nonlinear optical processes together with the susceptibility tensors that describe them.
Figure 3.1: Schematic description of the SHG process showing the involved optical transitions at fundamental frequency $\omega$ and at the second-harmonic frequency $2\omega$ among real (thick line) and virtual levels (dashed line). The initial, intermediate and final energetic levels are denoted by $|1\rangle$, $|2\rangle$, and $|3\rangle$, respectively.

where the optical transitions take place among $|1\rangle$, $|2\rangle$ and $|3\rangle$ states, which denote the initial, intermediate and final state, respectively. The density of electrons per volume was noted by $N e^3$ with the Fermi distribution factor being $f_1(k)$ for the state $|1, k\rangle$ with the electron wave vector $k$. The cartesian coordinate operator is $r_{i,j,k}$ and the $\hbar \Gamma$ is the linewidth of the transitions between two electronic states. The non-resonant susceptibility terms are denoted by $\chi^{NR}$.

As it can be observed, just the resonant part of the nonlinear tensor is written explicitly, as is the relevant part for our future discussions. It is clear that the SHG can be resonantly enhanced if the photon energies of the involved transitions match either the energetic interval between states $|1\rangle$ and $|2\rangle$ at fundamental frequency or between $|1\rangle$ and $|3\rangle$ at $2\hbar \omega$. These two situations are illustrated in the figure 3.1 b,c.

For a better illustration of the resonance condition that might appear in a SHG process, we have simulated the magnitude of the susceptibility tensor and of the corresponding phase for a resonance situation at $2\hbar \omega$ and $\hbar \omega$ according to eq. 3.10 (for simplicity without matrix elements and the Fermi function). At this point the phase of the second-order susceptibility can be understood as the phase of a complex number: $\chi^{(2)} = |\chi^{(2)}| \cdot e^{i\varphi}$. The result of the computation is displayed in the figure 3.2. Here we observe a sharp increase of $|\chi^{(2)}|$ and a $180^\circ$ phase change as the photon energy is crossing the resonance at the fundamental $\hbar \omega$ or at the second-harmonic $2\hbar \omega$ photon energy. Thus, in a SHG measurement one can identify the presence of a SHG resonance by monitoring the behavior of the SHG signal (SHG intensity scales with the magnitude of $|\chi^{(2)}|$, see eq. 3.18) and of the phase. The phase can be retrieved in a separate measurement that is described in detail in chapter 5. The values of involved parameters in the simulation are $\Gamma_{31}=1/20$ and $\Gamma_{21}=1/40$.

3.2.2 SHG - symmetry considerations

As we have seen above the second-order nonlinear effects are governed by a third-rank susceptibility tensor $\chi^{(2)}$. It consists of 27 independent components and because generally is a complex number the total number of components which should be take into account
Figure 3.2: The calculated magnitude of the second-order susceptibility tensor and of the corresponding phase change in the case of a double resonance with $\omega_{\text{res}}$ equal to $2\omega$ and $\omega$ photon frequencies, according to the first term in the formula 3.10. Note the 180° phase change for each of the encountered resonance.

is 54. This fact makes the evaluation of the SHG response of a certain medium in a quantitative manner a difficult task. It is the symmetry of the involved system which reduces the number of non-zero tensor components and thus simplifying the computation of the SH signal. A general symmetry framework is developed on the base of Neumann’s principle [98], which states that the symmetry exhibited by a certain system is possessed by every physical property of that system. In other words, the system properties should be invariable with regard to the symmetry operations that define the space group of the system.

As an example, let us take the case of centrosymmetric medium i.e. a medium that possesses inversion symmetry. This type of medium symmetry is the widest met in nature and is also relevant for our further considerations. Now one can write eq. 3.7 in a compressed manner for the case of a SHG process:

$$P = \varepsilon_0[\chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + ...]$$  \hspace{1cm} (3.11)

Under the inversion symmetry operation the $P$ and $E$ should change the sign since both are polar vectors. Under the effect of the inversion operation relation 2.11 becomes:

$$-P = \varepsilon_0[-\chi^{(1)}E + \chi^{(2)}EE - \chi^{(3)}EEE + ...]$$  \hspace{1cm} (3.12)

The above equations are both valid when $\chi^{(2)}=0$. That means, in general, for these type of materials the even order susceptibility tensors are 0, within the electric-dipole approximation. However, there are regions of the centrosymmetric materials where the
Nonlinear magneto-optics - theoretical aspects

Inversion symmetry is broken. For instance, at the surface of a medium or at the interface between two materials where locally the inversion symmetry is lifted. Therefore, for centrosymmetric materials and within the electric-dipole approximation, the SHG process has an intrinsic sensitivity to surfaces and interfaces where the inversion symmetry is broken.

Coming back to our discussion regarding the number of non-vanishing independent components of $\chi^{(2)}$, for the particular case of the SHG process, owing to the identical frequency of involved photons the total components number is reduced from 27 to 18. This is determined by the identity $\chi^{(2)}_{ijk} = \chi^{(2)}_{ikj}$. Thus, one can write the SHG nonlinear polarization expression under the following form:

$$\begin{pmatrix}
P_x \\
P_y \\
P_z
\end{pmatrix} =
\begin{pmatrix}
\chi_{xxx} & \chi_{xyy} & \chi_{xzz} \\
\chi_{yxz} & \chi_{yyz} & \chi_{yyz} \\
\chi_{zxx} & \chi_{zyy} & \chi_{zzz}
\end{pmatrix}
\begin{pmatrix}
E_xE_x \\
E_yE_y \\
E_zE_z
\end{pmatrix}$$

(3.13)

The elements of $\chi^{(2)}$ tensor can be further reduced by taking into account the particular symmetry of the system. Moreover, choosing a certain crystallographic orientation of the surface and experimental geometry (light polarization, azimuthal orientation of the sample) the number of tensor components that contributes to the generation of SH signal is further decreased.

Since we are interested in the hcp(0001) surface, in the following the calculation of tensor components for this particular surface orientation is presented. The deduction of the tensor components is straightforward since one has to check the invariability of these components under each symmetry operation of the group that defines the symmetry of the system. This can be written under the following form:

$$\chi_{ijk} = \sum_{ij'k'} T_{ii'}T_{jj'}T_{kk'}\chi_{ij'k'}$$

(3.14)

For instance, the transformation matrix $T$ has the following elements for the case of rotation with the angle $\Psi$ along $z$ axis (normal to the surface):

$$\begin{pmatrix}
\cos \Psi & \sin \Psi & 0 \\
-\sin \Psi & \cos \Psi & 0 \\
0 & 0 & 1
\end{pmatrix}$$

The hcp (hexagonally closed-packed) unit cell of bulk gadolinium has a $D_{6h}$ symmetry whereas the (0001) surface posses an effective $C_{6v}$ symmetry. By surface here is meant the first two atomic layers that form the stacking sequence along $c$ axis in the hcp unit cell. At the first sight, considering the first two layers at the Gd(0001) surface one ends up with a $C_{3v}$ symmetry. However, an effective $C_{6v}$ symmetry of the Gd(0001) surface has been revealed by a combined X-ray photoelectron diffraction (XPD) and LEED study [99]. Also we have checked this issue by applying an additional rotation operation of 60° to the tensor components obtained for $C_{3v}$ symmetry. Both even and odd tensor components reproduce the tensor elements of $C_{6v}$ symmetry. Therefore, in our further consideration we take the Gd(0001) surface as having a $C_{6v}$ symmetry.
3.2 Second Harmonic Generation (SHG)

Table 3.2: List of the allowed tensor components for a \( C_{6v} \) surface symmetry for various polarization geometries and magnetization directions. For simplicity we denote the tensor components just by their indices.

<table>
<thead>
<tr>
<th></th>
<th>p-P</th>
<th>p-S</th>
<th>s-P</th>
<th>s-S</th>
<th>mix-P</th>
<th>mix-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>even ((M\parallel y))</td>
<td>(zzz,zzx,xzx)</td>
<td>-</td>
<td>(zxy)</td>
<td>(-zzz,zzx,xzx,zyy)</td>
<td>(yzy)</td>
<td></td>
</tr>
<tr>
<td>odd ((M\parallel x))</td>
<td>(xxx,xzz,zzx)</td>
<td>-</td>
<td>(zxy)</td>
<td>(-xxx,xyy,xzz,zzx)</td>
<td>(yxy)</td>
<td></td>
</tr>
<tr>
<td>odd ((M\parallel z))</td>
<td>-</td>
<td>(yxx,yzz)</td>
<td>-</td>
<td>(yyy)</td>
<td>(yxx,yyy,yzz)</td>
<td></td>
</tr>
</tbody>
</table>

Applying relation 3.14 for a system with a \( C_{6v} \) symmetry one ends up with the allowed tensor components for hcp(0001) surface:

\[
\chi_{xxz} = \chi_{yyz}; \quad \chi_{zxx} = \chi_{zyy}; \quad \chi_{zzz}
\]

In the presence of magnetization the symmetry of the system is lowered but the inversion symmetry is not lifted since the magnetization is an axial vector i.e. does not change the sign under inversion symmetry. Thus, the surface and interface sensitivity is not lost for a magnetized system but the expression for the \( \chi^{(2)} \) tensor becomes more complicated since one has to deal with a higher number of components. For the transversal geometry (see figure 3.4) used in this work, magnetization lies in the plane of the sample which lowers the symmetry from \( C_{6v} \) to \( C_2 \). Considering the magnetization direction parallel to \( y \) axis and the optical incidence plane determined by \( x \) and \( z \) axes, the additional allowed tensor components are:

\[
\begin{pmatrix}
\chi_{xxz}^{odd} & \chi_{yyz}^{odd} & \chi_{zxx}^{odd} & 0 & \chi_{yyz}^{even} & 0 \\
0 & 0 & 0 & \chi_{zzz}^{even} & 0 & \chi_{zyy}^{odd} \\
\end{pmatrix}
\]  

(3.15)

Some of the new tensor components behave odd with respect to magnetization reversal i.e. \( \chi^{(2)}(M) = -\chi^{(2)}(-M) \) while some do not change the sign \( \chi^{(2)}(M) = \chi^{(2)}(-M) \). From now on, the latter ones will be denoted under even tensor components while the former ones under odd tensor components. The even and odd tensor components of \( \chi^{(2)} \) for a \( C_{6v} \) surface symmetry as a function of magnetization orientation and polarization geometry are listed in the table 3.2.

The effect of the even and odd tensor components on the SHG process can be readily seen by considering two cases with different magnetization direction: transversal and longitudinal (see figure 3.4) for a s-polarized incident light. According to table 3.2 for transversal geometry we have two tensor components: one even \( \chi_{zyy} \) and one odd \( \chi_{xyy} \) i.e. for a s-polarized fundamental. Both of them give a p-polarized SHG output. For longitudinal geometry we have the same even component \( \chi_{zyy} \) but an odd term \( \chi_{yyy} \), which means a p-polarized SHG from the even term and a s-polarized SHG from the odd term. Thus, upon magnetization reversal, one obtains in the transversal geometry a change in the SHG intensity whereas for the longitudinal configuration the effect is the rotation of the SHG polarization.
One way to obtain the even and odd components is to expand susceptibility tensor in powers of magnetization $M$:

$$
\chi^{(2)}(M) = \chi^{(2)}(0) + \frac{\partial \chi^{(2)}}{\partial M} M + ... \quad (3.16)
$$

The first term in right-hand side represents the even tensor component and the next term in the development is the odd term that is proportional to the magnetization. Based on these considerations, one can write an effective tensor that describes the total SHG response from a magnetized material under the form:

$$
\chi^{\text{eff}}(M) = \chi^{\text{even, eff}} + \chi^{\text{odd, eff}} \quad (3.17)
$$

where $\chi^{\text{even, eff}}$ and $\chi^{\text{odd, eff}}$ are linear combinations of tensor components and the corresponding Fresnel factors that are allowed by system symmetry and experimental geometry. Such a simplification is valid when the Fresnel coefficients $f_{ijk}$ might be considered constants and when only the relative changes in $\chi^{(2)}_{ijkl}$ are relevant. Thus one can write the expression for the SH intensity as:

$$
I(2\omega) = \left| \sum_{i,j,k} f_{ijk} \chi^{(2)\text{eff}}_{ijkl} \right|^2 I(\omega)^2 \quad (3.18)
$$

**Bulk contributions to $P^{(2)}(2\omega)$**

It should be noted, that at the surface one can encounter high electric field gradients due to the boundary existence, that can add higher order contributions to the second order nonlinear polarization. These contributions have a non-local character and are described by a fourth-rank tensor which is allowed in the bulk of centrosymmetric materials. Therefore, beside probing the surface/interface one might have also components to the SHG yield that contain information about the bulk of the investigated system. Moreover, when the volume of the studied system is considerable the small bulk contribution might add together and thus having a significant contribution to the total SHG response. In order to account for the bulk contributions to the SHG response, the equation 3.8 can be written now in the following form:

$$
P^{(2)}(2\omega) = P^D(2\omega) + P^Q(2\omega) = \varepsilon_0 \chi^{(2)}(2\omega)E(\omega)E(\omega) + \varepsilon_0 \chi^{(Q)}(2\omega)E(\omega)\nabla E(\omega) \quad (3.19)
$$

Here, the D and Q superscripts stand for dipole and quadrupole contributions, respectively. In general, the non-local component of total polarization consists of electric quadrupoles and magnetic dipoles sources which according to [97] are described by:

$$
P^Q(2\omega) = \alpha [E(\omega)\nabla |E(\omega)| + \beta E(\omega)[\nabla E(\omega)] + i \left( \frac{2\omega}{c} \right) \gamma [E(\omega) \times B(\omega)] \quad (3.20)
$$

where $\alpha$, $\beta$ and $\gamma$ are phenomenological constants. The first two terms in equation have electric quadrupole character whereas the last term describes the magnetic dipole contribution.

In the electric-dipole approximation one takes into account just the local contributions.
to the total induced polarization of the medium. Experimentally, it is difficult to distinguish between surface and bulk contributions to the total SHG response from a certain material. However, there are reports [100, 101] in literature where it has been shown that under special circumstances (employing certain experimental geometries) one can separate these contributions. Since during this work we never observed a measurable bulk (i.e. nonlocal) contribution to the SHG response of the investigated systems of Gd(0001) and Y(0001) films on W(110) substrate, we neglect this in our further considerations. It has been shown [44], that in the case of second harmonic generation the local and nonlocal contributions are of comparable strength if there is a non-resonant transition involved. We will see later for the case of gadolinium that the SHG response is resonantly enhanced via the surface state components [102], a fact that makes us more confident in excluding any bulk contribution to the total SHG yield for this particular system.

3.2.3 SHG radiation depth

An interesting point is the spatial extent over which the SH signal is radiated. A general answer to this issue is the region over which the bulk electronic density exhibits a variation due to the presence of a surface (or interface) that produces a perturbation of the translational symmetry along the $z$ axis i.e. normal to the surface. Thus, from symmetry considerations only, a quantitative information cannot be retrieved.

Another way of viewing these variations of the charge density at the surface is qualitatively reproduced in the framework of jellium model [103] by the so called Friedel oscillations. In this model the discrete positions of the ionic charges are replaced by a continuous positive background and the electronic density exhibits a damped oscillatory behavior inside the jellium in order to screen the background. The damping length is proportional to the background density. Usually the charge density of jellium is specified by the corresponding Wigner-Seitz radius in atomic units. For the case of Gd, the Wigner-Seitz cell radius is $r_s = 3.762$ a.u. [105] (the inverse value of $r_s$ denotes the background density) and therefore the source of SHG in this case is restricted within two atomic layers (one Gd layer is $2.89 \, \text{Å}$).

This link between the jellium model and SH polarization is illustrated in the figure 3.3, which displays the case of a metal with $r_s=4$ (i.e. close to Gd value) and consequently a large distance over which the electronic density oscillates. Here are depicted the calculated electronic density (determines the linear optical response) and the second-order polarization produced by an electric field normal to the surface. What is interesting here is the spatial distribution of the second harmonic polarization $P_2(z)$: the dominant contribution to $P_2(z)$ comes from a surface layer as thin as $\approx 4\, \text{Å}$ (accounting for both sides of the surface) and its maximum lies in the vacuum region where the equilibrium electron density decays exponentially. Thus we come to the same result as above that for Gd with $r_s=3.762$ a.u. the SHG source is located within a region of around two atomic layers. We have to be aware that jellium model is just a simple approximation of the real electronic structure at the surface of metals. However, it can give an important insight about the spatial extent that contributes to the generation of SH radiation.

Beside its intrinsic surface sensitivity derived from symmetry constraints, SHG is particular sensitive to electronic structure at the surface e.g. surface states [106], interface
3 Nonlinear magneto-optics - theoretical aspects

Figure 3.3: Illustration of the spatial distributions of the second harmonic polarization (solid line) and first order electronic polarization (dashed line) produced by an electric field at a metal surface (with \( r_s = 4 \)), calculated within a semi-infinite jellium model. The dashed-dotted line represents the normalized electronic density in equilibrium and the \( z_1 \) and \( z_2 \) indicate the centroid positions of \( n_1(z) \) and \( P_2(z) \), respectively. From [104].

states [107] and quantum-well states [108]. The sensitivity is furthermore increased if the optical transitions involved in the SHG process are resonant. This brings us to the case of Gd(0001) surface, which exhibits a \( d_{z^2} \)-like surface state that is localized in the top-most atomic layer (89% of the surface state charge density is located in the first atomic layer [27]). We will see in chapter 5 that at the Gd(0001) surface the SHG process is resonantly enhanced via the surface state (see figure 5.11). Thus we can say that for the case of Gd(0001) surface the SHG process is extremely surface sensitive, probing most likely the first two atomic layers (accounting for the charge gradient of the surface state). This arises partially from the common symmetry restriction (within electric-dipole approximation) of the SHG source at the surface, and due to the presence of the surface state via which the SHG process evolves resonantly enhanced.

3.2.4 SHG - macroscopic formalism

For a quantitative evaluation of the SHG response of a certain material one can use the phenomenological formalism developed by Sipe et al. [109]. Following their approach one can compute the second-harmonic field using as input parameters the Fresnel coefficients for fundamental \( f(\omega) \) and SH frequencies \( F(2\omega) \), the susceptibility tensor \( \chi^{(2)} \), the effective depth over which SHG is radiated \( \zeta \) and the incident laser intensity \( |E(\omega)|^2 \). The condensed
3.2 Second Harmonic Generation (SHG)

Figure 3.4: Experimental configuration of the SHG process in reflection employed in this work. The fundamental and second harmonic beams are depicted by the dashed and solid lines, respectively, while their polarization orientation is described by \( \phi \) (fundamental) and \( \Phi \) (second harmonic) angles. \( \varphi \) is the angle of incidence and the external magnetic field \( \mathbf{H} \) sets the magnetization orientation of the system and determines the transversal magneto-optical geometry.

formulation of this expression is given as \([110, 44]\):

\[
E(2\omega) = \frac{2i\omega}{c} \mathbf{F}(2\omega) \chi^{(2)} f(\omega)|E(\omega)|^2 \zeta
\]

(3.21)

The Frenel coefficients are given by:

\[
\mathbf{F}(2\omega) = \begin{pmatrix}
A_p F_c \cos \Phi \\
A_s \sin \Phi \\
A_p N^2 F_s \cos \Phi
\end{pmatrix}; \quad 
\mathbf{f}(\omega) = \begin{pmatrix}
f_c^2 t_p^2 \cos^2 \phi \\
t_s^2 \sin^2 \phi \\
f_s^2 t_p^2 \cos^2 \phi \\
2 f_s t_p t_s \cos \phi \sin \phi \\
2 f_c f_s t_p^2 \cos^2 \phi \\
2 f_c t_p t_s \cos \phi \sin \phi
\end{pmatrix}
\]

(3.22)

for the second harmonic and fundamental radiation, respectively. In the above relations the following contracted notation was used:

\[
f_s = \frac{\sin \varphi}{n(\omega)}, \quad f_c = \sqrt{1 - f_s^2}, \quad t_p = \frac{2 \cos \varphi}{n(\omega) \cos \varphi + f_c}
\]

\[
t_s = \frac{2 \cos \varphi}{n(\omega) f_c + \cos \varphi}, \quad A_{p/s} = \frac{2\pi T_{p/s}}{\cos \varphi}, \quad N = n(2\omega)
\]

(3.23)

where \( \phi \) and \( \Phi \) denotes the polarization direction for fundamental and second harmonic, respectively (0° for p polarization and 90° for s polarization, see figure 3.4). The lower-case letters describe the quantities at the fundamental frequency whereas capital letters denotes SH related quantities. The angle of incidence is denoted by \( \varphi \). \( N \) and \( n \) are the refractive indexes at second-harmonic and fundamental frequency, respectively, \( A_{p/s} \) denotes the amplitude of the output SHG for p and s polarized light, \( t_{p/s} \) the transmission
coefficients for p and s polarized light, while \( f_s \) and \( f_c \) represent the projection of the fundamental wavevector on the coordinate system of the sample.

The Fresnel coefficients reflect the linear optical response of the medium at the fundamental and the second-harmonic frequencies, and enter in the SH field formula (and consequently in the SHG intensity) as multiplying factors. This fact is useful since one can increase the SHG yield by choosing the optimal geometry (angle of incidence, wavelength). On the other hand, the fact that the SH field (eq. 3.21) depends on the optical properties of the system at both, SH and fundamental frequency, makes a straightforward interpretation of the SHG response, sometimes, to be difficult. Thus, one should be aware of this fact when trying to obtain quantitative information from the SHG transients in general [111].

From eq.3.21 we have seen that the SH field is proportional to the square of the incident electric field, which gives the same square dependence between the SH \( I_{2\omega} \) and the fundamental \( I_\omega \) intensities. It is of interest here to see what are the experimental parameters that influence the SHG intensity. The SHG intensity is given by:

\[
I_{2\omega} \propto \int |\chi^{(2)}(t)|^2 dt \propto \frac{(E_p/A)^2}{\tau}
\]

(3.24)

where \( E_p, A, \tau \) are the pulse energy, laser focus area, and pulse duration respectively. We notice that the SHG signal is material dependent through \( \chi^{(2)} \) and it can be optimized by varying one or more parameters that enter in the above equation.

### 3.3 Magneto-Optics

#### 3.3.1 Linear magneto-optics

The interaction between the light and matter, with the latter one being magnetized - either under the influence of an external magnetic field or showing a spontaneous magnetization - is described in the framework of magneto-optics. Assuming moderate level of incident optical intensities the response of the medium is a linear one (see previous section). The magneto-optical effects manifest themselves as a change in the state of polarization and/or intensity upon light reflection or transmission from magnetized material. In reflection this effect is known as magneto-optical Kerr effect (MOKE), and in transmission under Faraday effect. Both these phenomena resemble similar features, namely are proportional to the magnetization and scale with the thickness of the medium under investigation.

Classically, the MOKE effect can be explained by the action of the Lorentz force on the electrons excited by the incident electromagnetic wave. Although this picture has for sure a high pedagogical usefulness, it does not account for the reality since one needs magnetic fields in order of \( 10^4 \) tesla to obtain the observed amplitude of the MOKE signal. Macroscopically, in a phenomenological approach, the dielectric tensor that describes the optical response of the medium (optically isotropic) can be written as:

\[
\varepsilon(\omega) = \begin{pmatrix}
\varepsilon_{xx} & 0 & 0 \\
0 & \varepsilon_{xx} & 0 \\
0 & 0 & \varepsilon_{xx}
\end{pmatrix}
\]

(3.25)
Figure 3.5: Experimental geometries for linear and nonlinear magneto-optics that are defined by the orientation of magnetization \( \mathbf{M} \) direction with respect to the optical incidence plane (dashed rectangle) and the sample. For the polar case the magnetization is perpendicular to the sample surface and in the plane of incidence, for transversal geometry the \( \mathbf{M} \) vector lies in the plane of the sample and perpendicular to the plane of incidence while for the longitudinal situation \( \mathbf{M} \) is parallel with the plane of incidence and the sample surface.

In the presence of magnetization the medium becomes optically anisotropic, the effects induced by the presence of magnetization being described by the off-diagonal tensor components. These ones fulfill the Onsager identity [112] which illustrates the breaking of the time-reversal symmetry in the presence of magnetization:

\[
\varepsilon_{ij}(\mathbf{M}) = -\varepsilon_{ij}(-\mathbf{M})
\]

Taking this expression into account the dielectric tensor for a magnetized medium becomes:

\[
\varepsilon(\omega) = \begin{pmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & -\varepsilon_{xz} \\
-\varepsilon_{xy} & \varepsilon_{xx} & \varepsilon_{yz} \\
\varepsilon_{xz} & -\varepsilon_{yz} & \varepsilon_{xx}
\end{pmatrix}
\]

In eq. 3.26 the formula of the dielectric tensor is deduced for the general case when the magnetization has an arbitrary orientation.

As for the second-order susceptibility, expanding \( \varepsilon_{ij} \) in powers of \( \mathbf{M} \) one obtains:

\[
\varepsilon_{ij}(\mathbf{M}) = \varepsilon_{ij}(0) + \frac{\partial \varepsilon_{ij}}{\partial \mathbf{M}} \mathbf{M}
\]

where the part independent of magnetization (in a first approximation) denotes the diagonal components of the dielectric tensor while the part proportional with magnetization determines the antisymmetric off-diagonal tensor components in equation 3.26.

Until now we have seen that the MO effects are due to the off-diagonal components of the dielectric tensor. But the question is what is the physical picture behind these effects or how the magneto-optics comes about? For sake of simplicity let us follow the Kerr effect scenario: the incident linearly polarized light can be described as a superposition of left and right circularly polarized components with equal amplitudes. As the light travels through the magnetized medium, its constituent parts will "see" different medium with different refractive indexes. This will result, first, in different propagating velocities and implicitly there will be a phase shift between the two modes which produces the rotation of the polarization plane. Second, different absorption rates for the two circularly polarized...
waves will change their relative amplitudes and modify the polarization state from linear to elliptical. Their combined effect will produce an elliptically polarized output radiation with the polarization plane rotated with respect to the incident wave polarization axis.

These two effects are quantified by Kerr ellipticity $\varepsilon_K$ and rotation $\theta_K$ contributions to the complex Kerr angle: $\Theta_K = \theta_k + i\varepsilon_K$. Writing these quantities in terms of dielectric tensor components, one obtains e.g. for a magnetized medium in the polar geometry ($\vec{M} \parallel z$):

$$\Theta_K \sim \frac{\varepsilon_{xy}}{\varepsilon_{xx}} \sim M$$

The above relation shows the origin of the small linear magneto-optical effects, which is the low magnitude of the magnetization-induced off-diagonal components of the dielectric tensor in comparison to the diagonal ones. We will see that this is not the case for the nonlinear magneto-optics, as detailed in the next section.

Depending on the involved MOKE geometry (see figure 3.5) one can map out the magnetization orientation in real space. For example in longitudinal geometry the in-plane magnetization can be probed, this characteristic being used in magnetic domains imaging. In polar configuration the projection of magnetization along $z$ axis is determined, this geometry finds applications in magneto-optical recording [113]. Although MOKE is primarily a bulk sensitive technique since it averages over the optical penetration depth, one can resolve thicknesses in monolayer or even sub-monolayer range of a ferromagnetic material [114].

On a microscopic level, there is the combined effect of the spin-orbit coupling and the exchange interaction together with the selection rules for optical transitions that give rise to the observed magneto-optical effects. The optical transition in the electric-dipole approximation have different absorption probabilities for left and right circularly polarized light as can be seen in the figure 3.6. Writing the imaginary part of the non-diagonal component of conductivity tensor that determines the magneto-optical activity [115], one can identify on a microscopic scale the source of the magneto-optical effects:

$$\sigma_{xy}(\omega) = \frac{\pi e^2}{4\hbar \omega m^* \Omega} \sum_{i,f} f(E_i)[1 - f(E_f)][|i|p_-|f>|^2 - |i|p_+|f>|^2] \delta(\omega_{fi} - \omega) \quad (3.28)$$

with $f(E)$ representing the Fermi-Dirac function, $\hbar \omega$ being the energetic interval between the initial $|i>$ and final state $|f>$ and $\delta(\omega_{fi} - \omega)$ describing the energy conservation. If the difference between the matrix elements for dipole transitions corresponding to left $|i|p_+|f>$ and right $|i|p_-|f>$ circularly polarized light vanishes (the case of a paramagnet) than there is no net magneto-optical effect.

The above picture provides just a qualitative understanding regarding the origin of MO effects on a microscopic level. It was shown [116, 117] that is the change of the electronic wavefunctions due to the spin-orbit coupling rather than the energy eigenvalues shift which accounts for the proper order of magnitude of the MO effects.

### 3.3.2 Magnetization-induced second-harmonic generation

Previously we have discuss in detail the linear magneto-optical effects since these resemble several common features with, and are the basis for understanding of the nonlinear
magneto-optics, that is the topic of this section. Due to its linear optical character MOKE gives information about the magnetization behavior in the bulk region (within the optical penetration depth) of the materials. Although can reach atomic monolayer sensitivity \[113, 114\] of ferromagnetic films, MOKE lacks the surface or interface specificity.

Magnetization-induced second-harmonic generation, also known as the nonlinear magneto-optical Kerr effect (NOLIMOKE or NOMOKE), as a nonlinear optical process provides (within electric-dipole approximation) the surface and interface sensitivity (see preceding sections) and simultaneously gives a measure of the magnetization in the probed region. Similar to MOKE, the MSHG is linear in magnetization \( \mathbf{M} \) but is nonlinear in the optical field. Beside these characteristics, MSHG can access buried interfaces of e.g. magnetic multilayered structures, with evident applications in magnetic data storage.

Although the SHG was first demonstrated in early 1960-ties \[96\], MSHG is a relatively young tool of investigation of ferromagnetic materials. The MSHG effects were first predicted in the theoretical work of Pan et al. \[11\], where it was shown that magnetization could induce a component of measurable magnitude to the total SHG response from a ferromagnetic material. The first experimental proof came from the work of Reif et al. \[118\] performed on the iron Fe(110) surface. Since then, the nonlinear magneto-optics field experienced a tremendous development which was partially triggered by the continuous interest in the physics of magnetic multilayered structures and their potential applications as well as the development of the ultrafast laser sources. The application range of MSHG covers a large spectrum starting from imaging of magnetic domains to investigation of spin dynamics on ultrafast time scales, and from investigation of spin reorientation transition of thin magnetic films to magnetic quantum wells. These are just a few examples that give a rough overview about the applicability of MSHG. For a better overview of the work done in this field, the reader is referred to the review of Kirilyuk \[107\].

**Figure 3.6:** Microscopic picture of linear magneto-optical effects on a ferromagnetic material: the initial degeneracy of the ground electronic states is lifted by the presence of spin-orbit coupling while the exchange interaction produce a energetic shift \( \Delta_{\text{ex}} \) of the electronic states with different spin orientation. The optical transitions for left (LCL) and right-handed (RCL) circularly polarized light evolve according to the selection rules \( \Delta l = \pm 1 \) and \( \Delta m_l = \pm 1 \). The overall effect is a different absorption probability for LCL and RCL that produces the rotation of polarization plane for the outgoing light \[115\].
As for the case of linear magneto-optics, the origin of the nonlinear magneto-optical effects rely on breaking of the time-reversal symmetry. In addition, breaking of space-inversion symmetry provides a high surface and interface sensitivity. These two symmetry considerations being fulfilled simultaneously, make the nonlinear magneto-optics in general and especially MSHG a very reliable investigation method of electronic and magnetic properties at surfaces and interfaces. Analogous to MOKE, in the case of MSHG the magnitude of the magnetization-induced effects is proportional to the ratio between the magnetic and non-magnetic tensor components \( i.e. \) odd and even with regard to magnetization reversal, respectively. Thus, both effects, MSHG and MOKE, resemble a similar feature namely are proportional with the magnetization of the investigated system. For the case of MOKE, the odd (off-diagonal) tensor components are usually small which explains the low magnitude effects encountered in linear magneto-optics. This is not the case of MSHG where the even and odd tensor components are of comparable magnitude, and therefore giving rise to much higher effects compared to linear magneto-optics. An illustrative example here is Ni, where for the same wavelength range, a ratio of the odd and even tensor components of 0.03 was found for linear magneto-optics whereas for the nonlinear magneto-optics a value of 0.27 was determined [117].

In general, for a ferromagnetic material the nonlinear source of the SH signal can be described by the second-order nonlinear polarization having the following form [107, 119]:

\[
P^{(2)}_s(2\omega) = \chi^{(2)}_{ijk} E_j(\omega) E_k(\omega) + \chi^{(3)}_{ijkl} E_j(\omega) E_k(\omega) M_l
\]

(3.29)

where the first term on the right-hand side describes the non-magnetic effects while the second is determined by the presence of magnetization. Defining [119] the magnetization-induced susceptibility tensor as:

\[
\chi^{(2)}_{ijk}(M) \equiv \chi^{(3)}_{ijkl} M_l
\]

(3.30)

one can express the susceptibility tensor giving rise to MSHG effects as a sum of second-order susceptibility components that behave even and odd with respect to magnetization reversal. Thus, one can write:

\[
\chi^{(2)}_{ijk} = [\chi^{(2)}_{\text{even}}]_{ijk} + [\chi^{(2)}_{\text{odd}}(M)]_{ijk}
\]

(3.31)

Experimentally one measures the SHG intensity for opposite magnetization directions, which can be written as:

\[
I^{\uparrow\downarrow}(2\omega) \propto |E^{\text{even}}(2\omega) + E^{\text{odd}}(2\omega)|^2
\]

(3.32)

where \( E^{\text{even}}(2\omega) \) and \( E^{\text{odd}}(2\omega) \) are the even and odd SH fields generated by the nonlinear polarization described in eq. 3.29. The magnetization orientation is denoted by up and down arrows in the formula. Further on, the above equation becomes:

\[
I^{\uparrow\downarrow}(2\omega) \propto |E^{\text{even}}(2\omega)|^2 + |E^{\text{odd}}(2\omega)|^2 \pm 2 |E^{\text{even}}(2\omega)||E^{\text{odd}}(2\omega)| \cos \phi
\]

(3.33)

where \( \cos \phi \) represents the relative phase between the even and odd second harmonic fields. From here we see that the magnetization effects come from the cross term in the right-hand side of eq. 3.33, which gives the interference between the even and odd SH fields.
and contains also their mutual phase $\phi$. Hence, the phase between odd and even fields is a non-negligible quantity and should also be evaluated from experiment. Its importance can be seen immediately by assuming a $\phi = 90^\circ$ value that gives a zero value for the cross term, which is equivalent with no magnetization-induced SHG signal. How to measure the relative phase between even and odd fields and the involved formalism will be presented in the chapter 5.

In this work we have used the transversal magneto-optical geometry in a p-P polarization configuration. This experimental geometry has been chosen since we are interested in the in-plane magnetization component (of ferromagnetic Gd(0001) films) and the highest number of even and odd tensor components contribute to the SHG response (see table 3.2). The latter fact ensures a high sensitivity of the SHG process to the magnetized medium through the cross term in eq 3.33. Also for the p-P geometry the magnitude of the Fresnel factors is higher that further enhances the SHG efficiency (see eq. 3.21).

In order to get information about the magnetization of the probed region, one can determine from the measured SH intensities the magnetic contrast or magnetic asymmetry. This is defined as the relative variations of the SHG intensity for opposite magnetization directions and it has the below form:

\[
\rho = \frac{I^\uparrow(2\omega) - I^\downarrow(2\omega)}{I^\uparrow(2\omega) + I^\downarrow(2\omega)}
\]

(3.34)

Taking into account the relation 3.33 one can write the magnetic contrast as:

\[
\rho \approx 2 \frac{|E_{\text{odd}}|}{|E_{\text{even}}|} \cos \phi
\]

(3.35)

considering that \(\frac{|E_{\text{odd}}|}{|E_{\text{even}}|} \ll 1\). Since the magnetic contrast and the phase can be measured in the experiment, one can deduce the value of the even and odd SH fields. Moreover, accounting for the eq. 3.30 one obtains a direct relationship between the magnetic contrast and magnetization of the probed area:

\[
\rho \approx 2 \frac{\chi^{(3)}_{\text{odd}}}{\chi^{(2)}_{\text{even}}} M \cos \phi
\]

(3.36)

Based on the above considerations, we can consider the magnetic contrast as a good measure of the magnetization in the probed region.

**Time resolved MSHG**

The measured observable in a time-resolved MSHG experiment is the intensity of second harmonic signal for opposite directions of magnetization and as a function of delay time between pump and probe beams. As has been shown previously, the SH intensity consists of even and odd fields with respect to magnetization reversal, which monitor the electron (phonon) and spin subsystems, respectively. We are interested in the time evolution of the second-harmonic fields as a function of pump-probe delay. The first step

\[\text{The validity of the condition } \frac{|E_{\text{odd}}|}{|E_{\text{even}}|} \ll 1 \text{ is demonstrated in chapter 5 for the case of Gd(0001) surface.}\]
in their determination is computing the sum and difference of SHG intensities for opposite magnetic fields, accounting for eq. 3.33:

\[ I^\uparrow(t) + I^\downarrow(t) = 2[E^2_{\text{even}}(t) + E^2_{\text{odd}}(t)] \] (3.37)

\[ I^\uparrow(t) - I^\downarrow(t) = 4E_{\text{even}}(t)E_{\text{odd}}(t) \cos \phi(t) \] (3.38)

To deduce the transient SH fields, the ratios between the measured intensities for positive and negative time delays (in absence of the pump pulse) are computed under the form:

\[ R(t) = \frac{I^\uparrow(t) \pm I^\downarrow(t)}{I^\uparrow(t_0) \pm I^\downarrow(t_0)} \] (3.39)

In obtaining the upper expression in terms of transient SH fields we neglect the factor \( |E_{\text{odd}}(2\omega)|^2 \) since \( |E_{\text{odd}}(2\omega)|^2 \ll |E_{\text{even}}(2\omega)|^2 \) (as shown above). The resulting pump-induced variations in the second-harmonic fields are written as:

\[ \frac{E_{\text{even}}(t)}{E_{\text{even}}(t_0)} = \sqrt{R^+(t)} \] (3.40)

\[ \frac{E_{\text{odd}}(t) \cos \phi(t)}{E_{\text{odd}}(t_0) \cos \phi(t_0)} = \frac{R^-(t)}{\sqrt{R^+(t)}} \] (3.41)

The normalized ratio of the even field denote the dynamics of the electron system while the ratio of the odd fields gives measure of the magnetization dynamics in the probed region [17]. In the following, and throughout the thesis, the time-resolved SHG data will be presented under the following form:

\[ \Delta_{\text{even}} = \sqrt{R^+(t)} - 1 \approx \frac{E_{\text{even}}(t)}{E_{\text{even}}(t_0)} - 1 \] (3.42)

\[ \Delta_{\text{odd}} = \frac{R^-(t)}{\sqrt{R^+(t)}} - 1 \approx \frac{E_{\text{odd}}(t) \cos \phi(t)}{E_{\text{odd}}(t_0) \cos \phi(t_0)} - 1 \] (3.43)

Accounting for the expression 3.30 one can write the \( \Delta_{\text{odd}} \) as [119]:

\[ \Delta_{\text{odd}} \approx \alpha(t,\omega) \frac{M(t)}{M(t_0)} - 1 \] (3.44)

with the prefactor defined as:

\[ \alpha(t,\omega) = \frac{\chi^{(3)}_{\text{odd}}(t)}{\chi^{(3)}_{\text{odd}}(t_0)} \cdot \frac{\cos \phi(t)}{\cos \phi(t_0)} \] (3.45)

From the above equations we notice that \( \Delta_{\text{odd}} \) measures the transient magnetization of the system multiplied by a factor that depends on the relative phase between the SH fields and the normalized ratio of the third-order susceptibility. In principle one can measure the relative phase in a time-resolved manner. For the case of Gd(0001) such measurements
are hindered by the relatively low SHG signal and the inherent technical difficulty of measuring SHG phase in UHV. However, spectroscopic measurements of the phase \[ \phi \approx 20^\circ \] (see chapter 5) in the static case performed on Gd(0001) yield a value \( \phi < 20^\circ \) that gives \( \cos \phi(t_0) \approx 1 \). Time-resolved MSHG measurements performed on Ni samples in air [120] showed the pump-induced variations of the phase to be small and consequently \( \frac{\cos \phi(t)}{\cos \phi(t_0)} \approx 1 \). Accounting for the Ni experiment and since for the Gd(0001) surface \( \cos \phi(t_0) \approx 1 \) we can conclude that \( \frac{\cos \phi(t)}{\cos \phi(t_0)} \approx 1 \) is valid for time-resolved MSHG measurements performed on Gd(0001). From the spectroscopic behavior of the \( \Delta_{\text{odd}} \) and \( \Delta_{\text{even}} \) we deduce a minor role of the susceptibility ratio in the dynamics of \( \Delta_{\text{odd}} \) [119]. Thus, we can conclude that the quantity \( \Delta_{\text{odd}} \) reflects, mostly, the dynamics of the surface magnetization.
4 Experimental details

This chapter is devoted to the description of the experimental setup involved in the present work, which consists mainly of two parts:

1. the ultra-high vacuum (UHV) chamber
2. the femtosecond laser system

The UHV chamber is used for the preparation and characterization of thin films, and also for the optical measurements. The femtosecond laser is the light source, providing ultrashort and high energy pulses necessary for the steady-state and time-resolved linear and nonlinear optical spectroscopy.

In the following, the experimental devices together with the employed measurement techniques, the second harmonic generation (SHG) and the linear reflectivity (LR), will be presented.

4.1 UHV chamber

Accounting for the high reactivity exhibited by rare-earth elements, and in particular by gadolinium, an ultra-high vacuum environment is necessary for the preparation of high quality rare-earth thin films. Generally, ultra-low pressures are obtainable after a careful bake-out of the UHV vessel and additional chemical pumping using e.g. ion-getter pumps and/or titanium sublimation pumps. In this way pressures in the $10^{-11}$mbar range are achievable. The UHV chamber used in this work - depicted in figure 4.1 - is pumped by a turbomolecular pump (Leybold Turbovac 361) together with a pumping stage (Pfeiffer) consisting of a turbomolecular pump and a diaphragm pump, the latter one serving as a pre-vacuum pump. In order to get lower pressures, a titanium sublimation pump (TSP) is employed. In this context the high reactivity of gadolinium is very useful since one can utilize it as an additional modality of chemical pumping. By combining its effect with the TSP pumping, the achieved base pressure is around $2\times10^{-11}$mbar. The residual gas analysis of the obtained vacuum is performed with a quadrupole mass spectrometer (QMS). The QMS is also used as a detector for the desorbed species in the temperature desorption spectroscopy (TDS) measurements.

The UHV chamber, sketched in the figure 4.1, is structured on two levels: the preparation level for thin film deposition and characterization and the optical level for the linear and nonlinear optical measurements. In the preparation level three home-build evaporators are installed, which provide us with enough provisions of gadolinium (Gd), yttrium (Y) and terbium (Tb). Thin films of these materials are prepared by electron-beam evaporation from tungsten (W) crucibles with the film thickness and deposition rate being monitored by a quartz microbalance (QMB). For checking the morphology and the long-range structural
ordering of the deposited films and also for the substrate quality, a low electron energy diffraction (LEED) device is used. A pair of leak valves are utilized to dose xenon (Xe) and oxygen (O\textsubscript{2}) in UHV.

For the optical level, a special entrance flange has been designed, allowing the positioning of the focusing lens closer to the sample. Hence a better focus of the laser beam is achieved (diameter in focus $\approx$70 $\mu$m), that results in higher laser fluences\(^1\) (typical $\approx$1mJ/cm\textsuperscript{2}). Fused silica UHV windows were used for entrance and exit of laser beams, a material exhibiting high transmission ($\geq$95\%) over a wide spectral range (250 nm to 2 $\mu$m). Also, an electromagnet (not shown) is installed, producing magnetic fields up to 500 Gauss, which is sufficient to magnetize the films in saturation along the easy axis. The sample holder is attached to the cold finger of a continuous flow cryostat, which can be used either with liquid nitrogen or liquid helium. The whole construction is mounted on a differentially pumped manipulator that allows displacements along $x$, $y$, and $z$ axis (vertical) as well as 360° rotation.

\(^1\)The laser fluence is defined as the ratio $E_p/A$, where $E_p$ is the energy per pulse in mJ and $A$ is the laser illuminated area in cm\textsuperscript{2}.
4.1 Sample preparation

Both materials investigated in this work, Gd and Y, have been grown on a tungsten(110) substrate. Since we have used a similar preparation procedure for the Gd(0001) and Y(0001) thin films, we focus in the following on the Gd(0001)/W(110), being the most investigated system in this work.

Growing of rare earth metals on refractory materials substrates like W(110) (also Mo(110)), presents several advantages that makes this substrate very feasible in preparing high quality rare-earth thin films. One of the reasons is the high surface energy of the W surface that favors a layer-by-layer type of growth and the fact that the deposited material does not form alloys with the substrate. Also the bcc(110) surface is atomically smooth that results in a high mobility of the adsorbed atoms. Moreover, there is a relatively good matching between the support substrate and the deposited film, with a lattice mismatch for the Gd(0001)/W(110) system that amounts to ≈15%. This causes a Gd lattice distortion that becomes weaker and disappears by strain release after 4 monolayers (ML) of Gd(0001) film [24]. Furthermore, this substrate is paramagnetic having no influence on magnetic properties of the deposited overlayer. Cleaning the substrate can be performed in a easy manner and is not a time consuming procedure in comparison with sputtering+annealing cycles, that are necessary for other systems e.g. Ni/Cu(001). From technical point of view this constitutes a major advantage.

One necessary condition for a good quality of deposited film is that the substrate is clean, showing no impurities. The W(110) substrate is cleaned by short (several seconds) cycles of heating up to ≈2600 K, a process known as flashing. The usual contaminants, which diffuse from the bulk upon heating, are carbon and sulfur. These can be removed after several cycles of heating the sample to ≈1600 K in partial pressure of oxygen (p = 2x10^{-7}mbar). During this procedure the contaminants are oxidized and desorbed. For a clean substrate an additional cycle of flashing is required in order to remove the more stable tungsten oxides. Normally, the above mentioned procedure should be repeated after the preparation of 30 to 40 films, as has been done in the present work.

As mentioned above, gadolinium grows epitaxially on W(110) in a layer-by-layer mode
4 Experimental details

Figure 4.3: The dependence of the Gd(0001) films morphology on the annealing temperatures for various film thicknesses, as was measured with ac susceptibility by Aspelmaier et al. [121]. One can obtain 3D islands or 2D films by choosing the appropriate annealing temperature. Taken from [122].

(Frank-van der Merwe mode) [122, 33] owing to the bigger free energy of tungsten surface, which favors a two-dimensional (2D) type of growth. After a short annealing cycle, the film acquires a long range crystalline order. This is illustrated in the figure 4.2, where the LEED pattern from a 10 nm Gd(0001) film annealed to 680 K is shown. Making use of even higher annealing temperatures the film morphology changes to a Stranky-Krastranov mode i.e. three-dimensional (3D) islands on top of a flat film [123]. In the present work, a relatively similar procedure in growing thin gadolinium films on W(110) substrate has been used, as was described by Aspelmaier et al. [121]. They performed a thorough study of critical annealing temperatures for Gd films with different thicknesses, at which the transformation from a 2D film to 3D islands takes place. Their results are shown in the figure 4.3.

Our daily used recipe in growing thick gadolinium films is as follows: a 20 nm (the typical thickness) gadolinium film is deposited on the tungsten substrate held at room temperature, at a deposition rate of $\sim 6 \, \text{Å/min}$ followed by 10 min annealing to 680 K. This produces a smooth and well ordered film, which can be judged from the LEED picture shown in the figure 4.2.

Before we end the section regarding the sample preparation, is worthwhile mentioning how the residual gases of the UHV environment can influence the surface quality of the prepared rare-earth films and what is special for our case. Even for base pressures in the $10^{-11}$ mbar range a freshly prepared film will be covered by a layer of adsorbed residual gas molecules in a time interval of $\approx 3$-4 hours, accounting for the definition of one langmuir $1 \, \text{L}=10^{-6}$torr·s. Upon adsorption of various residual gases the surface electronic structure is significantly affected. For the case of Gd(0001) surface, the exchange-split surface state (see chapter 2) can be used as an indicator for the cleanliness of the surface. Photoemission measurements on Gd(0001) use the signal arising from the surface state as a signature for the surface quality [124] and report a degradation and a subsequent disappearance of the
Figure 4.4: The variation of the SHG signal (of the probe beam) with the H\textsubscript{2} exposure for a sequential opening and closing of the pump beam. The pump and probe beams are spatially and temporally overlapped. During the measurement the sample is continuously exposed to H\textsubscript{2} at various partial pressures. Note the logarithmic scale of the y axis.

surface state signal after a few hours with a vacuum in the $10^{-11}$ mbar range [125]. Since the surface quality is of utmost importance for us, we have performed a test measurement by exposing a freshly prepared Gd(0001) film to molecular hydrogen at various partial pressures. Simultaneously we monitor the SHG signal, that arises mainly from the surface state (see chapters 3 and 5). The result is plotted in the figure 4.4, where the SHG yield (from the probe beam) is displayed for open and closed pump beam (more intense than the probe beam - see section 4.3). We observe initially for a closed pump a decrease of the SHG signal with step-like features, that corresponds to different exposure pressures of H\textsubscript{2}: from $2 \times 10^{-9}$ mbar to $5 \times 10^{-7}$ mbar. This indicates a degradation of the surface quality by the H\textsubscript{2} adsorption. A sharp increase of the SHG yield (almost one order of magnitude) appears for a H\textsubscript{2} partial pressure of $2 \times 10^{-6}$ mbar, that might indicate a SHG resonance enhancement via an adsorbate electronic state. When the pump is open a sudden decrease of the SHG yield to the initial level, before adsorption, is noticed. The sequence is repeated and the same level of SHG signal are detected for the open and close pump. Therefore we can conclude that we produce a very efficient laser-induced cleaning
Experimental details

of the surface based on the laser-induced desorption process. We have to keep in mind that for the real measurements the residual gases are at much lower concentrations than the exposures used here. This result is corroborated by the features of the time-resolved measurements, which were showing a similar quality even for films that were four days old.

4.1.2 Sample holder

Along this work two different types of sample holder were used: one which was optimized for photoemission measurements, but having the drawback of low cooling efficiencies (used in earlier stage of the present work), and the second one being an improved version in terms of robustness and cooling. For comparison both sample holders are sketched in the figure 4.5.

The fundamental difference between them, rely on sample mounting: while in the first case the tungsten crystal is mounted between a W stick and a W wire, for the second variant the crystal is actually wrapped by the tungsten wires. Hence, the thermal contact is different: for the first variant the contact with the cooling reservoir is done just through the sharpened W stick via the tantalum block and the Ta screw, whereas for the second variant, a better thermal contact is realized between the cooling source and the sample via the W wires and Cu legs. Therefore, the latter solution provides an extended contact surface between sample and the cooling reservoir, which increased significantly the efficiency of cooling (cooling the sample with liquid helium, 20 K could be achieved with the improved version whereas just 60-70 K with the old version). In the following the second variant of the sample holder is described.

The W(110) crystal is mounted with the help of two tungsten wires (diameter 0.3 mm), which are wrapped around and tightly fixed on the sample holder legs. This is done by pressing the W wires between a 1 mm thick tantalum plate and the sample holder leg. The copper legs are covered with a thin tantalum foil as a safety precaution in order to prevent any damage, which can be produced during flashing. Electrical isolation and good thermal conductivity at low temperatures, are ensured by employing a pair of sapphire plates (thickness 1 mm), which are mounted between the main rod and the Cu legs. The sapphire plates are polished in order to provide a better contact with the main rod and the holder legs. A protective Cu shield (not shown) is mounted in order to hinder the deposition of metal films on the sapphire plates during flashing. By this, the appearance of electrical short-circuits is avoided.

The sample holder components are made of high purity copper and are gold-coated to reflect the thermal radiation. This latter fact together with a radiation shield (mentioned above) made of Cu, that is mounted concentric around the sample holder, assure a good cooling efficiency in the low temperatures range. The entire construction is attached to the cryostat coldfinger, which is used mainly with liquid helium. With this type of sample holder the lowest achieved temperature is around 20 K. Heating of the sample can be done in two ways: either by resistive heating via the tungsten wires which hold the sample or by electron bombardment using the a tantalum filament (diameter 0.3 mm) installed behind the sample. The filament has a spiral-like shape in order to produce a spatially homogeneous heating of the W sample. For direct heating currents between
15-20 A are used to obtain temperature above 1200 K. In the case of indirect heating, the electrons produced by a 5 A current flowing through the filament, are accelerated by +700 V voltage applied between sample and ground. The high temperatures required for flashing are obtained with the latter method.

For temperature measurement, an appropriate sensor should be used taking into account the wide temperature range, i.e. from 20 K to 2600 K in which the setup is operated. The only available tool covering such a temperature region is W/Re (W5%Re/W26%Re) type C thermocouple. This is installed in a 0.3 mm hole made in the W crystal, and is mounted uninterrupted from sample to thermovoltage display (Keithley 2000 multimeter) through a UHV flange where is glued. Thus, unwanted additional junctions are avoided and a better accuracy in temperature reading is obtained. This is very important in the low temperature range where the W/Re thermopower variations with temperature are very small. This can be seen in the left panel of figure 4.6, where the temperature variation between 20 K and 100 K corresponds to a thermovoltage value of $\approx 200 \mu V$. A step forward in improving the temperature accuracy was made using an electronic ice reference point (Newport) instead having the reference junction in an ice bath. The latter one can exhibits temperature gradients in the ice-water mixture, that can influence the temperature reading in an uncontrollable way. Even with this precautions, the measured thermovoltage can be influenced by a series of factors, which introduce errors in temperature reading e.g. bad contact sample - sensor. Thus, after each sample mounting a temperature calibration procedure has been done. In the low temperature range the calibration has been made
4 Experimental details

Figure 4.6: Calibration of the temperature reading of the W/Re thermocouple using TDS measurements from the W(110) substrate Left: Variations of the W/Re thermovoltage with temperature: the tabulated values (dashed line) together with the measured TDS desorption temperatures for Xe and O$_2$ (dots) used to obtain the calibration curve (solid line). Both curves are described by a fifth order polynomial. Right: typical TDS spectrum of Xe from W(110) substrate, showing the multilayer (low temperature) and the monolayer (higher temperature) desorption peaks.

employing thermal desorption spectroscopy, by using the measured desorption temperatures of physisorbed O$_2$ and Xe on W(110) sample. An exemplary TDS spectrum of the thermally desorbed Xe from the W(110) substrate is shown in the right panel of the figure 4.6. From here one can deduce the desorption temperatures (actually the measured thermovoltage) for the monolayer and the multilayer coverage of Xe. The same procedure is done also for the O$_2$. By comparing the measured desorption temperatures with the literature data one can get an estimation about the encountered deviation from the real temperature. Thus, the three low temperature points together with the room temperature point are used for the determination of the calibration curve (solid curve in fig. 4.6 left) employing the same polynomial fit function utilized to fit the tabulated values of thermovoltage vs. temperature for the W/Re thermocouple (dashed curve in fig. 4.6 left). From here an error in the temperature reading $\leq$10K is estimated. In the high temperatures (above 600°C) region a pyrometer has been utilized.

4.2 Laser system

As mentioned earlier in this section, we use as a light source for the static and time-resolved linear and nonlinear optical measurements a home-made Titanium:sapphire (Ti:Al$_2$O$_3$) oscillator. There are two regimes in which the laser can be used:

1. the normal oscillator mode

2. the cavity dumping mode
4.2 Laser system

![Absorption and emission (fluorescence) spectra of Ti:Sa crystal as a function of wavelength. Maximum in the Ti:Sa absorption (514 nm) is close to the wavelength of Nd:YVO₃ pump laser (532 nm). The broad bandwidth of the fluorescence spectrum supports the generation of ultrashort laser pulses. From [126].]

In the normal oscillator regime, the typical operating parameters are: pulse energy around 6 nJ at a repetition rate of 76 MHz and thus an average power of 500 mW. In the cavity-dumping mode, the pulse energies are increased by almost an order of magnitude to \( \sim 42 \) nJ at an adjustable repetition rate controlled by the cavity dumper control unit. For both regimes, pulses as short as 35 fs are delivered. Due to the higher pulse energy and the possibility of having a variable repetition rate, the cavity dumping variant has been chosen for all time-resolved measurements presented here. For some of the static measurements and the MSHG phase determination (see chapter 5) the oscillator variant has been employed. In the following, a short introduction in the theory of the femtosecond laser pulse generation and mode-locking technique is given, followed by the description of cavity-dump working mode of the oscillator.

### 4.2.1 Ultrashort laser pulse generation

Titanium doped Al₂O₃ crystal as an active laser medium presents several advantages, which makes it a very feasible choice in the construction of nowadays ultrafast lasers. First of all it exhibits a broadband gain/emission spectrum centered at 790 nm (see figure 4.7) and therefore having the capability to produce ultrashort (femtosecond) laser pulses. Generally, the laser pulse duration \( \tau_p \) is determined by the time-bandwidth product \( \Delta \nu \cdot \tau_p \geq C \), where \( \Delta \nu \) represents the spectral bandwidth and \( C \) a constant factor that depends on the pulse profile e.g. \( C=0.441 \) for a gaussian pulse. Thus broader the spectral profile shorter is the laser pulse. Also, the excellent thermal properties and hardness makes from Ti:Sapphire the most utilized solid state laser material in building femtosecond laser oscillators and amplified laser systems.

The pulsed operation of Ti:Sa laser is obtained by means of the so-called mode-locking technique. This describes the operation of the laser with all the resonator frequency modes
Figure 4.8: Illustration of the optical Kerr effect in the soft-aperture type of mode locking. The Kerr medium acts as a lens on the focused laser beam, producing a selective amplification of the higher intensity modes. These ones experience a bigger gain than the lower ones having the largest overlap with the excited gain medium.

Phase locked (under the gain envelope). As a competing regime is continuous wave (CW) mode, when exists a arbitrary phase among the cavity modes. Mode locking is achieved through the *nonlinear optical Kerr effect* which produces the

- self focusing
- self-phase modulation

of the pump laser intracavity mode in the Ti:Sa crystal. This is due to dependence, in the high intensity regime, of the refractive index on the intensity according to the following relation:

\[ n(\omega, t) = n_0(\omega) + n_2 I(\omega, t) \]  

(4.1)

with \( n_2 \sim \chi^{(3)} \) where \( n_0 \) and \( n_2 \) are the normal (complex) and the nonlinear part of refractive index, respectively, while \( \chi^{(3)} \) is the third-order nonlinear susceptibility tensor that describe the bulk optical properties of the crystal (see chapter 3).

How the self focusing works is illustrated in the figure 4.8. As it travels through the nonlinear medium with a \( n_2 \) positive, the gaussian shaped laser pulse *i.e.* higher intensities in center then at the edges, encounters regions with different refractive index, which focus the beam being similar to a lens (Kerr-lens effect). Thus, the stronger intensity modes will experience a stronger focusing than the weaker ones which implicitly results in lower amount of losses for the former ones. This together with the insertion of a variable aperture in the cavity, suppress the weak intensity modes and the competing CW mode. This method is known as hard-aperture mode locking. The intrinsic character of self-focusing can be used for mode-locking without introducing any additional element in the laser cavity. The excited region of the gain medium forms by itself an "aperture" determined by spatial variation of the refractive index across the incident gaussian wavefront. Using this property one can initiate ML operation of the laser, this method being known as soft-aperture mode locking. The construction of the oscillator used in this work is based on the latter mentioned type of mode locking.

Beside the self-induced spatial variation of the refractive index *i.e.* self-focusing, there is also a variation in time due to the temporal distribution of the intensity in an ultrashort
4.2 Laser system

Figure 4.9: The cross-correlation signal (dots) between the pump and probe pulses measured on the gadolinium sample. Fitting (solid line) the CC curve with a gaussian one obtains a pulse duration of 33 fs.

laser pulse. This produces a change in the phase of the electric field of the pulse in a similar manner as in the aforementioned self-focusing: distribution in the intensity at the leading and the falling edge of the pulse results in the appearance of new frequency components in the pulse i.e. a chirped pulse. This is equivalent to a broader spectral width of the pulse that gives the possibility of generation of even shorter laser pulses. The ultimate pulse duration is given by the subtle interplay of the above mentioned phenomena with the group velocity dispersion (GVD), this point being discussed in the next paragraph.

Hence, the intensity dependent losses in the laser medium give rise to the initial build up of the pulsed regime. But the steady state operation of the laser depends on a series of factors. Generally speaking, the laser pulse duration is determined by the competition between group velocity dispersion and the quality of self-focusing in laser cavity. Taking into account the large emission bandwidth (according to the figure 4.7) of the Ti:Sapphire medium and the time-bandwidth product, pulses of 4 fs duration could be generated. But the positive GVD encountered by the laser pulse while it travels in the resonator, makes the pulse much longer. This limitation can be compensated, to some extent, by introducing in laser cavity optical components producing a negative GVD e.g. a prism compressor. Depending on the prisms material the compensation of positive GVD can be make up to second order dispersion term. Higher orders dispersion can be compensated by using chirped mirrors. Hence, having the prisms as an active control over GVD delay is possible to generate pulses as short as 10 fs. With the actual oscillator configuration pulses around 35 fs are produced as can be deduced from cross-correlation curves measured directly on the sample (see figure 4.9).
4.2.2 Cavity-dumped Titanium:Sapphire oscillator

The cavity-dump version of the Ti:Sapphire laser is an intermediate solution between the high repetition rate but low pulse energies delivered by oscillators (≈80 MHz repetition rate and few nJ pulse energy) and the amplified systems with variable repetition rate and high peak powers (hundreds of KHz repetition rate and pulse energy in the mJ range). This cavity-dump variant is well suited for nonlinear optical experiments and in general for time-resolved experiments because it provides ultrashort laser pulses at a variable repetition rate with a medium pulse energy and more important keeping the thermal load of the sample at insignificant levels. The cavity dump version of the Ti:Sa oscillator used in this work is schematically illustrated in the figure 4.10.

The oscillator is constructed in a X configuration with two asymmetric length branches. For pumping the Ti:Sa crystal, the second-harmonic (532 nm) of a diode laser (Millenia 5W, Spectra Physics) is used, which is coupled into the oscillator via a periscope. This serves also as a polarization rotation device, the output pump laser polarization being perpendicular to the plane of laser table. The CW pump beam is focused on to the Ti:Sa crystal, which is Brewster-oriented for minimizing the losses due to reflection. The optical resonator comprises six mirrors: two spherical mirrors around the Ti:Sa crystal, that
are highly transmissive for pump light (532 nm) and highly reflective for laser radiation centered at 800 nm; another two high reflective (HR) mirrors enclose the cavity with one of them acting as an output coupler (OC). Depending on the used configuration i.e. cavity dumping or normal oscillator regime the OC transmission has been 4\% or 10\%, respectively. In addition, two curved mirrors are inserted in the shorter arm which form the Bragg cell together with a fused silica crystal. The dumped pulse train is deflected out of the oscillator by the pick-off mirror. In the longer arm a combination of two fused silica prisms mounted in a double-pass configuration are installed for GVD compensation. This material possess a small third order dispersion therefore having a small contribution to the pulse broadening. A knife is inserted before the second prism in order to tune the laser wavelength. The residual light reflected from the knife detected by a photodiode, is used to monitor (with an oscilloscope) the pulse train in the oscillator. The mode-locking regime is initiated by slightly tapping the high reflective mirror, that encloses the oscillator cavity. This can be done also by moving back and forth the prism in the laser beam at the dispersive branch of the resonator. In order to improve stability of the laser running in the mode-locked regime, the oscillator is covered with a plastic box, which stops any air flow and dust particles to enter in the laser cavity.

Coming back to the cavity dumper regime, the underlying physical principle is the diffraction of laser light from an acoustically induced optical grating i.e. spatially modulation of the refractive index in the crystal. The acoustic wave is produced by a piezoelectric transducer attached at the bottom of the fused silica crystal. For this regime an output coupler with 4\% transmission has been installed, which decreases the losses compared to the normal oscillator mode (a 10\% OC is used) and thereby increasing the amount of energy stored in the cavity. By switching on and off the high frequency acoustical wave, the first order diffracted pulse train is coupled out of the cavity. An example of such dumped pulse train is presented in the figure 4.11.
With this method the pulse energy could be increased by roughly one order of magnitude with little effect on the pulse duration. Without the Bragg cell installed in the laser cavity, the oscillator could deliver pulses around 25 fs duration [127]. In principle, additional dispersion introduced by the Bragg cell can be compensated by increasing the separation length between prisms or using chirped mirrors. However, the 35 fs pulse duration is enough for the purposes of the present thesis. The cavity dumper regime has been implemented with the help of the above mentioned Bragg cell controlled electronically by a driving unit (APE Berlin). This one is synchronized at the repetition rate of the laser, being triggered by the signal of a fast photodiode. In the feed-back circuit an amplifier and a constant fraction discriminator are employed due to the low signal level during dumping and that keep a clean triggering signal. The jitter of control unit is smaller than 50 ps with an electronic rise/fall time around 2 ns which is small compared to round trip in the oscillator 13 ns. Variable dumping repetition rates in the range of 1:20 to 1:5000 with regard to seeding laser frequency are available with the present setup. Similar diffraction efficiencies were obtained with the 1:50 and 1:100 ratios, which have been used in this work. These two ratios that correspond to 1.52 MHz and 760 KHz repetition rates, respectively, have been selected since they provide a high pulse energy with a negligible thermal load of the sample and, very important, a stable operating regime of the oscillator. For more technical details about the oscillator construction the reader is referred to Uwe Conrad’s thesis [127].

4.3 Pump-probe scheme for TR measurements

The layout of the optical pump-probe scheme together with the laser beam paths on the laser table, in the UHV chamber and in the detection block are depicted in the figure 4.12. The UHV chamber is installed near by the laser table.

At the exit from the oscillator a second prism compressor is installed for compensating any additional GVD acquired along the optical path from oscillator to the sample e.g. air, mirrors, UHV window. The prisms are made of SF11 material which provide, in a double-pass path, a negative GVD in order of -4550 fs$^2$ [127]. Here, a reference channel detecting the SHG signal from a nonlinear crystal is installed, in order to monitor the fluctuations in the laser intensity. It consists of a beam splitter, lens, beta barium borate (BBO) crystal and a photodiode. A small part of the laser output is reflected by the beam splitter onto the lens and focused in the BBO crystal, that produces SHG in transmission which is detected by the photodiode.

The layout of the pump-probe scheme is shown in figure 4.12: after a beam splitter which separates the pump and probe beams in a 4:1 ratio, the pump beam is delayed with respect to probe by a delay stage (Physik Instruments). The smallest delay step is 0.5 fs. A chopper working at a frequency of 700 Hz, is inserted in the pump beam that makes possible to measure pump-induced variations of the detected signal i.e. to measure the probe signal for on and off pump. From here, both beams are directed to the UHV chamber in a collinear manner and focused on the sample using a plano-convex lens (fused silica f=100 mm). For a better focusing condition a special flange has been designed, which allows positioning of the focusing lens very close to the sample. Hence, a
4.3 Pump-probe scheme for TR measurements

Figure 4.12: General view of the optical setup on the laser table. In the lower part the laser oscillator together with the reference channel (P-photodiode, BBO nonlinear crystal), prisms compressor and the pump-probe scheme, while in the upper part the beams path (λ/2 half-wave plate, λ/4 quarter-wave plate) in the UHV chamber and in the detection block (P-photodiode, A-analyzer, F-filter, M-monochromator, PMT-photomultiplier tube) are depicted.
bigger laser fluence is obtainable: $\sim 0.9 \text{mJ/cm}^2$ for a focus diameter of $\sim 70 \ \mu\text{m}$ and a pump pulse energy of 34 nJ. The focus quality and the position of the laser beams on the sample is checked with a microscope and a CCD (charge coupled devices) camera. This imaging part is used also for the spatial overlap of pump and probe beams on the sample. At this point is worthwhile mentioning the way of determination of the beam diameter in focus. Due to the actual configuration of the setup we had to measure the focused beam diameter on the laser table by using the sliding knife-edge technique [128]. The laser optical path to the sample has been mimic by using the same focusing lens and the same type of UHV window as in the real setup. For the single-beam scheme the obtained beam diameter is $\approx 52 \ \mu\text{m}$ while for the pump-probe scheme a diameter of $\approx 70 \ \mu\text{m}$ has been deduced. The last result is presumably due to the fact that the collinear pump and probe beams are incident on the focusing lens in off-centered positions and thus a less efficient focusing condition is encountered. Hence the resulting laser fluences for the single-beam and pump-probe schemes are $\sim 2 \text{mJ/cm}^2$ and $\sim 0.9 \text{mJ/cm}^2$, respectively.

A stable and flexible optical table has been made, that is attached to the UHV chamber, on which the mirror that directs the beams to the chamber and the focusing lens are mounted (typically). Due to its design the optical table offers a higher degree of freedom in collimating and focusing the laser onto the sample, allowing various optical items and optical schemes (e.g. SHG phase measurement in chapter 5) to be installed. After hitting the sample at $45^\circ$ incidence angle, the beams are collimated and directed to the detection part. Note, that the entrance and exit UHV windows are made of fused silica since this material exhibits a high transmittance coefficient ($\geq 95\%$) from UV throughout the visible spectral range and do not produce any residual SHG signal.

For polarization dependent measurements, and in general for changing the polarization of
4.3 Pump-probe scheme for TR measurements

the incident beams, a \( \lambda/2 \) half-wave plate is used (yellow rectangle in figure 4.12) or/and a \( \lambda/4 \) quarter-wave plate. In the detection block, a Glan-Taylor polarizer is used as an analyzer of the output SHG polarization.

The detection scheme consists of two branches: one is detecting the linear reflectivity \( i.e. \) at fundamental wavelength 800 nm (typical) and another one detecting the second harmonic (400 nm) signal. The linear reflectivity is recorded with the help of a photodiode and a lock-in amplifier whereas the SH reflectivity is measured with a photomultiplier and a photon counter. Both, the lock-in and the photon counter, are synchronized with the chopper (see fig. 4.12). The fundamental and the SH beams reflected-off the sample are separated with a dichroic mirror. For time resolved measurements, the pump and the cross-correlation signals are closed with a knife mounted on a translation stage (see figure 4.14). This can be done for both, fundamental and SHG signal, since they are reflected in a collinear geometry.

The SH signal from the sample is detected in the single photon counting mode due to the relatively low SHG efficiency from the gadolinium films. Owing to the relatively low SHG yield from Gd and Y surfaces, a special care is devoted to eliminate the potential noise in the measurement. Hence, spectral filtering and low noise level are obtained by using a monochromator together with a thick (2 mm) BK39 filter. Also the photomultiplier (R4220P Hamamatsu) has a spectral response centered at 410 nm and several orders of magnitude smaller sensitivity for 800 nm \( i.e. \) fundamental wavelength. As an additional way to avoid any environmental stray light to enter in the detection block, the whole optical scheme (together with the oscillator and the UHV chamber) is installed under a light protective tent.

The photocurrent generated by the SH photons in the photomultiplier (quantum efficiency of around 23% at 400 nm) is subsequently amplified and fed into the photon counter. Here, the signal is measured in two channels corresponding to ”on” and ”off” chopper phase. This is illustrated in the figure 4.13.

For a pump-probe measurement, opening and closing the chopper is equivalent to the detection of the probe signal for positive and negative delays, respectively (assuming chopper in the pump and the pump and the cross-correlation signal suppressed). In the case of a static measurement, during the ”on” phase the signal plus noise is detected while for ”off” phase just the noise is measured. Additional substraction of the signal measured in the two channels, remove the noise (mainly environmental) measured in the dark phase of the chopper.

A relatively similar measurement procedure is used to detect the pump-induced variations in linear reflectivity. The reflected probe beam is incident onto silicon photodiode (BPX61 Siemens) and the produced photocurrent is fed into a specially designed amplification stage. This one allows a simultaneous detection of the time-integrated \( (R_0) \) and time-modulated \( \Delta R \) linear reflectivity signal. With this setup we can resolve relative variations in the transient linear reflectivity \( \Delta R/R_0 \) down to \( 1 \times 10^{-5} \).

The entire setup is remotely controlled by a computer under a LabView programming environment. The instruments are interconnected in a GPIB (General Purpose Interface Bus) driven circuit. The LabView environment has been implemented during this work, which increases the data acquisition speed and ensures an efficient data-collection and
Figure 4.14: Schematic description of the detection geometry in the pump-probe scheme: the pump and probe beams are focussed on the sample and in reflection one can distinguish, assuming that the pump and probe are overlapped in space and time, the SHG signal coming from the pump, probe and the cross-correlation (CC) beams. These beams are denoted in the figure as having gaussian profile. For a time-resolved measurement the pump and the cross-correlation signal are blocked with the knife, only the probe signal being detected.

averaging. Therefore, the statistics in measured data has been sensitively improved, a fact that is very important for demanding measurements with an increased level of noise due to variation of an external parameter e.g. the temperature-dependent data in chapter 5. Also, for the temperature-dependent measurements and generally for the annealing procedure and running temperature ramps in the TDS measurements, a PID (Proportional Integral Differential) software has been developed. By this, an accuracy in temperature stabilization of $\pm 1$ K in the low temperature range and $\pm 0.1$ K at higher temperatures is obtained.

4.4 Measurement description

At the end of this experimental chapter, a day-by-day measurement workflow is described as is relevant for an interested reader and for getting a better understanding regarding the entire experimental setup.

After the Gd(0001) thin film is deposited and annealed, the crystalline quality is checked with LEED. The next step is to align the oscillator, first getting the optimal output power in CW mode and afterwards in the mode-locked mode. The laser wavelength is tuned and the spectral shape of the pulse is displayed with the help of CCD spectrometer and the PC monitor. In the case that one runs the oscillator in cavity-dump regime, the pick-off mirror is slightly inserted in the laser beam. Running a cw acoustical wave through the fused silica crystal in the Bragg cell, one can mimic the normal CD regime, and by this the output power can be checked. The power is optimized by changing the $z$ position, the rotation coordinate and the tilting angle of the Bragg crystal, trying to get the maximum power and in the same time a stable laser regime. Afterwards, a more fine adjustment is done by varying the parameters of cavity-dumper control unit i.e. phase, delay, acoustical pulse width.

In the next stage, the alignment of the external compressor is done, which is made by positioning the laser beam on the standard height (pinhole like) plates, and keeping the beams at the very edge of the prisms in order to get as small as possible the positive GVD. In case of a time-resolved measurement, the pump-probe scheme is employed by inserting a pair of mirrors in the laser beam path, and the shape and parallelism of pump
and probe beams are verified. After this, the beams are guided to the UHV chamber from where are focussed onto the sample. Focussing is made with the entrance lens, mounted on a special holder which allows movement in $x$, $y$, and $z$ directions. The reflected beam from the sample is adjusted in the detection block by rotating the sample and optimizing the position of the collimating lens. The position and the overlap of the beams on the sample are checked with the microscope and the CCD camera. The photon counter and the high-voltage power supply of the photomultiplier are turned on, and the SHG signal level is measured in the two channels, which correspond to pump on/off or signal+noise and dark-phase noise (see preceding section) for the one-beam scheme. The probe signal is optimized by moving the focusing lens and also adjusting the prisms position in the external compressor, that compensate the positive GVD. After this, the pump signal is closed with the knife and the cross-correlation signal is optimized by overlapping the pump and probe beams on the sample. At this point, the CC curve is measured and the zero time delay between the pump and probe pulses is checked and eventually modified. After the zero delay is set, the CC signal is also closed, the photon counter measuring just the probe signal for open and closed pump. The last point is to optimize the signal from photodiode, that measures linear reflectivity. After all this sequential steps have been performed, one can starts the time-resolved (static) SHG and LR measurements.
5 Electron, lattice and spin dynamics on Gd(0001)/W(110)

This chapter is devoted to the static and dynamic nonlinear magneto-optical investigations of the ferromagnetic Gd(0001) system. In the first part the static properties of the system as measured by MSHG are detailed while the following part of the chapter is focused on the time-resolved response of the system. Here the ultrafast magnetization dynamics encountered at the Gd surface and the newly discovered phenomenon of the coupled coherent phonon-magnon mode, that evolves in the THz frequency range, are described.

5.1 MSHG on Gd(0001): static properties

Before starting any time-resolved investigation of a certain system, a detailed knowledge about its characteristic static properties is necessary. With respect to the MSHG investigation of ferromagnetic materials, precise information regarding the polarization dependence of the SHG yield and magnetic contrast as well as the behavior of the relative phase between the even $E_{\text{even}}(2\omega)$ and odd $E_{\text{odd}}(2\omega)$ second-harmonic fields are required. For instance, information about the origin of the SHG response can be retrieved from polarization dependent measurements of the SHG intensity since this quantity is sensitive to e.g. surface symmetry, electronic structure and photon energy [129]. Furthermore, the magnetic contrast defined in eq. 3.34 renders the magnitude of the magnetic effects in the investigated region. The relative phase $\phi$ between the SHG fields is of utmost importance since together with the SHG intensity (see formula 3.33) provides a complete characterization of the nonlinear response of the system. By investigating the photon energy dependence of the phase $\phi$, the presence of a resonance in the SHG process can be detected [102, 106].

In this section, the quantities characterizing the MSHG static response (i.e. polarization dependence, magnetic contrast and the relative phase $\phi$), measured on the Gd(0001) surface under an UHV environment, will be presented.

As a reminder, all the measurements presented in this chapter are performed in situ on 20 nm Gd films grown epitaxially on W(110) substrate, in a transversal configuration at 45° incidence angle with the external magnetic field oriented along magnetization easy axis, unless otherwise specified.

5.1.1 Polarization dependent MSHG response

The first issue one should investigate when working with magneto-optics on ferromagnetic materials is the existence of a measurable magnetic contrast. This can be done simply by measuring the magnetization hysteresis that renders not only the value of the magnetic
contrast but also information about magnetic anisotropy, magnetization orientation [114] etc. In the case of Gd(0001) thin films, we have been primarily interested in the orientation of the magnetization easy axis direction. At the employed film thickness of 20 nm, the easy axis of magnetization is oriented in the film plane [130] its direction being determined by the higher demagnetization energy compared to the magnetocrystalline anisotropy. As a check for this, a MSHG hysteresis has been recorded by measuring the SH intensity as a function of the applied external magnetic field. The MSHG measurements has been performed in the transversal geometry (with magnetic field in the plane of the sample) in a p-T polarization configuration (p-polarized input fundamental, SHG detected without preferential polarization). One such example is presented in figure 5.1 where one notices immediately the square shape of the hysteresis that indicates a measurement performed along easy axis, and thus the orientation of magnetization in the plane of the sample.

After this initial check one can proceed to the polarization dependent MSHG measurements. One information that can be retrieved from polarization dependence of the SHG response is related with the structural symmetry of the surface. Also valuable information can be deduced regarding the optimal experimental geometry in terms of SHG intensity, magnetic contrast, the particular susceptibility $\chi^{(2)}$ tensor elements involved etc. In the following the polarization dependent MSHG measurements performed on Gd(0001) are presented.

The measurements described in this section are performed at a sample temperature of 110 K (well below Curie point of 293 K) and with the femtosecond laser running in the oscillator regime (see chapter 4). Although in this regime the laser pulse energy is smaller ($\approx 6$ nJ) than for the cavity dumper ($\approx 42$ nJ) due to the higher repetition rate (76 MHz) the produced SHG yield is higher\(^1\). This is required since one can encounter certain polarization configurations where the SHG efficiency is low and therefore a higher incident power is useful. For the polarization measurements a combination of $\lambda/2$ plate and a Glan-Thompson polarizer is used, that are inserted in the fundamental (laser beam

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\(^1\)According to eq. 3.24 the SHG signal scales proportionally with the incident laser pulse energy and inverse proportionally with the laser beam diameter and pulse duration.
5.1 MSHG on Gd(0001): static properties

Figure 5.2: Variation of the SHG signal (upper panel) and magnetic contrast (lower panel) as a function of analyzer angle for a p-polarized fundamental measured on a 20 nm Gd(0001) film at a temperature of 110 K. The solid lines are guide for the eye.

of $\omega$ photon frequency) and the SH beam, respectively. The $\lambda/2$ plate is used to rotate the polarization of the incident laser beam whereas the Glan-Thompson polarizer is analyzing the polarization of the output SH signal. The measurements are done either by varying the polarization of the fundamental and detecting the SHG signal at a fixed polarization orientation (P or S polarized output)\(^2\) or the opposite way. The azimuthal dependence of the SHG yield \textit{i.e.} as a function of sample rotation, could not be investigated since the sample mounting system in the UHV chamber does not offer such a capability. In principle one can circumvent this drawback, by simultaneous variation of the polarization and analyzer angle for fundamental and SH beam, respectively, and thus obtaining the same information as measuring the SHG azimuthal dependence.

In figure 5.2 the behavior of the SHG intensity and of the magnetic contrast as a function of analyzer angle is depicted for an incident p-polarized fundamental laser beam. In the upper part of the figure the SHG yield for opposite magnetization direction is shown. In the p-P geometry the contribution of the susceptibility tensor components (see table 3.2)\(^2\)The capital letters denote the SHG polarization orientation whereas small letters are used for fundamental beam polarization.
Figure 5.3: Variation of the SHG signal (upper panel) and of the magnetic contrast (lower panel) as a function of analyzer angle for a s-polarized fundamental beam. The solid lines in the top panel represent the fitting curves according to eq. 5.1.

to the SH signal interfere constructively that together with the bigger amplitudes of the Fresnel factors (eq. 3.21) for p-polarized fundamental and SH light produces a high SHG yield. As expected, for p-P polarization geometry the highest SHG signal is obtained. The magnetic contrast displayed in the lower panel is around 10% for p-P, a value that stays almost constant (within scattering of the data points) for all SHG polarization directions. The exception is the p-S geometry where the SHG signal and the magnetic contrast become zero since in this configuration no SHG tensor component is allowed (see table 3.2) i.e. due to symmetry constrains for this particular polarization combination.

The situation for a s-polarized input is presented in the figure 5.3. In comparison to the case of p-polarized input, the SHG intensity is one order of magnitude lower while the magnetic contrast is increased by at least a factor of two. Another difference compared with the previous case relies on the appearance of a shift between the curves for up and down magnetization direction. This shift represents the nonlinear Kerr rotation (analogous to linear MOKE) that is evaluated to 7±1 degrees. For the p-polarized input no Kerr rotation can appear since the even and odd tensor components give a P-polarized component (see


Figure 5.4: Variation of the P-polarized SHG signal (upper panel) and of the magnetic contrast (lower panel) as a function of polarizer angle measured from a clean Gd(0001) film. The solid lines are guide for the eye.

tabulated 3.2) to the total SHG signal. The value of the Kerr rotation is deduced from fitting the data with the expression (deduced from eq. 3.21):

\[ I_{\alpha}(2\omega, \pm M) = F_1 \cdot \cos^2(\alpha \pm \delta) \cdot \pi/180 + F_2 \]  

(5.1)

that renders the SHG signal amplitude through \(F_1\) and the Kerr angle \(\delta\). In the argument of the cosine function \(\alpha\) is the analyzer angle and while \(F_2\) is an offset included for a better fitting.

Summarizing this part, the p-P polarization combination gives the highest contribution to the SH signal with a relatively high magnetic contrast. Although the magnetic contrast is larger in the s-P configuration the SHG efficiency is low and therefore this geometry is not reliable for further pump-probe measurements. Since we are primarily interested in a high SHG intensity, the p-P configuration has been chosen as the experimental geometry for all the following static and time-resolved experiments performed in this work.

Generally, owing to its sensitivity, SHG is used to study the symmetry of the surface.
Figure 5.5: Variation of the P-polarized SHG signal (upper panel) and of the magnetic contrast (lower panel) as a function of polarizer angle measured from an oxidized (1 L O₂) Gd(0001) film. The solid lines are guide for the eye.

For this type of measurements, a clean and an oxygen-covered Gd(0001) surface have been investigated. The idea is that upon oxidation the exchange-split surface state is shifted in energy below Fermi level (both components are occupied) but remaining exchange-split [31, 124]. Consequently the possible resonance in the SH generation pro-
cess will be lost. The Gd(0001) surface is oxidized upon exposing it to a nominally 1 Langmuir (1L=10^{-6}torr s) of oxygen at a sample temperature of 300 K. The oxidation of Gd(0001) surface results in a dramatic adsorbate-induced change of the surface electronic structure that affects the energetic position of the surface state. Therefore, the totally different electronic surface configuration obtained after oxidation might be used as a check for the SHG resonance enhancement. The results obtained for a clean and O₂ covered Gd(0001) surface for a P-polarized SHG output are depicted in figure 5.4 and 5.5, respectively. First, one notices the 10-times higher SHG signal generated from the clean Gd film in comparison to the oxygen-covered surface. Furthermore, two small additional peaks appear with the maximum centered the s-P orientation, that shows a 4-fold symmetry of the oxidized surface region which generates the SH signal. Regarding the magnetic contrast, a decrease of ≈35% is observed upon oxidation with the appearance of additional maxima. This value is in a good agreement³ with the measurements of the surface oxide layer magnetization performed with magnetic circular dichroism in photoemission [124], that gives a reduction of ≈50% of magnetization relative to the clean Gd(0001) surface.

A general conclusion that can be drawn is related with the sensitivity of the SHG process to the surface electronic structure. After the formation of the oxide layer, the surface state is shifted below Fermi level [27, 124] with the majority and minority components positioned (for T=80 K.) at -0.8 eV and -0.35 eV binding energies, respectively [124]. The used photon energy (1.55 eV) does not match the energetic separation between the oxygen-formed surface state and the unoccupied d band positioned ≈1.5 eV above E_F (see figure 5.11). Therefore, the SHG optical transitions evolve non-resonant in this case and consequently the SHG efficiency is low. Thus, one can suggest that for the case of a clean Gd surface the SHG process evolve resonantly enhanced. In order to prove this proposal the MSHG phase measurements are required, which is the topic of the next section.

5.1.2 Phase-sensitive MSHG measurements

As mentioned earlier in this chapter, the relative phase \( \phi \) between the even \( E_{even}(2\omega) \) and odd \( E_{odd}(2\omega) \) SH fields constitutes an important parameter that together with the SHG intensity provides a complete description of the MSHG response from a ferromagnetic sample (see eq. 3.33). Therefore, a simultaneous measurement of the SH intensity and phase is a prerequisite for the identification of a resonance in the SHG process and for a detailed understanding of the investigated system. In this section, the MSHG phase measurements performed on epitaxially grown Gd(0001)/W(110) thin films under UHV conditions are presented. The first part gives a short introduction regarding the phase concept in a SHG experiment and the practical modalities of measuring it. Thereafter, the actual phase measurements on Gd(0001) and the data analysis are presented in a step-by-step manner. Based on the combined measurements of the SH yield, relative phase and magnetic contrast we will show how one can conclude about the presence of a resonance in the SHG process.

We have seen in chapter 3, that the SHG response from a magnetized sample consists of even \( \chi^{(2)}_{even} \) and odd \( \chi^{(2)}_{odd} \) contributions i.e. which behave symmetric and anti-symmetric

³Accounting for the different depth sensitivity of the SHG and the photoemission techniques.
with respect to magnetization reversal, respectively. In other words, the \( \chi_{\text{odd}}^{(2)} \) exhibits a phase shift of 180° upon magnetization reversal \( i.e. \) it changes the sign, whereas \( \chi_{\text{even}}^{(2)} \) is unaffected. These effective susceptibility tensors (see eq. 3.18) are linear combinations of tensor components multiplied by the corresponding Fresnel factors \( f_{ijk} \) (see eq 3.21). They determine the SH field that can be written as:

\[
E(2\omega) \propto \sum_{i,j,k} f_{ijk} \chi_{ijk} \equiv \chi_{\text{eff}}
\]

(5.2)

Since the emitted SH field is a complex quantity (the Fresnel coefficients and the susceptibility tensors are complex numbers) one can write its expression in terms of amplitude and phase as:

\[
E(2\omega) = |E(2\omega)|e^{i\varphi}
\]

(5.3)

with the phase \( \varphi \) being the sum of phases of all the complex numbers involved in eq 5.2. Now one can see that measuring the SH intensity \( I(2\omega) \propto |E(2\omega)|^2 \) the phase content is lost. However, employing interferometric techniques the phase information can be retrieved [131, 132, 133].

In a MSHG experiment the measured observable is the magnitude of the SHG signal for opposite magnetization directions. For sake of clarity we write again the expression of the SHG intensity as:

\[
I_{2\omega}^{\uparrow \downarrow} \propto |E_{\text{even}}(2\omega)|^2 + |E_{\text{odd}}(2\omega)|^2 \pm 2|E_{\text{even}}(2\omega)||E_{\text{odd}}(2\omega)| \cos \phi
\]

where \( I_{2\omega}^{\uparrow \downarrow} \) denotes the SHG intensity for up and down magnetization directions and \( \phi \) is the relative phase between the even and odd SH fields. It is immediately obvious that the phase information can not be obtained directly by measuring only the SH intensity, since we do not have an independent information about the \( E_{\text{even}} \) and \( E_{\text{even}} \). Therefore, one has to employ the interference between the SHG light generated from the sample and from a reference source (usually a nonlinear crystal) in order to recover the phase information. For understanding of the relative phase concept in the framework of a MSHG experiment.
5.1 MSHG on Gd(0001): static properties

Figure 5.7: Schematic description of the time-domain (left) and frequency-domain (right) phase measurements. For time-domain measurements the pulses at $\omega$ and $2\omega$ are temporally overlapped (also spatially overlapped on the sample S) and the interference pattern (due to the dispersion of air between S and R) is obtained by translating the reference crystal (R). Frequency-domain phase measurements are necessary due to the presence of the UHV window that produces a time delay $\Delta t$ between the pulses of duration $\tau$. The frequency-domain interference pattern has a width $\approx 1/\tau$ and a period of modulation $\approx 1/\Delta t$. The reference crystal is fixed.

Let us have a look at the figure 5.6. Here the even $E_{\text{even}}$ and odd $E_{\text{odd}}$ SH fields are plotted as vectors in the complex plane together with their sum $E(\mathbf{M}) = E_{\text{even}} + E_{\text{odd}}$ that determines the measured signal. Upon magnetization reversal the odd component changes the sign $-E_{\text{odd}}(-\mathbf{M})$ and consequently a phase shift $\theta$ between $E(\mathbf{M})$ and $E(-\mathbf{M})$ will appear. The relationship between phase shift $\theta$ that is measured in an interferometric MSHG investigation and the relative phase $\phi$ between $E_{\text{even}}$ and $E_{\text{odd}}$ is given by:

$$\cos \phi = \frac{1 - I^\dagger/I^\dagger}{\sqrt{(1 + I^\dagger/I^\dagger)^2 - 4(1 + I^\dagger/I^\dagger)^2 \cos^2 \theta}^{1/2}}$$

(5.4)

Another quantity of interest here is the magnetic contrast that can be directly obtained by measuring the SHG intensity for opposite magnetization directions. In connection with the relative phase $\phi$ it carries useful information regarding the relative contributions of the even and odd SH fields to the total SHG response, that can be deduced from the formula:

$$\rho = \frac{I^\dagger(2\omega) - I^\dagger(-2\omega)}{I^\dagger(2\omega) + I^\dagger(-2\omega)} = 2 \frac{E_{\text{odd}}/E_{\text{even}}}{1 + (E_{\text{odd}}/E_{\text{even}})^2} \cos \phi \approx 2 \frac{E_{\text{odd}}/E_{\text{even}}}{\cos \phi}$$

(5.5)

where the assumption $(E_{\text{odd}}/E_{\text{even}})^2 \ll 1$ (see chapter 3) has been used. This assumption is demonstrated later in this section. Therefore, knowing the phase and contrast one can evaluate the ratio between the magnetic and nonmagnetic components $E_{\text{odd}}/E_{\text{even}}$ of the SHG response. Moreover, once the ratio $E_{\text{odd}}/E_{\text{even}}$ is deduced we can disentangle the
values of the $E_{\text{even}}$ and $E_{\text{odd}}$ second-harmonic fields, since $E_{\text{even}}$ is easily obtained from $E_{\text{even}} \approx \frac{I_{\uparrow} + I_{\downarrow}}{2}$. In the following the measured data will be presented in terms of the relative phase $\phi$ and the ratio $E_{\text{odd}}/E_{\text{even}}$.

**How to measure the relative phase $\phi$?**

As has been discussed in the beginning of this section, by measuring the intensity alone the phase $\phi$ content of the SHG response is lost. However, it can be detected in an interferometric manner [131, 133] using the SHG signal produced by a nonlinear reference source. As shown schematically in the figure 5.7 left, by superimposing the SHG signal from the sample and from the reference source, an interference pattern is observed when the optical phase delay between the pulses is varied. The optical phase delay arises from the different phase-velocity dispersions of the medium (air in this case) for the propagating fundamental and SH light. Alteration of the optical phase delay can be done either by changing the refractive index of the medium or by varying the reference source-sample distance [131] (as in the figure 5.7). Such a time-domain measurement is conditioned by the time-overlap of SH pulses. This condition is not fulfilled when a strong dispersive element is involved in the experimental scheme e.g. when the phase measurement is performed under UHV conditions (see figure 5.7 right). Due to the different group-velocity ($v_g$) dispersion in the UHV window for the fundamental and the second-harmonic beam, a time delay $\Delta t = d(v_1^{-1}(2\omega) - v_1^{-1}(\omega))$ appears between the pulses. Such a time delay is usually much bigger than the width $\tau$ of the laser pulses and consequently the time-domain interference is lost. Nevertheless, for measurements performed under UHV conditions the interferometric phase detection can be done in the frequency domain.

As was first demonstrated by Veenstra et al. [133], one can use the fact that in the frequency domain the femtosecond pulses have a broad bandwidth. Thus, a time delay $\Delta t$ between the laser pulses (of width $\tau$) is equivalent in the frequency domain to a spectral interference pattern of $1/\tau$ width, modulated at $1/\Delta t$ frequency (see figures 5.7 right and 5.8 middle). The phase of the modulation can be retrieved without the need to translate the reference source. In the measurements presented here a $z$-cut quartz crystal (0.25 mm thick) is used as a reference source, providing a large enough SHG intensity in order to match the level of SHG signal arising from the sample.

An example of spectral interferogram measured on Gd(0001) surface at $T=100$ K for up and down magnetization directions is displayed in the figure 5.8 middle. For this particular measurement the wavelength of the fundamental pulse is centered at 815 nm. One observes the interferogram peaks separated by an interval of 1.02 nm that corresponds to a time delay $\Delta t$ of 0.5 ps superimposed on spectral envelope of 6.32 nm HWHM (half-width half-maximum). The phase shift $\theta$ is obtained in the following way: the measured interferometric pattern is Fourier transformed and the so-called autocorrelation function [133] is obtained that exhibits a central peak with two satellites situated at $\pm \Delta t$ as displayed in the inset of figure 5.8. The central peak reflects the envelope of the laser pulse in

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4Optical phase delay is given [133] $P(d) = \frac{4\pi\Delta n_{\text{air}}d}{\lambda}$ where $\Delta n_{\text{air}}$ is the difference in the refractive index for fundamental and SH beams, $d$ is the beams travelling distance, $\lambda$ the fundamental wavelength.

5For a fused silica window of 3 mm thickness and a pulse duration of 35 fs of the fundamental beam, the resulting delay $\Delta t$ is around 0.5 ps.
5.1 MSHG on Gd(0001): static properties

Figure 5.8: Example of interferometric pattern (middle panel) as measured on Gd(0001) surface for up (solid curve) and down (dotted curve) magnetization directions. The inset shows the Fourier transform of the modulated interference spectrum. The pure oscillatory component (middle panel) of the raw data results from the back Fourier transform of the satellite peaks displayed (framed) in the inset. The resulting phase shift $\theta$, displayed in the top panel, is extracted by making the difference of the oscillatory data obtained for opposite magnetization direction at their zero point. For clarity, a zoom in the framed region of the oscillatory component is depicted in the lower panel.
Figure 5.9: The spectral dependence of the relative phase $\phi$ (solid line) and of the amplitude ratio $E_{\text{odd}}/E_{\text{even}}$ measured on Gd(0001) at 90K.

The measured values of the relative phase $\phi$ between 1.48 eV and 1.68 eV fundamental photon energy, determined as described above, are plotted in the figure 5.9. From the magnetic contrast, that is measured simultaneously with the relative phase (deduced from the SHG yield), the $E_{\text{odd}}/E_{\text{even}}$ ratio is calculated according to eq. 5.5. Hence, we plot together with the relative phase also the dependence of the $E_{\text{odd}}/E_{\text{even}}$ ratio on the photon energy. The spectral dependence of the magnetic contrast and of the SHG intensity are displayed separately in the figure 5.10.

The main purpose of the spectral investigation of the relative phase and SHG yield is to determine whether or not the SHG process evolves resonantly at the Gd(0001) surface. As was shown in chapter 3, the presence of a resonance in the SHG optical transitions
results in an increased magnitude of the susceptibility tensor and a phase change of 180°, as the optical transitions crossed the resonance (see figure 3.2). The magnitude of $\chi^{(2)}$ is reflected in the SHG intensity and therefore one expects an increased SH signal at the resonance. In a real experiment, the increased SHG yield, solely, can not be considered as an indication for the presence of a resonance since it can be influenced by many factors e.g. morphology, adsorbates etc. However, the simultaneous observations of a phase change and an increased SHG signal as the incident photon energy is varied, it is considered as an evidence for the resonance [106, 102].

Such a behavior is observed for the SH signal on the Gd(0001) surface, as shown in the figure 5.10. Over the investigated photon energy range, the SHG intensity increases gradually by almost one order of magnitude, from 1.48 eV with a maximum around 1.67 eV. Simultaneously, the relative phase, displayed in figure 5.9, varies within an interval of 150°. The dependence of the relative phase $\phi$ on the photon energy exhibits a complex structure by changing its sign several times and showing pronounced modulations between 1.62-1.66 eV. Such phase changes are difficult to interpret as a resonance signature. However, the magnetic contrast varies strongly with the photon energy showing a sign change, that is a typical signature at the resonance [102, 106], in the region of maximum SHG intensity. Accounting for the behavior of the SHG signal and magnetic contrast (see fig. 5.10) we deduce that the resonance maximum is around 1.7 eV which is also confirmed by the DOS structure in fig. 5.11.

Although the spectral dependence of the phase is within 150°, does not show a gradual variation as has been measured for longitudinal geometry [102]. This behavior might arise
Figure 5.11: The valence electronic structure of Gd(0001) at Γ as measured by photoemission [17], inverse photoemission [32] and scanning tunnelling spectroscopy [48]. The arrows involving the exchange-split bulk state and the surface state close to $E_F$ depict the fundamental optical transitions at a photon energy of 1.5 eV that define the spin-up and spin-down contributions to the SHG response (see text). For clarity, the other optical transitions of the SHG process are not shown here. The resonant SHG process, enhanced by the unoccupied $S^\downarrow$ surface state component as an intermediated state, is displayed in the upper part of the figure.

from the higher number of allowed tensor components (each carrying a phase content) in the transversal geometry, that can lead to a complex interplay of their phases as the photon energy is varied, which eventually gives the observed relative phase behavior. However, the combined observation of the SHG intensity, of the magnetic contrast spectral dependence as well as the dramatic SHG yield decrease upon surface oxidation (see preceding section) lead us to conclude that the SHG process encounter a resonance at the Gd(0001) surface. Our conclusion corroborates earlier MSHG measurements [102] of the Gd(0001) surface performed in the longitudinal geometry, that have shown the presence of the SHG resonance.

In order to understand how the resonance process can explain the presented results let us have a closer look at the valence electronic structure of Gd(0001) depicted in the figure 5.11. Here one sees that the optical transitions at fundamental frequency (in this case 1.5 eV) are nearly matching the energetic separation between the $5d$ bulk state and the unoccupied surface state for the spin-down channel. For the spin-up channel the optical transitions evolve between the surface state and the broad unoccupied bulk state, that is rather flat in this spectral region. Thus, the unoccupied minority surface state and majority bulk state can be considered as intermediate states for the SHG process.
Inspecting the spin-up optical transitions at the Gd(0001) surface, one notices that the final state is a broad ($\approx 1.2$ eV) and flat bulk state. On the other hand, the optical transitions in the spin-down channel evolves via a narrow surface state component (linewidth of $\approx 100$ meV at 100 K [33]). Hence, as the photon energy is increased, one can consider the spin-up transitions to have a rather constant contribution to the total SHG response in comparison to the transitions in the spin-down channel. This is due to the specificity of the Gd(0001) electronic structure within the employed photon energy. Based on these considerations, we can ascribe the strong variations in all the measured SHG quantities with the laser photon energy to the relative weight of the spin-up and spin-down optical transitions to the SHG response, with the latter ones having the dominant contribution.

This point is supported by the observed dependence of the magnetic contrast and SH signal on the photon energy. Both quantities plotted in the figure 5.10 exhibit initially a constant level between 1.48 and 1.52 eV range. Starting with 1.52 eV, that coincides with the onset of the spin-down transitions, pronounced variations in $\rho$ and $I(2\omega)$ set in, that reach a minimum respectively a maximum at 1.67 eV. The interpretation of the SHG signal dependence is based on the magnitude of the susceptibility tensor (see fig. 3.2) as the electronic transitions approach the resonance. This is described as follows. In the low photon energy range the spin-down transitions evolve off-resonant while the spin-up give a constant contribution. Increasing the photon energy, the energy separation between spin-down bulk and surface state is gradually better matched, the resonance condition is better fulfilled, that explains the SHG signal increase. Also one can interpret the SH intensity behavior in the view of equation 3.33. Here the absolute values of the even and odd fields contribute to the SH signal while the $\cos(\phi) \approx 1$ throughout the investigated energy interval (except the oscillatory feature). A simple estimation of the the contributions of the even and odd field to the total SHG intensity shows that even component prevails (is a factor of 10 to 100 higher along the investigated spectral range). Thus, the SHG intensity is mainly determined by the $E_{even}$, whose value increases with the photon energy due to the resonance presence. The variations in odd field add up to the even field and produce the observed monotonous increase of the SHG yield. But how can we explain the magnetic contrast dependence?

The variation of the SHG magnetic contrast has been shown [102, 119, 106] to be determined by the relative contributions of the spin-up and spin-down optical transitions that have different signs. Thus, the spin-up channel provides a nearly constant (due to the broad final state) and positive contribution whereas the spin-down channel contribution is negative and increases with photon energy. Starting with 1.52 eV (the onset of transition see fig. 5.11) the contribution increases considerably and eventually overcomes the positive one at 1.67 eV (see the contrast sign change in figure 5.9). The constant level of $\rho$ at 1.48 eV is also explained since for the spin-down channel, off-resonant transitions take place below 1.52 eV while the spin-up contribution is nearly constant (due to the small variations with photon energy). Consequently, we show that the balance between optical transitions involving electrons with opposite spin orientations via the surface state describes the magnetic contrast behavior. Therefore, the magnetic contrast is a measure of the spin polarization of the surface state on the Gd(0001) surface, in agreement with literature [17, 119].
The behavior of the magnetic contrast can be simulated in the framework of a simple model that describes a double resonance condition and accounts for the relative contributions of the optical transitions in the spin-up and spin-down channels. The expression used in the model reads:

\[ \rho = f_0 + \frac{f_{\text{up}}}{\hbar \omega - E_{\text{up}} + i\hbar \Gamma_{\text{up}}} + \frac{f_{\text{down}}}{\hbar \omega - E_{\text{down}} + i\hbar \Gamma_{\text{down}}} \] (5.6)

where \( \hbar \omega \) is the photon energy, \( E_{\text{up}} \) and \( E_{\text{down}} \) are the energetic separations in the spin-up (surface state-unoccupied bulk state) and spin-down (occupied bulk state-unoccupied surface state) channel at a temperature of 100 K (see figure 5.11), \( \Gamma_{\text{up}} \) and \( \Gamma_{\text{down}} \) represent the linewidth of the optical transitions determined by the convolution of the linewidth of the initial and final state with the experimental resolution (given by the laser pulse). The \( f_{\text{up}} \) and \( f_{\text{down}} \) are the factors that describe the matrix elements for the majority and minority electrons, respectively, whereas the non-resonant contribution is given by \( f_0 \). The non-resonant contribution contains the contributions from all possible optical transitions over the bandstructure. The resulting fit curve is plotted in upper panel of the figure 5.9. As discussed above, if the dependence of the contrast is determined by contributions from optical transitions involving electrons with opposite spin than the matrix elements would have also opposite signs. This result is found by fitting the contrast with the model formula. The input fixed parameters are: \( E_{\text{up}} = 1.7 \text{ eV}, \) \( E_{\text{down}} = 1.8 \text{ eV}. \) The output fit values are \( \Gamma_{\text{up}} = 2.182 \pm 0.1 \text{ eV} \) and \( \Gamma_{\text{down}} = 1.072 \pm 0.05 \text{ eV} \), \( f_{\text{up}} = 0.00337 \pm 1 \cdot 10^{-5} \), \( f_{\text{down}} = -2.312 \pm 0.006 \) and \( f_0 = 2.3772 \pm 0.006 \). Despite of the simplicity of the model we see that gives a good description of the measured magnetic contrast (see fig. 5.10) reproducing even the sign change around 1.67 eV. Moreover, it confirms our assumption of positive and negative signs of the matrix elements for the spin-up and spin-down optical transitions, respectively, that determine the spectral behavior of the magnetic contrast.

Finally, we address the modulation observed in the phase and the amplitude ratio of the SH fields. This modulation appears in the spectral range where the strength of the spin-down transitions reaches a maximum, as judged from the behavior of the SHG signal and magnetic contrast. The peak-to-peak splitting amounts to 13 meV that represents a frequency of 3.1 THz. This value is in a good agreement with the observed (reported in section 5.3 and [17]) phonon-magnon mode at the Gd(0001) surface that oscillates at a frequency of 2.9 THz in time domain. Thus, one might consider [119] the oscillatory feature of the phase and \( \frac{E_{\text{odd}}}{E_{\text{even}}} \) measured in the frequency-domain to be related to the oscillation of the surface state peaks due to the surface phonon mode. However, this issue requires further detailed investigations for a clear identification of the modulation source.

### 5.1.3 Conclusions

The polarization-dependent measurements performed on Gd(0001) revealed the p-P polarization geometry to be optimal in terms of SHG efficiency and the magnitude of the magnetic contrast. From now on this will be the experimental geometry of choice for all static and time-resolved MSHG measurements. For the case of a s-polarized incident fundamental beam, a Kerr rotation is detected that amounts to approximately 7°. The high surface sensitivity exhibited by the SHG process has been demonstrated by measuring the...
nonlinear response of a clean and oxygen-covered Gd surface. The dramatic decrease of the
SHG signal after the oxidation of the Gd surface has been considered as an indication for
the resonant character of the SHG process that evolves via the surface state components.
This suggestion has been proved by the spectral dependence of the SHG intensity and of
the magnetic contrast. The relative phase varies over a large interval (≈150°) showing a
complex structure with a pronounced oscillatory feature in the high photon energy range.

5.2 Laser-induced magnetization dynamics on Gd(0001)

With the provided detailed knowledge about the static properties of the ferromagnetic
Gd(0001) from the previous section, one can proceed in investigation of the dynamic
properties of the system. That means the time-dependent behavior of the constituent
sub-systems: electrons, lattice and spins after a femtosecond laser pulse excitation. These
properties are investigated employing the pump-probe technique in which the system is
excited by an intense pump pulse. The temporal evolution after excitation is monitored
by a weaker, time-delayed probe pulse that takes actually "snapshots" i.e. frozen pictures
in the time-domain of system’s behavior after excitation. The time delay is realized by
varying the optical path length between pump and probe pulses.

Here, the pump-probe magnetization-induced second harmonic generation MSHG is
employed. The Gd(0001) surface is excited by a pump pulse with a wavelength of e.g.
λ=800 nm and the pump-induced variations are detected by a probe pulse at the second-
harmonic photon frequency i.e. λ=400 nm. This technique possesses the advantage of
simultaneous detection of the electrons/phonons as well as the magnetic system behavior
(see chapter 3).

The time-resolved MSHG is used in order to investigate the photoinduced changes in
the magnetization of the ferromagnetic Gd(0001) surface. The main goal is to determine
and disentangle the elementary spin-dependent scattering processes that drive the laser-
induced demagnetization and their characteristic time scales. The nonlinear magneto-
optical investigations, which have been considered within the present thesis, are comple-
mented by time-resolved photoemission spectroscopy (TRPS) performed under comparab-
le experimental conditions by Martin Lisowski and Panos Loukakos in our lab. The latter
investigation tool is used to acquire additional information about the transient evolution
of the electronic system after laser excitation.

This section is organized as follows: in the first part the photoinduced femtosecond
demagnetization dynamics is presented whereas the magnetization relaxation evolving on
several 100 ps time scale covers the second part.

5.2.1 Femtosecond demagnetization dynamics

As a starting point to our discussion regarding the laser-induced magnetization dynamics
on Gd, a short remainder concerning the previous work done in the field and the magnetic
properties of Gd in equilibrium, is considered. As detailed in section 2.5, the common be-
lieve in the community is that photoinduced demagnetization takes place within the first
several 100 fs after the laser excitation [14]. Although various spin-scattering processes like
spin-orbit, electron-magnon, phonon-magnon have been invoked in order to explain this ultrafast demagnetization, an unambiguous identification of the responsible microscopic mechanism is still missing. For a better understanding a more systematic approach is necessary namely involving different investigation techniques on the same system. Thus, the combined insights gained from different experimental approaches provide a much clearer picture. Such an experimental strategy has been followed here in the case of ferromagnetic Gd(0001) surface using MSHG and TRPE as complementary investigation techniques.

Of central interest in our combined investigation is the exchange-split surface state present at the Gd(0001) surface [29, 33]. This can be considered as a model system due to the fact that reflects the degree of magnetic ordering on Gd(0001), due to its localization (spatially and energetically) and large exchange splitting that amounts e.g. $\Delta_{ex}=0.6$ eV at 100 K [33, 34]. Therefore, the effect of laser excitation on the magnetization behavior is monitored by measuring the transient spin polarization (with MSHG) and the $\Delta_{ex}$ (with TRPE) of the surface state.

It is important at this point to clarify in how far one can make the connection between the spin polarization of the surface state and the surface magnetization. As shown in chapter 3, with MSHG one can measure the transient magnetization dynamics accompanied by a spectroscopic factor (see eq 3.44), that gives the optical response of the system within the involved photon energy range. For an exchange-split band structure one measures the spin polarization of the probed electronic states. This is valid for any magneto-optical investigation technique e.g. time-resolved MOKE. The Gd(0001) surface state is energetically localized in the band gap of the bulk band structure and is exclusively probed by SHG due to the resonance condition. Thus the spin polarization of the surface state is measured with MSHG. Spatially the surface state is localized in the upper surface layer with a radial charge distribution localized on the atomic site. Hence, the surface state is sensitive to a local magnetic moment (gives the local quantization axis) or local magnetic ordering that does not vanish even above Curie point, being responsible for the observed residual exchange splitting. Within our spatial resolution (laser beam diameter) we average over these local magnetic ordering areas which give the overall spin orientation in the probed area and thus the magnetization. In conclusion, with MSHG we probe the surface magnetization via the spin polarization of the surface state within the spectral range given by the employed photon energy and with a spatial extent given by the damping of the surface state wavefunction.

These characteristic attributes of the surface state have been measured before under equilibrium conditions in order to clarify the origin of magnetic ordering on Gd(0001) at finite temperatures. It has been shown [36, 33] that neither of the invoked models, Stoner and spin-mixing (see chapter 2), is reliable to explain the experimental observations since these models are idealized pictures of itinerant and localized spins, respectively. The present understanding relies on a combination of these models i.e. the exchange splitting and spin polarization decrease with temperature down to Curie point where the $\Delta_{ex}$ remains finite while the spin polarization vanishes. It will be interesting to see

\footnote{It was shown [31] for magnetic lanthanides that the exchange splitting of the surface state scales with the magnitude of the 4f moments which governs the magnetism of these elements.}

\footnote{Employing much higher photon energies ($\approx 9$ eV) one could measure the 4f moments that give 90% of the total magnetic moment in Gd.}
5.2 Laser-induced magnetization dynamics on Gd(0001)

![Figure 5.12: The evolution of SHG magnetic contrast as a function of temperature at the Gd(0001) surface. The filled and open circles represent the magnetic contrast measured in the static case (in absence of the pump pulse) and at a pump-probe delay of 1 ps, respectively. Note that both curves have been measured simultaneously by opening and blocking the pump beam that correspond to an excited and unexcited sample, respectively. From [134].](image)

which of these models prevail under high non-equilibrium conditions provoked by the laser excitation.

In the previous section we have shown that the SHG process at the Gd(0001) surface evolves resonantly enhanced via the surface state components [102, 119]. Hence, apart from its intrinsic surface sensitivity based on symmetry considerations, the SHG is particularly sensitive to the exchange-split surface state present at the Gd(0001) surface. From the spectroscopic investigation of the SH response, presented in the preceding section, we have concluded that MSHG measures the magnetization at the surface via the spin polarization of the surface state [17].

An illustrative example of how sensitive is the MSHG to magnetic ordering at the surface is presented figure 5.12. Here the variation of the SHG magnetic contrast $\rho$ (defined in eq. 3.34) with the temperature resembles clearly the well-known $M(T)$ Curie-Weiss law dependence [135]. The dependence of $\rho$ on temperature is quasi-linear until it is approaching the critical region in the vicinity of Curie temperature. This quasi-linear behavior in $M(T)$ is usually ascribed to the reduced dimensionality of the magnetic thin films [37]. This is most likely also the case here, since the probed region is restricted to the upper two layers of Gd(0001) (see chapter 3). Such a behavior has been reported for Gd(0001) thin films investigated with surface sensitive techniques [35]. The bulk Curie point of $T_C=293$ K is well reproduced\(^8\) while above $T_C$ the magnetic contrast is vanishing. These results are evidence for the absence of an enhanced surface $T_C$, which also confirm earlier investigation [35] regarding this issue.

The second curve in the figure displays the magnetic contrast measured at 1 ps delay after pump pulse excitation. Both curves, measured in equilibrium and non-equilibrium conditions, show a similar temperature dependence but for the excited case a decrease of $\approx 60\%$ from the equilibrium value is observed. From here one can conclude that the laser excitation produces a partial demagnetization of Gd(0001) sample within 1 ps. Such\(^8\)

\(^8\)The Curie temperatures of a 20 nm thick Gd(0001) film is 293 K, which is identical to bulk $T_C$ [136].
Figure 5.13: The pump-induced variations in the odd SH field, that measures the dynamics of the spin-polarization at Gd(0001) surface after excitation with a 35 fs pump pulse (the curve centered at zero delay scaled to $\Delta_{\text{odd}}$). The sudden breakdown of $\Delta_{\text{odd}}$ take place within pulse duration, reaches the minimum at 1.5 ps and comes to the initial level at 500 ps (right panel). The line denotes the incoherent (non-oscillatory) contribution to the signal after subtraction of the oscillatory part (see text).

an interesting observation gives us a flavor about the ultrafast demagnetization dynamics encountered on Gd, that will be the topic of the following part.

We further proceed in presenting the time-resolved MSHG data measured on Gd(0001). From the detected second-harmonic intensities for opposite magnetization directions and as a function of pump-probe delay, the normalized intensities $R(t) = \frac{I^{(t)}(t) \pm I^{(t)}(t)}{I^{(t)}(t) \pm I^{(t=0)}}$ are computed, where $t_0$ denotes negative time delays. The measured data are presented as pump-induced variations in the even and odd SH fields, that are denoted by (see for details chapter 3): $\Delta_{\text{even}} = \frac{E_{\text{even}(t)}}{E_{\text{even}(t_0)}} - 1$ and $\Delta_{\text{odd}} = \frac{E_{\text{odd}(t)}}{E_{\text{odd}(t_0)}} - 1$, respectively.

The pump-induced variations in the odd SH field, which reflect the transient spin polarization of the surface state, are displayed in the figure 5.13. In the first place we notice (for a pump fluence of $\approx 1 \text{mJ/cm}^2$) a sudden drop that amounts to 50% from the equilibrium spin polarization value (at negative delays). Second, this abrupt decrease takes place within laser pulse duration depicted in the figure by the curve centered at zero delay. The minimum (60% decrease) in the transient odd field is reached around 1.5 ps and remains at this value up to 40 ps delay time. The spin polarization recovers on a 500 ps time scale (the right panel of the figure 5.13) and it will be discussed in the next section.

The pronounced oscillations with a period of 340 fs that are superimposed on the incoherent (non-oscillatory) background have been ascribed to a coherent phonon-magnon mode [17] excited at the Gd(0001) surface. A detailed investigation of their excitation and relaxation will be presented in the next section. For the discussion of the incoherent
5.2 Laser-induced magnetization dynamics on Gd(0001)

Figure 5.14: Pump-induced variations in the odd SH field as a function of laser fluence. **Left**: The measured $\Delta_{odd}$ dynamics for various relative laser fluences. The solid, dashed and dotted lines denote the incoherent part of $\Delta_{odd}$, that reflect the transient spin polarization after excitation. **Right**: The measured drop in $\Delta_{odd}$ close to zero delay as a function of laser fluence, where 100% represents 1mJ/cm$^2$. The 100% data point is from figure 5.13. The solid line is a linear fit to the data.

ultrafast drop in $\Delta_{odd}$ the coherent oscillations are not of interest and their contribution is subtracted\(^9\) from the measured signal. The remaining incoherent component of $\Delta_{odd}$ (the full, dashed, dotted lines) is displayed in figure 5.14 left, for different pump fluences. As plotted in the figure 5.14 right, the breakdown in $\Delta_{odd}$ scales linearly with the pump fluence which indicates an ultrafast loss of spin polarization mediated by the photoexcited electron population. Note that the state-filling or bleaching effects \cite{85} (see chapter 2 for details) can not be invoked here since the drop in the spin polarization persists up to 40 ps while the excited electron population is already relaxed to the lattice on 1 ps time scale (see fig. 5.16 upper panel and fig. 2.7).

As pointed out earlier, the spin polarization and the exchange splitting of the surface state are the two main ingredients that offer a rather complete picture about the magnetism-electronic structure interplay on Gd(0001) under equilibrium conditions. Hence, apart from the transient spin polarization at the surface measured with MSHG we want to investigate also the time evolution of the surface state exchange splitting upon laser excitation. For this purpose the time-resolved photoemission TRPE technique has been employed.

The TRPE provides a direct measurement of the electronic structure of the system under investigation in a time, energy, and angle-resolved manner. The technique relies on the detection the photoemitted electrons after laser pulse absorption via photo-electric effect. The measurement principle of the TRPE is schematically shown in figure 5.15 for

\(^9\)The separation of the coherent and incoherent components of the MSHG response as well as the fitting procedure of the oscillations are presented in detailed in appendix B.
the case of Gd(0001) electronic structure in the vicinity of $E_F$. An intense laser pulse (the pump) of energy $h\nu_1$ (here 1.5 eV) excites electrons from the bulk states and the occupied surface state component $S^\uparrow$, which are photo-ejected above vacuum level $E_{vac}$ by a less-intense, time-delayed probe pulse $h\nu_2$ (here 6 eV) (when $h\nu_2$ is above the work function $\Phi = E_{vac} - E_F$). The kinetic energy $E_{kin}$ of the emitted electrons is detected by a time-of-flight spectrometer (TOF). Due to the limited escape depth of electrons that amounts to several Å in the used photon energy range, the PE is also a surface sensitive technique. Considering the energy conservation of the entire process, one can obtain the energetic positions $E_i$ of the initial states (binding energies) of the detected electrons:

$$E_i - E_F = E_{kin} + \Phi - h\nu_2$$  \hspace{1cm} (5.7)

The resulting time evolution of the energetic positions for surface state components, upon laser excitation, is depicted in the figure 5.16. The binding energy of the $S^\uparrow$ varies gradually in a time interval of 2 ps by an amount of 45 meV towards $E_F$. Such a small energy gradient could not be detected in the case of the $S^\downarrow$ component due to its low intensity and larger linewidth. However, computing the sum between the measured binding energy transients for $E(S^\uparrow)$ and $E(S^\downarrow)$ one obtains the surface state exchange splitting $\Delta_{ex} = E(S^\uparrow) + E(S^\downarrow)$ as plotted in the inset of figure 5.16. The resulting observation is that $\Delta_{ex}$ stays constant within error bars 0.6±0.06 eV in the investigated time range of 1 ps.

Another information that can be retrieved from the TRPE spectra is the photo-injected excitation strength of the electronic system that is described by the transient energy density $\varepsilon el(t)$. According to the reference [56] the electronic energy density can be calculated as $\varepsilon el(t) = 2\int_{0}^{2eV} N(E, t) |E|dE$, where $N(E, t)$ is the electronic population measured in the photoemission spectra and the factor 2 before integral accounts for equal contribution from electrons and holes. The computed $\varepsilon el(t)$ is shown in the lower part of the figure 5.16 together with the transient population of the $S^\uparrow$ state (inset). One can observe that the
maximum in \( \varepsilon_{el}(t) \) is reached around 100 fs and it decays in 1 ps time interval, usually via e-e, e-p and ballistic as well as diffusive transport \([44, 56]\). On the same time scale of 100 fs, a drop of 19% in the population of majority surface state is detected that levels out to a constant value close to 1 ps delay. A simple estimation of the excited electronic temperature gives a value of \( \varepsilon_{el}/k_B=1900 \) K, that quantifies the high excitation regime.

Summarizing the experimental observations, we notice that upon an intense laser excitation the spin polarization of the surface state decreases with 50% while its exchange splitting remains constant. This happens on the time scale when the electronic system is in a highly non-equilibrated state and e-e scattering dominates, as deduced from the transient energy density and the estimated value of the electronic temperature. Based on these observations, we can rule-out a demagnetization mechanism based on the Stoner model \( i.e. \Delta_{ex} \) scales with \( M(T) \), and conclude that for the Gd(0001) surface, on the femtosecond time scale, the spin-mixing behavior dominates.

In order to develop a microscopic understanding of the observed phenomena one can

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**Figure 5.16:** Upper panel: the transient binding energy for the \( S^\uparrow \) and \( S^\downarrow \) surface state components. The inset displays the resulting surface state exchange splitting \( \Delta_{ex} \). Lower panel: the time evolution of the energy density \( \varepsilon_{el}(t) \) (dots) and the fit according to the 2TM (solid line). The inset shows the change in the \( S^\uparrow \) surface state population after excitation. From \([13]\).
start by considering some potential spin-scattering processes responsible for laser-induced demagnetization in Gd, having in mind the particularities (localized magnetic moment, strong electron-magnon coupling) of this ferromagnetic system:

- the phonon-magnon scattering or the spin-lattice interaction has been shown ([79, 80] and the next section) to evolve on a 100 ps time scale in case of Gd(0001) and therefore can not be considered here
- the spin-orbit interaction, that is considered the main mechanism responsible for angular momentum transfer between the spin and orbital degrees of freedom, it is small for Gd [137] and thus of minor importance here
- secondary electron effects combined with transport processes
- electronic spin-flip scattering among spin-mixed states

In the following we will focus on the last two listed processes that will be discussed within the framework of figure 5.17. The upper part of the figure displays the optical excitation and the subsequent secondary electrons generation in the spin-resolved Gd(0001) band structure (calculated by Kurz et al. [26]). In panel (a) of the figure 5.17 the two channels of pump-induced optical transition are shown for a photon energy of 1.5 eV. There are transitions between the bulk bands as well as transition involving the surface state (also introduced earlier in the figure 5.11). The latter ones promote majority electrons from the surface state to bulk whereas minority electrons are excited from the occupied bulk state into the $S\downarrow$ surface state. As a result the spin polarization\textsuperscript{10} of the surface state is reduced after excitation while for the bulk states it should be increased. The higher spin-polarization of the bulk states might be relaxed by transport into the bulk of the sample through ballistic and diffusive transport, that are taking place on this early time range after excitation.

Generally, the highly excited electron-hole pairs relax through inelastic $e$-$e$ scattering that produces secondary electron cascades (see chapter 2). As plotted in panel (b), the generated secondary electrons might preserve the spin orientation (processes 1 and 2) or not (processes 1 and 3). The latter case accounts for Stoner excitations \textit{i.e.} excited electron-hole pair with opposite spin orientation. Both type of processes lower the spin polarization of the surface state on the time scale of $e$-$e$ scattering \textit{i.e.} $<100$ fs but do not influence the spin polarization of the bulk states. Taking into account the linewidth $\Gamma$ of the surface state components that amounts to \approx100 meV at 100 K [48], one obtains a scattering rate of 0.1 $fs^{-1}$ and a short carriers lifetime ($\tau = \hbar/\Gamma$ of \approx10 fs). Therefore, frequent scattering events are taking place between the surface state and bulk electrons which will restore the electronic spin polarization to the equilibrium value before excitation. Such a process will evolve on the hot electrons relaxation time scale \textit{i.e.} within the first 100 fs. We do not observe such a rapid recovery of spin polarization since the drop in the $\Delta_{odd}$ signal persists up to 50 ps. Therefore, the spatially redistribution of the spin polarization between the surface and bulk and the secondary electrons effects are not explaining the observed ultrafast loss of spin polarization.

\textsuperscript{10}By spin polarization of the surface state is meant the difference between the majority and minority spin population of the surface state components
Figure 5.17: The description of the laser-induced ultrafast demagnetization scenario in the spin-resolved band structure of Gd(0001), calculated by Kurz et al. [26]. The green and the red filled areas are the majority and minority bulk states, respectively, while the thick lines close to Fermi level depicts the position of the exchange-split surface state. The panels display: (a) laser excitation of electron-hole pairs; (b) the e-e scattering; (c)(d) the spin-flip scattering among spin-mixed states involving surface state components (panel c) and bulk states (panel d). The dashed lines in panel (c) and the hatched areas in panel (d) represent the opposite spin states that together with the full lines and filled areas, respectively, generate the surface and the bulk spin-mixed states. From [13].

The remaining mechanism is the spin-flip scattering of hot electrons among spin-mixed states, that is discussed in the following. As pointed out earlier, the presence of a constant exchange splitting unaffected by the high electronic photoexcitation led us to the conclusion that spin-mixing behavior prevails on this ultrashort time scale. This is equivalent to the existence of degenerate spin-mixed electronic states as displayed in the panel (c) and (d) of figure 5.17, for the case of surface and bulk states, respectively. Hence, an electron in the majority surface state can scatter quasi-elastically with a minority electron situated at the same energetic position (dashed line), flip its spin, and consequently lower the surface state spin polarization. The conservation of angular momentum requires that the reduced momentum through the spin-flip event to be compensated by the absorption of magnon of energy $\hbar k_m$. The absorption and emission of magnons take place in the conduction band but might involve also the $4f - 5d$ exchange interaction. The calculated [138] exchange coupling between $4f - 5d$ electrons amounts to $\approx 100$
meV that corresponds to $\approx 5$ fs and thus in agreement with the observed drop of spin-polarization within the laser pulse duration. The probability of the electronic spin-flip with emission/absorption of magnons is governed by the strength of the electron-magnon coupling, that was shown to be comparable with the $e$-$p$ coupling or even higher \[57, 58\] for Gd. Thus, the occurrence of this process will be also on the femtosecond time scale.

The spin-mixing behavior was encountered under equilibrium conditions also for the 5$d$ bulk states on Gd(0001) \[36\]. Therefore we can extend this scenario for the bulk states and expect that spin-flip scattering is active also here as depicted in panel (d) which will lead to a spin polarization lowering in the bulk. To check this point a bulk sensitive technique is required, like time-resolved MOKE, that will be integrated soon in the actual MSHG setup.

Summarizing, we have identified the spin-flip scattering of hot electrons among spin-mixed states facilitated by a strong $e$-$m$ interaction, as the responsible mechanism for the ultrafast loss of spin-polarization of the surface state on Gd(0001). The proposed demagnetization mechanism might be extended to even shorter time scales of the highly non-equilibrated electron bath since the measured spin polarization breakdown by MSHG takes place within the pulse duration of 35 fs (see figure 5.13).

### 5.2.2 Remagnetization dynamics on Gd(0001)

In the preceding section we have focused on the early time dynamics of the magnetization upon femtosecond laser excitation. The observed loss of magnetization (see figure 5.13) as measured by MSHG was on the 100 fs range. This partial (60 %) demagnetization of the system persists on a 40 ps time scale and it recovers the equilibrium magnetization value around 500 ps. The observed remagnetization process is studied in detail in this section.

Figure 5.18 illustrates the time evolution of the odd field together with the transients of even field $\Delta_{\text{even}}$ and the linear reflectivity $\Delta R/R$. The latter two quantities monitor the surface and bulk electron dynamics \[44, 17, 70\], respectively, and offer additional information that helps the interpretation of the observed transients. Upon laser excitation one observes rapid changes in all measured quantities. The sudden increase in the $\Delta_{\text{even}}$ and $\Delta R/R$ reflects the elevated electronic temperature reached after excitation through $e$-$e$ scattering processes (see chapter 2). The hot electron population cools down to the lattice on a sub-picosecond time scale and a common temperature will be reached on a few picosecond range. The thermal gradient in the excited region will be spatially redistributed via thermal diffusion to the bulk of the sample and the substrate. Thus, the transients in $\Delta_{\text{even}}$ and $\Delta R/R$ during the 0.5 ns delay interval shown in figure 5.18, reflect the dynamics of lattice cooling in the laser spot region. One notices the difference between $\Delta_{\text{even}}$ and $\Delta R/R$ with the former one showing higher pump-induced variations and a quicker relaxation (steeper slope). This can be explained by the higher temperature reached in the surface layer (measured exclusively by $\Delta_{\text{even}}$) in comparison to deeper region of the excitation profile (measured by $\Delta R/R$). The more rapid cooling observed in nonlinear signal might also be ascribed to a different $e$-$ph$ coupling at the surface than in the bulk. These points are not further develop here since they require more detailed investigations and are in the context of long-time magnetization behavior of minor importance.
5.2 Laser-induced magnetization dynamics on Gd(0001)

Figure 5.18: The pump-induced variations in the linear reflectivity (dashed curve), even (solid curve) and odd (dots) SH fields measured on a 20 nm Gd film at T=100 K.

Inspecting closely the odd field behavior in figure 5.18, one notice mainly three time scales: the one where the quasi-instantaneous breakdown is taking place (see preceding section), an intermediate one between 2-40 ps where $\Delta_{\text{odd}}$ levels-out to a constant value and a delayed, much slower one on hundreds of ps time interval, on which the equilibrium magnetization recovers.

On the last time scale 40-500 ps, we observe the remagnetization of the sample after the sudden photoexcitation. This process corresponds to the thermalization of the spin population and proceeds via coupling to the lattice [1, 81, 79]. This can be seen in the figure 5.19 where the transients in $\Delta_{\text{even}}$ and the scaled $\Delta_{\text{odd}}$ coincide starting to $\approx 150$ ps. Since the even field monitors here the lattice cooling dynamics and the odd field the magnetization of the system, one can conclude that at 150 ps the lattice and the spin systems reach a common temperature. The characteristic time of the energy transfer between the lattice and the spin system defines the so-called spin-lattice relaxation time.

As shown previously (see fig. 5.16 and fig. 2.7), around 1 ps the electrons and the lattice are equilibrated and the later dynamics represents the lattice cooling through thermal diffusion.
\[ \tau_{s-l}, \text{ which is determined by the coupling strength between these baths.} \] Hence, the measured spin-lattice relaxation time for Gd is \( \approx 150 \text{ ps} \) and it is in a good agreement with the earlier reported [79] \( \tau_{s-l} \) of \( 100 \pm 80 \text{ ps} \) measured with spin-polarized photoemission. Below 150 ps the magnetization recovery shows a slower dynamics than the lattice cooling, thus does not follow the classical M(T) behavior.

A possible interpretation might be as follows: in 100 fs after the excitation the spin-flip scattering of hot electrons produces magnons that introduces disordering of the 4f moments; after thermalization of the hot "source" of magnons (\( \approx 1 \text{ ps} \)) the 4f moments remain in a disordered state and due to their localization i.e. less interaction with the surrounding energy baths, a slow relaxation is encountered.

\( \tau_{s-l} \) of Gd is estimated to be around 2 ns. This time interval is one order of magnitude bigger than the measured relaxation time, which ask for an additional relaxation mechanism beside spin-orbit coupling. This last fact is not completely understood and further measurements are required. On a speculative level, one can involve the electron-magnon interaction which is specifically strong in gadolinium.

\[ 12 \text{The values of the exchange interaction constants } J_{4f-5d}=94 \text{ meV}, J_{5d-5d}=531 \text{ meV} [138] \text{ and } J_{4f-4f}=3 \text{ meV} [105] \text{ give coupling times in the fs time range and thus can not be invoked here to explain such a slow dynamics.} \]
5.3 Coherent optical phonons and magnons on Gd(0001) surface

In summary, from the remagnetization behavior on ferromagnetic Gd(0001) after laser excitation we could retrieve a spin-lattice relaxation time of $\tau_{s-l}$ of 150 ps, with the initial equilibrium magnetization of the surface being totally recovered after 500 ps. The slower magnetization relaxation than the lattice cooling below 150 ps has been ascribed to the localization of the 4f moments.

5.2.3 Conclusions

We have employed time-resolved magnetization-induced second-harmonic generation and photoemission measurements on the ferromagnetic Gd(0001) surface, in order to investigate the laser-induced demagnetization behavior of this material.

The main observations are that upon laser excitation an ultrafast breakdown ($<100$ fs) in the spin polarization of the surface state is taking place while its exchange splitting remains constant (in the investigated interval from 0–1 ps). Accounting for transient behavior of the surface state spin polarization and exchange splitting upon laser excitation, we could conclude that the Stoner model is inadequate for the ultrafast, non-equilibrium conditions and the measured data are well described in the framework of the spin-mixing model.

Based on these observations, we have identified the spin-flip scattering of hot electrons among spin-mixed states accompanied by magnons emission as the elementary spin-scattering process responsible for the ultrafast loss of magnetization on Gd(0001) surface. The suggested demagnetization mechanism is particularly efficient in Gd owing to its strong electron-magnon interaction.

On a longer time scale, we assist at the remagnetization of the system with a time constant of $\approx 150$ ps that has been attributed to the spin-lattice relaxation. This has been concluded from the similarity between the transients of even SHG field and linear reflectivity (measures the electron/lattice dynamics) with the odd SHG field starting with this delay time.

5.3 Coherent optical phonons and magnons on Gd(0001) surface

This section presents the novel phenomenon of a coupled coherent phonon-magnon mode [17] measured at the ferromagnetic Gd(0001) surface by means of time-resolved MSHG. This coupled quasiparticle constitutes itself in new type of phonon-magnon interaction whose coupling is mediated by the exchange interaction. Moreover, the present study reports the first time observation of a coherent optical phonon on a metal surface.

5.3.1 Phonon-magnon coupling in equilibrium

The interaction between lattice and spins or between their quasiparticle excitations i.e. phonons and magnons is typically ascribed to spin-orbit coupling [81, 140]. Through the spin-orbit interaction the spin bath can relax to the surrounding lattice and thus has been considered as a major relaxation channel in ferromagnets since decades [135]. For the magnetic rare-earth elements, the evidence for the phonon-magnon interaction has been considered the appearance of energy gaps (or avoided crossings) in the magnon dispersion curves. These gaps have been observed [141] at the crossing points between the
unperturbed magnon and phonon dispersion curves (see the figure 5.20 for Tb). At this quasiparticle momentum, the eigenmode of the system has a mixed phonon-magnon character derived from the strong hybridization of the normal modes produced by the phonon-magnon interaction [142]. An illustrative case is e.g. Terbium which has eight electrons in the 4f shell and therefore a L=3 orbital contribution to the total magnetic moment. As it can be seen in the left part of the figure 5.20, along ΓA direction in the Brillouin zone, two gaps (denoted by $\Delta_1$ and $\Delta_2$ in the figure) show up in the magnon dispersion curve. Similar behaviors have been encountered also for dysprosium and Tb$_{0.9}$Ho$_{0.1}$ alloy [140]. No such an effect has been observed for Gd (see figure 5.20 right), which has L=0 and thus a weak spin-orbit coupling [137] coming from the valence electrons. By comparison of the dispersion curves for Gd and Tb, it has been concluded [141, 140, 142] that the observed energy gaps in the magnon dispersion curves ascribed to the phonon-magnon interaction are the effect of the spin-orbit coupling.

5.3.2 Coherent lattice and spin excitations

We have seen above that in equilibrated systems the phonon-magnon interaction is considered to be mediated by spin-orbit coupling. Here we propose a different type of magnetoelastic interaction between the phonons and spin waves, that relies on the modulation of exchange coupling strength $J$ with lattice vibrations.

Employing time-resolved magnetization-induced second-harmonic generation on the ferromagnetic Gd(0001) surface, a pronounced oscillatory contribution to the transient SHG signal has been observed [17] upon laser excitation. A typical example of such a measurement is displayed in the figure 5.21a, for a sample temperature of 90 K and a laser wavelength of 815 nm. The upper panel of the figure displays the time evolution of linear reflectivity $\Delta R/R$ and of the even SH field $\Delta_{\text{even}}$ while in the lower panel the transient odd SH field $\Delta_{\text{odd}}$ is shown. One notices immediately the conspicuous oscillatory component present in the transient SH fields while in the linear reflectivity, at the first glance, is not evident. Since $\Delta R/R$ does not show the oscillatory feature, the presence of the oscillations in the surface sensitive SHG signal points to the surface origin of the oscillatory pattern. Owing to the symmetry of the SH fields with respect to magnetization reversal [11], one has simultaneous access to the electron and lattice dynamics$^{13}$ described by the even field and to the surface magnetization monitored by the odd field (see chapter 3, section 5.1 and [17]). Thus, the observed oscillations describe a simultaneous, periodic modulation of the electron/lattice system and of the magnetization at the Gd(0001) surface.

The monotonous increase of the $\Delta R/R$ between 0-3 ps is ascribed to the hot electron temperature formation via $e-e$ scattering (within 100 fs) and relaxation to the lattice through $e-p$ scattering (up to 3 ps) of the system after laser excitation [17]. Such an incoherent behavior originating from electron and electron-phonon thermalization, is observed also in the $\Delta_{\text{even}}$ on which the oscillatory component is superimposed. Based on the similar incoherent contributions in $\Delta_{\text{even}}$ and $\Delta R/R$, the former one is also assigned to $e-e$ and $e-p$ scattering processes. The origin of the initial drop and the subsequent levelling

$^{13}$Since any structural change of the lattice is reflected in the electronic structure of the system, the lattice dynamics is also measured by even SH field.
of the incoherent odd field has been detailed in the preceding section and is attributed to spin-flip scattering of hot electrons among spin-mixed states.

For the separation of the oscillatory and incoherent contributions to both SH fields the following procedure\(^\text{14}\) has been used. An initial smoothing is done by fitting the original data with a polynomial function within a certain time window for consecutive time delays. The degree of the polynomial and the width of the time window is optimized by an autocorrelation criterion. The function 5.8, that simulates the oscillatory fraction of the signal, is subtracted from the smoothed data by adjusting \(A, \tau, \Omega\) and \(\varphi\) in order to minimize the oscillating component in the incoherent background. The obtained incoherent background \(\Delta^{\text{incoh}}\) is subsequently smoothed and removed from the smoothed raw data, that renders \(\Delta^{\text{coh}}\). The resulting oscillatory components \(\Delta_{\text{even}}^{\text{coh}}\) and \(\Delta_{\text{odd}}^{\text{coh}}\) are displayed in figure 5.21b. The frequency of the oscillation is retrieved from the Fourier transformation

\(^{14}\)The data analysis procedure is presented in detail in appendix B.
Figure 5.21: (a) Exemplary data set measured on Gd(0001)/W(110) at T=90 K and a laser wavelength $\lambda=815$ nm, showing the transient even (red curve), odd (blue curve) transient SH fields and linear reflectivity (green curve) behavior after laser excitation. For clarity $\Delta R/R$ is scaled by a factor 15. The pronounced oscillations in the transient SH fields are attributed to a coupled coherent phonon-magnon mode [17]. (b) Oscillatory component (dots) of $\Delta_{\text{even}}$ and $\Delta_{\text{odd}}$ obtained after removing the incoherent background (see text) together with the fitting curves (solid lines) according to eq. 5.8. The inset displays the Fourier transform of the $\Delta_{\text{even}}^{\text{coh}}$ and $\Delta_{\text{odd}}^{\text{coh}}$, that gives an identical frequency of $2.9\pm0.3$ THz for both fields, as indicated by the arrow.

of the oscillatory signal, that is plotted in the inset of the figure. From here an identical frequency of $2.9\pm0.3$ THz is observed for both fields, even and odd, that indicates the coupled nature of the oscillations. To analyze the transient oscillatory behavior, a fitting function that models an exponentially damped cosine-like oscillation has been introduced:

$$f(t) = Ae^{-t/\tau} \cdot \cos[2\pi(\Omega \cdot t + c \cdot t^2 + \varphi)]$$

(5.8)

where $A$, $\tau$, $\Omega$ and $\varphi$ represent the amplitude, decay time, frequency and the phase, respectively. Also a linear chirp of the frequency $c = \frac{1}{2\pi} \frac{\partial \Omega}{\partial t}$ has been introduced in order to account for a possible frequency change in time. That such a chirp in frequency is indeed observed will be detailed in section 5.4. The fits of the oscillating SH fields according to eq. 5.8 are displayed in figure 5.21b as the solid lines.

In order to develop an understanding of the observed results let us have a look at the dispersion curves for phonons in bulk Gd as plotted in the right panel of figure 5.20. Here, the calculated phonon $E(q)$ spectrum (solid curve) [145, 143] predicts for the longitudinal-optical branch (LO) at $\Gamma$ point ($q=0$) a frequency of 3.15 THz. This value gives a reasonable good agreement with the phonon frequency of $2.9\pm0.3$ measured at the surface in the
5.3 Coherent optical phonons and magnons on Gd(0001) surface

time-resolved experiment, since for a surface phonon mode one expects a lower frequency in comparison to the bulk value, due to the reduced coordination number. Consequently, we conclude that the observed modulations in the $\Delta_{\text{even}}$ are coherent optical phonons excited at the Gd(0001) surface. In the bulk, the LO phonon mode denotes the out-of-phase vibration of two hcp basal planes. By analogy, the longitudinal surface mode represents the vibration along surface normal of the topmost layer against the underlying bulk.

At this point we want to remark that the oscillatory part of $\Delta_{\text{even}}$ do not represent the real amplitude of the lattice vibration produced by the coherent phonon, which is measured in a time-resolved x-ray diffraction experiment. Here we measure the modulation of the $\chi^{(2)}$ (see eq. 2.18) determined by the coherent lattice oscillation via the electron-phonon deformational potential (see chapter 2). Therefore, further on, when refer to coherent phonon we understand the oscillatory component of the SH signal that arises from the coherent lattice motion.

The observation of a coherent optical phonon on a metal is a remarkable fact since such coherent lattice vibrations have been measured in semiconductors and semimetals only [15, 65, 68, 73, 77]. This can be attributed to the strong screening due to the high density of conduction electrons present in metals, that results in low efficiencies of coherent lattice excitation. The case of ferromagnetic Gd(0001) is special due to the presence of the spatially and energetically localized exchange-split surface state, through which the lattice vibration can be excited efficiently. Only very recently, Hase et al. [64] succeeded in detecting coherent optical phonons in hcp metals Zn and Cd employing high sensitivity LR detection.

Before explaining the coherence in the odd field, we focus on the excitation mechanism of the coherent optical phonon on the Gd(0001) surface. As reviewed in chapter 2, for the excitation of coherent phonons in THz frequency range two main mechanisms are invoked: impulsive stimulated Raman scattering (ISRS) and the displacive excitation of coherent phonons (DECP). The former one is mainly the inelastic Raman scattering effect under non-resonant excitation conditions encountered in transparent materials, whereas DECP triggers the coherent lattice dynamics under resonant excitation of the electronic population for opaque (absorbing) media. These two limits can be distinguished by considering the initial phase of the lattice oscillations: cosine-like for DECP and sine-like for ISRS (see figure 2.8).

In order to identify how one can excite coherent phonons on Gd and which is the involved excitation mechanism, we consider the pump-induced optical transitions via the specific electronic structure of Gd(0001) surface plotted in figure 5.11. The presence of the exchange-split surface state offers two excitation channels according to the spin orientation of the excited electrons. The majority channel that promotes an electron from the occupied surface state $S^\uparrow$ to unoccupied bulk states leaving behind a hole and the minority channel where the electrons are excited from bulk states to the unoccupied surface state $S^\downarrow$. Estimations of the lifetimes of the photoexcited electrons and holes are provided by STS measurements of the surface state components linewidth: at 80 K $\Gamma^\uparrow=70$ meV \textit{i.e.} $\tau^\uparrow=h/\Gamma^\uparrow=9$ fs for the hole and $\Gamma^\downarrow=175$ meV \textit{i.e.} $\tau^\downarrow=4$ fs for the excited electron. Based on the asymmetric lifetimes of electrons and holes in the surface state one can develop the following scenario: the photoexcited hole in $S^\uparrow$ lives longer than the
Figure 5.22: The influence of the Y adsorption on the coherent phonons dynamics at the Gd(0001) surface, as monitored by $\Delta_{\text{even}}$ and $\Delta_{\text{odd}}$ (a) and photoemission (b). Upon depositing 1 and 3 ML (nominally) of Y, the oscillation are gradually altered and eventually quenched in both transient SH fields. This behavior corresponds, according to the photoemission data, to an initial broadening of the surface state with an additional shoulder peak from Y surface state for 1 ML of Y, and to a suppression of the Gd surface state for 3 ML of Y. The photoemission measurements have been performed by O. Krupin (within the collaboration with our group [17]) under comparable conditions at BESSY light source with a photon energy of 36 eV at normal incidence. The $\Delta_{\text{odd}}$ curves are offset it for clarity.
5.3 Coherent optical phonons and magnons on Gd(0001) surface

excited electron in the $S_{\downarrow}$ and therefore an ultrafast charge redistribution take place at the surface in order to screen the photo-hole. This is equivalent with a modification of the equilibrium potential of the surface ions cores, that will try to restore the equilibrated potential by a collective ion movement to a new lattice coordinate. This will establish a new potential energy surface with a changed equilibrium position with respect to the equilibrium case. Due to availability of scattering channels typical for metals, the charge imbalance at the surface decays on a 10 fs time scale leaving the surface ions displaced. Such a sudden lattice displacement is the initial trigger of the coherent lattice oscillations.

From the above considerations we have seen that the presence of the exchange-split surface state plays a major role in the excitation of the coherent lattice motion. As a check of the excitation mechanism, we have performed an overlayer experiment where the 20 nm Gd film was covered with a thin layer of yttrium (Y). The hcp Y metal is non-ferromagnetic, has the same valency and almost the same lattice constant (lattice mismatch 0.5%) as Gd. It exhibits also a $d_{z^2}$-like surface state positioned at the Fermi level that is not exchange-split (see figure 6.6). Thus yttrium is a good candidate for the controlled modification of the Gd surface state. Covering the Gd surface with various Y layer thicknesses the exchange splitting of the Gd(0001) surface state should be affected and eventually quenched, whereas the Y(0001) surface state should remain. The idea is to demonstrate that the existence of an exchange-split surface state is the necessary condition for the coherent phonon excitation. The effect of Y deposition on the lattice vibrations is depicted in figure 5.22. Upon one monolayer (nominally) Y coverage the amplitude of the oscillations in $\Delta_{\text{even}}$ is drastically reduced and after three ML the oscillations are barely visible. Similar transients are encountered for the oscillatory $\Delta_{\text{odd}}$ behavior with a clear oscillatory signature for pure Gd and a decreasing amplitude upon Y absorption. Photoemission measurements performed with a 36 eV beam energy under comparable conditions [17], show the presence of the surface state for clean Gd(0001), a modified Gd surface state with an additional peak from Y at a coverage of 1 ML of Y, and quenching of Gd surface state at three ML Y coverage. Therefore, we have unambiguously demonstrated that the excitation of the coherent phonons at the Gd(0001) surface is conditioned by the presence of the exchange-split surface state. A non-split state at the surface, as is the case for Y(0001), is obviously not leading to excitation of the coherent mode. From this observation we conclude that two excitation channels are required. Later in section 5.5 it will be discussed that different probabilities for excitation of both channels are likely to be responsible for the excitation of the coherent phonon-magnon mode at the Gd(0001) surface.

Coming now to the periodic modulations in the magnetic signal, we see that the Fourier transformation of the oscillatory SH fields (5.21 inset) gives an identical frequency for odd and even fields, whereas in the time-domain a phase shift of $\pi$ is encountered between their oscillatory transients (see figure 5.21b). Furthermore, there is no evidence for the existence of a build-up time in the $\Delta_{\text{odd}}$ behavior, which means that the coherent spin excitation follows the lattice instantaneously. All these facts give evidence for coupled lattice and spin oscillations with a common origin, that proceed simultaneously after excitation, and thus a strong interaction should mediate their coupling. Now the major question that arises is: what kind of interaction determines the coupling ?.
One can address this questions starting from the phonon-magnon interaction in equilibrium. As has been described at the beginning of this section, the spin-orbit coupling is considered responsible for the interaction between spin and lattice. Bulk gadolinium exhibits a weak spin-orbit coupling that amounts to 16 µeV as calculated by Colarieti et al. [137]. Transforming this value in time units one ends up with a time scale of ≈4 ns that is four orders of magnitude slower than the encountered sub-ps lattice and spin dynamics. Therefore, one can be very confident in excluding the spin-orbit coupling as being responsible for the observed dynamics.

As a possible mechanism that mediates the coupling between the lattice and spins, we propose the exchange interaction $J$. $J$ depends on the wavefunction overlap between nearest neighbor atoms and thus might exhibit also the dependence $J = J(d_{12})$, where $d_{12}$ is the interlayer distance. The dependence of the exchange interaction on the $c/a$ ratio ($a$ and $c=2d_{12}$ are the hcp lattice constants) and implicitly on the interlayer distance $J = J(d_{12})$ has been calculated for bulk gadolinium, using density functional theory (DFT), by Turek et al. [105]. At the surface, due to the $d_{z^2}$ orbital symmetry of the surface state (see figure 2.3), the exchange interaction along $z$ axis will depend sensitively on the variation of the interlayer distance $d_{12}$. Thus any variation $\delta$ in the interlayer distance $d_{12} \pm \delta$ due to the coherent lattice vibration will be reflected in magnitude of the exchange interaction. As illustrated in fig. 5.24, the $J$ will increase or decrease with an amount $\delta J$ as the $d_{12}$ is larger or smaller relative to its value in equilibrium. The variation of the interlayer distance determines the appearance of a lattice strain, that has been shown to strongly affect the energetic position of surface states [146, 147, 148]. Thus, the lattice vibrations will be sensitively monitored by SHG signal since the SHG process evolves resonantly enhanced via the surface state. Another consequence of $J = J(d_{12})$ is the variation of the local magnetic ordering at the surface in parallel with the change in $d_{12}$. This affirmation is based on the Heisenberg model picture (see eq. 2.1) where the relative orientation of two nearest neighbors spins is determined by the sign and magnitude of the exchange interaction $J$. Such a periodic variation of the surface magnetic ordering is detectable with the transient odd SH field. Indeed, we observe periodic oscillations in the $\Delta_{odd}$, which corroborates this scenario. Thus, the exchange interactions seems to be the appropriate lattice-spin coupling mechanism since it is sensitive to changes in both
5.3 Coherent optical phonons and magnons on Gd(0001) surface

Figure 5.24: Schematic illustration of the coupling mechanism between lattice and spins oscillations within one oscillation period. At t=0 the lattice is contracted by an amount δ that increases the exchange interaction by δJ (see fig. 5.23), which results in an increased exchange splitting of the surface state and thus the SHG resonance enhancement via the surface state is less fulfilled. This explains the initial phases of the oscillatory lattice and spin coherence that show a minimum and maximum (fig. 5.21b), respectively. At t=T/2 the lattice is expanded, the J is decreased which means that ∆ex is decreased and the resonance enhancement is better fulfilled i.e. the coherent phonon shows a maximum while the spin oscillation shows a minimum. This scenario is repeated until the oscillations are damped.

subsystems. In how far will explain the observed phenomena is described in the following.

From the calculated dependence of J on the c/a ratio plotted in the figure 5.23, we notice an increasing magnitude of J with decreasing interlayer distance due to a better wavefunction overlap. Based on these facts one can suggest the following coupling mechanism. The coherent phonon excited at the surface produces periodical variations of the interlayer distance d12, which will modulate the exchange interaction strength according to J = J(d12). Hence, the degree of magnetic ordering at the surface (i.e. magnetization) determined by the magnitude of J, will also oscillate concomitant with the lattice vibration. In the same time, the modulations of d12 will build-up a periodically varying lattice strain that will periodically shift the surface state peak positions and implicitly modulates its exchange splitting i.e. a 'breathing' surface state. This scenario is depicted in figure 5.24 showing the presumable dynamics of J between two magnetic moments in adjacent layers and of the surface state exchange splitting ∆ex over one coherent phonon period. From the extrapolated phase to t=0 of the oscillatory component in SH fields (see figure 5.21b), one notices that ∆coh even starts with a minimum while ∆coh odd shows a maximum. The maximum in ∆coh odd reflects a better magnetic ordering and thus an increase of the exchange
coupling $J + \delta J$. The increased $J$ has been ascribed [105] (see fig. 5.23) to a compressive strain of the lattice i.e. the interlayer distance is decreased $d_{12} - \delta$. Also, the bigger the magnitude of $J$, the larger is the exchange splitting of the surface state and therefore less fulfillment of the SHG resonance condition, explaining the minimum in the $\Delta_{\text{even}}^{\text{coh}}$. At the half-period (the second instance in the figure), $\Delta_{\text{even}}^{\text{coh}}$ is maximum whereas $\Delta_{\text{odd}}^{\text{coh}}$ exhibits a minimum. Now the lattice suffers a tensile strain i.e. the interlayer distance is increased $d_{12} + \delta$ that results in a smaller exchange coupling $J - \delta J$ (produces minimum in $\Delta_{\text{odd}}^{\text{coh}}$) and thus a smaller exchange splitting of the surface state. The resonance enhancement via the surface state is better fulfilled and therefore one encounters a maximum in $\Delta_{\text{even}}^{\text{coh}}$. These sequential time-frames are repeated along the oscillatory transient and eventually damped after a time interval of $\approx 3$ ps.

The proposed model connects the lattice vibrations and the modulation of the surface magnetization via the exchange interaction $J$. Since the magnetization follows the lattice instantaneously (no build-up time in $\Delta_{\text{odd}}^{\text{coh}}$ observed within our time resolution of 35 fs), $J$ should provide a very strong interaction. This is indeed the case, with values for the intra-atomic exchange coupling $J_{4f-5d} = 94$ meV and $J_{5d-5d} = 531$ meV [138] that are much higher than the 12 meV energy of the coupled phonon-magnon mode, determined from the its measured frequency of 3 THz. The time equivalents of $J_{4f-5d}$ and $J_{5d-5d}$ are 6 fs and 1.2 fs, respectively. These values are smaller than our time resolution of 35 fs (laser pulse duration), which means that they provide a quasi-instantaneous coupling with regard to the experimental time resolution. Therefore, we can explain the quasi-instantaneous excitation of the lattice and spin coherence that proceed simultaneously within the time resolution of our experiment.

In the above considerations we have mentioned the exchange coupling constants between the 4f and 5d as well as 5d and 5d electrons. Accounting for their magnitude, both could explain the quasi-instantaneous coupling between lattice and spin excitations. Therefore the following question arises. What represents the periodic modulation of magnetization measured by the odd field – the oscillatory magnetic ordering of the 4f or the 5d magnetic moments? The MSHG measures the dynamics of the 5d valence electrons within the achievable spectral range between 1.48 - 1.7 eV. The 4f levels have a binding energy of $\approx 9$ eV [31] and thus are not directly accessible with the available laser photon energy. On the other hand, the dominant contribution to the SHG response on Gd(0001) comes from the exchange-split surface state whose energy splitting reflects the magnitude of the 4f moments [31, 30]. An oscillating exchange splitting (see fig. 5.24) will affect the orientation of the 4f due to the strong $J_{4f-5d}$ coupling between the surface state (5d$_{z^2}$ character) to the 4f electrons. Hence, a very plausible scenario is that the 4f moments will also oscillate with the same frequency as the lattice vibrations. Since we measure the dynamics of the 5d electrons and we have strong indications that the 4f moments are also involved in the observed coherent phenomenon, we conclude that the oscillations in the odd SH field represent the coherent modulation of the total magnetic moment in Gd.

Inelastic neutron scattering that measures directly the magnetic moments (the major contribution coming from the 4f moments in Gd case) of a ferromagnetic sample, gives for bulk Gd$^{15}$ [144] at $\Gamma$ point a magnon frequency of 3.4 THz, as can be seen in figure 5.20.

$^{15}$To the best of author’s knowledge, there are no reported measurements of the phonon and magnon
5.3 Coherent optical phonons and magnons on Gd(0001) surface

Figure 5.25: Time-resolved PE measurement of the $S^\uparrow$ surface state binding energy on the Gd(0001) surface at $T$=40 K. Upper panel: the transient behavior of the $S^\uparrow$ binding energy exhibits a continuous shift towards $E_F$ modulated by an oscillatory component. Lower panel: the oscillatory fraction of the binding energy (dots) obtained after subtraction of the incoherent part fitted (solid line) according to eq. 5.8. In the inset the Fourier transformation of the oscillatory signal gives a central frequency of $3.1\pm0.2$ THz. From [150].

Considering the lower coordinate of surface atoms such a value gives a good agreement with the observed frequency of $2.9\pm0.3$ THz. Moreover, we can argue that a lower frequency is required since an overlap of the surface phonon and magnon frequencies is a necessary condition in order to observe a coupled mode. Therefore, the magnon dispersion curves further support the idea of a coherent magnon involving the $4f$ moments.

As mentioned earlier for the coherent phonons, the SHG measures the modulation of the magnetic susceptibility and not the magnons as e.g. the neutron scattering does. Therefore, when mentioning coherent magnons we have in mind the oscillatory $\Delta_{\text{odd}}$ component.

To unambiguously proof the dynamics of the $4f$ moments it would be required to measure them directly with femtosecond resolution involving UV or x-ray UV sources from free-electron lasers or high-harmonics in rare-gas cells [149]. Also it would be interesting to perform a time-resolved x-ray magnetic circular dichroism (XMCD) experiment, that would monitor simultaneously the dynamics of the orbital and spin contributions to the total magnetic moment.

An independent experimental check for the proposed coupling mechanism has been done, within our lab, by time-resolved photoemission measurements of the Gd(0001) $S^\uparrow$ surface state component. These measurements have been performed by my colleagues P. Loukakos and M. Lisowski [150]. The experimental apparatus and conditions are identical with the one presented in section 5.2.1 except the sample temperature that is lower $\approx$40 K. Figure 5.25 shows the transient behavior in the binding energy of the majority surface state component. We observe a monotonous shift of the $S^\uparrow$ binding energy towards $E_F$ as a function of pump-probe delay, that is modulated by an oscillatory component with a
period of \(\approx 330 \text{ fs}\). After the subtraction of the incoherent background as has been done for the SH fields, one obtains the oscillatory contribution plotted in the lower panel of the figure 5.25. The result of Fourier transformation displayed in the inset of the figure, gives a central frequency of \(3.1\pm0.2 \text{ THz}\) that is in a very good agreement with the frequency measured by MSHG. Note that the required energy resolution in binding energy changes is \(\approx 1 \text{ meV}\), which has not been achieved for the unoccupied \(S^\downarrow\) component. Therefore, the suggested model of oscillating binding energy of the surface state with the lattice vibration, firstly proposed accounting only for the nonlinear optical measurements [17], is confirmed (at least for the \(S^\uparrow\) component).

A theoretical support of the proposed coupling mechanism comes from the DFT calculations performed by Blügel and coworkers [151]. They computed the change in the binding energy of the surface state due to a compressive lattice strain. The result for the majority surface state component is depicted in the figure 5.26. Upon a lattice contraction the \(S^\uparrow\) energetic position is shifted to lower binding energies. Based on this calculations one can evaluate the variation in the interlayer distance produced by the coherent phonon oscillation. Fitting the oscillatory binding energy data from figure 5.25 with the eq. 5.8, one obtains an initial amplitude (t=0) of 1.6 meV. According to the figure 5.25 this value corresponds to a contraction of 70 pm that represents 0.24% from the equilibrium \(d_{12}=2.89\AA\) [25] interlayer distance. Thus the observed oscillations represent a modulation of the interlayer distance of less than 1%.

5.3.3 Conclusions

Employing the pump-probe MSHG technique on the Gd(0001) surface we have observed coupled coherent lattice and spin excitations evolving with a common frequency of 2.9 THz. This has been deduced from the pronounced oscillatory features present in the SH fields, which measure simultaneously and separates the electron/lattice and spin dynamics owing to the symmetry of these fields with respect to magnetization reversal. A very re-
markable fact is that we measure for the first time the presence of coherent optical phonon on a metal. The excitation of the coherent phonon is attributed to the asymmetric excitation of the surface state components which produces an ultrafast charge redistribution at the surface that suddenly displaces the surface ions potential and sets the surface atoms into an oscillatory motion. From the initial cosine-like phase of the coherent phonons and taking into account that is a charge-driven coherent lattice vibration we identify the excitation mechanism as being DECP-like. The coupling between the lattice vibrations and the spin system is determined by a dynamic variation of the exchange interaction strength $J$ with the interlayer distance $d_{12}$. The magnitude of $J$ explains the observed quasi-instantaneous coupling between phonons and magnons. This type of coupling represents a new, dynamical interaction mechanism between phonons and magnons. The proposed excitation mechanism deduced from MSHG data, has been confirmed by TRPE measurements of the surface state binding energy. In time-resolved photoemission, a periodic modulation of the $S^1$ surface state binding energy has been observed having the same frequency as the coupled phonon-magnon mode measured with MSHG.

5.4 Coherent surface and bulk lattice vibrations on Gd(0001)

In the preceding section, the surface coherent phonon-magnon mode has been studied in detail by investigating its origin, excitation mechanism and the coupling between lattice and spin excitations. Since the coherent phonon mode corresponds to the vibration of the surface layer against the underlying bulk, the question arises whether the bulk phonon modes are also excited. This subject is investigated using the time-resolved linear reflectivity and second-harmonic generation techniques, and is presented in the following section.

5.4.1 Results

Inspecting the Gd phonon dispersion curves in the figure 5.20, one observes that the frequency of the measured surface phonon mode of 3 THz is laying in the proximity of the bulk mode with 3.14 THz at $q=0$. This suggests that the surface mode can, in principle, couple to the adjacent bulk layers and trigger an oscillatory motion of bulk atoms. The existence of bulk phonons in Gd(0001) after photoexcitation has been addressed employing the pump-probe linear reflectivity (LR), that is a bulk sensitive technique within the optical penetration depth\(^{16}\) (here $\delta \approx 20$ nm). Simultaneously, the SHG response has been measured that reflects the surface phonons dynamics. Hence, by the use of both techniques one can measure and separate the bulk and surface behavior.

Such a combined measurement performed at $T=90$ K is presented in the figure 5.27. In the upper side of the figure the measured transient dynamics of the even SHG ($\Delta^{2\omega}$) and linear reflectivity ($\Delta^\omega$) fields is displayed. $\Delta^\omega$ is defined as $\sqrt{\frac{I^\omega(t)}{I^\omega(t_0)}} - 1 \approx \frac{1}{2} \frac{I^\omega(t) - I^\omega(t_0)}{I^\omega(t_0)}$, where $I^\omega(t)$ and $I^\omega(t_0)$ denote the reflected intensities for positive and negative pump-probe delays, respectively. In the SHG signal pronounced oscillations are present while

\(^{16}\)The literature data regarding the imaginary part of the refractive index $k$ at $\lambda=800$ nm are very scattered, ranging from 1.55 to 3.46 that give optical penetration depths $\delta = \frac{\lambda}{4k}$ from 41 nm to 18 nm. [152]
in the pump-induced variations of LR, although weak, are also visible. After removing the incoherent background (the solid lines) as has been described earlier (section 5.3), the oscillatory fraction is obtained, which is plotted in the lower part of the figure 5.27. Now one can clearly notice the existence of an oscillatory component in the linear reflectivity, whose amplitude is in the $10^{-5}$ range i.e. three orders of magnitude smaller than the oscillations $\Delta_{\text{coh}}$ in the SH signal. This explains why its presence is not so evident in the raw LR signal. Based on the bulk sensitivity of the linear reflectivity, we ascribe the oscillatory signal measured by LR to coherent bulk phonons in the Gd(0001) sample.

Performing the Fourier transform of the oscillatory signals displayed in figure 5.28, one obtains two different central frequencies of $3.3 \pm 0.1$ THz and $2.9 \pm 0.1$ THz for bulk and surface phonons, respectively. First, the dissimilar frequencies of the phonon modes indicate that they originate from different environments i.e. bulk and surface. Hence, one can assign the measured frequency difference to the different coordinate number encountered at the surface (9) with respect to bulk (12) i.e. the chemical bonding is stronger in the bulk than at the surface, that yields a higher frequency for the latter one. The Fourier spectra in the figure 5.28 exhibit asymmetric peak shapes towards higher and lower frequency for the bulk and surface phonon mode, respectively. As will be shown in the following, this asymmetry can be related to a dynamical change of the frequency i.e. a frequency chirp. Such a behavior has been reported in literature [153, 154, 155, 156] for bulk coherent phonons in semimetals and semiconductors. This has been ascribed to anharmonic
5.4 Coherent surface and bulk lattice vibrations on Gd(0001)

Figure 5.28: Left The Fourier transformation of the oscillatory signals measured in SHG ($\Delta^{2\omega}_{coh}$) and LR ($\Delta^{\omega}_{coh}$) that give a frequency of 2.9 THz and 3.3 THz for surface and bulk phonons, respectively. The measured frequencies are indicated by the arrows. Note the asymmetric peak shapes which indicate a time-dependent frequency change. Right The oscillatory SH field plotted with and without a linear frequency shift. The measured data could be fitted properly only incorporating a frequency chirp, in this case of 0.17 THz/ps.

effects of the vibrational potential and/or to electronic softening of the inter-atomic bond strength under the effect of excited carriers [157].

In order to clarify the origin of the asymmetric shape of the Fourier spectra and of the opposite broadening for bulk and surface phonons, we have employed two methods to analyze the frequency evolution in the time domain. The first one is based on the phenomenological model of an exponentially damped oscillator defined in the eq. 5.8. In this expression the term $c = \frac{1}{2} \frac{\partial \Omega}{\partial t}$ describes a linear chirp of the frequency, which was necessary to be introduced in order to describe the oscillatory data for time delays > 1.5 ps. A comparison between the data with and without chirp for the $\Delta^{2\omega}_{coh}$ is plotted in figure 5.28. The fitting curves of the oscillatory signal according to 5.8 are plotted as solid lines in the lower part of the figure 5.27. The obtained values for the frequency, chirp and delay time from the fit are $\Omega_s=2.8\pm0.05$ THz, $c_s=0.17\pm0.01$ THz/ps, $\tau_s=0.86\pm0.02$ ps for the surface mode while for the bulk phonons $\Omega_b=3.44\pm0.05$ THz, $c_b=-0.12\pm0.05$ THz/ps, $\tau_b=0.9\pm0.01$ ps. The values and the signs of the chirp parameters give a quantitative evaluation of the observed asymmetric Fourier spectra, and confirm also their opposite broadening tendency. Plotting the time-dependence of the frequency chirp, as shown in the figure 5.29, we note that they cross each other around 2 ps delay time. This interesting feature will be detailed in the following.

The second analysis method has been employed in order to obtain further insight in the phonon dynamics, and evaluates the instantaneous values of frequency and amplitudes. For this purpose the following fit function has been used:

$$\Delta_{coh}(t') = \left[ A(t) + \frac{\partial A(t)}{\partial t}(t - t') \right] \cos[2\pi(\Omega(t)t' + \phi(t))]$$ (5.9)
Figure 5.29: The time evolution of the instantaneous amplitudes (top) and frequencies (bottom) of the bulk and surface coherent phonons obtained by fitting the oscillatory components of LR and SHG with the expression 5.9. **Top** The bulk and surface coherent phonons amplitudes denoted by $A^\omega$ and $A^{2\omega}$, respectively, decay exponentially with the same time constant $\tau=0.87$ ps. **Bottom** The transient frequency values of the bulk and surface phonon modes exhibit an opposite frequency chirp showed by the red and the blue lines: redshift for bulk phonons and blueshift for surface phonons. The frequency change of both modes reach a common level, denoted by the dashed line, at a frequency value $\Omega_0=3.15$ THz and around 2 ps delay time. This delay coincides with the $e$-$p$ equilibration as deduced from the saturation of the incoherent SHG signal (solid line) $\Delta^{2\omega}_{\text{incoh}}$. 
The analysis procedure has been carried out as follows. Within a time window of 0.4 ps centered at time \( t \), that is shifted in steps of 0.1 ps along the pump-probe delay, the oscillatory signal is fitted with \( A \) and \( \Omega \) as adjustable parameters. The values of \( \frac{\partial A}{\partial t} \) and \( \phi \) are determined by the \( A \) and \( \Omega \) from the previous and actual fitting frame. The resulting values for the instantaneous frequency and amplitude are displayed in figure 5.29. The frequency of the surface mode shows a monotonous increase with time i.e. blueshift, that goes along the extrapolated values of the linear chirp obtained from the previous fitting procedure. For the bulk mode, despite of the lower statistics, we observe a clear decrease in the frequency i.e. redshift, following the linear chirp values. Both data sets are merging to a common point around 2 ps, that corresponds to a frequency value of 3.15 THz, indicated in the figure 5.29 by the dashed line. This value agrees well with the calculated frequency of the bulk LO phonon mode \( \Gamma_{3+} \) in gadolinium at the \( \Gamma \) point.

Summarizing the experimental data, we measure the presence of oscillatory components in the pump-induced variations of the SHG and LR signals whose relative magnitude is in the \( 10^{-2} \) and \( 10^{-5} \) range, respectively. They exhibit different initial frequencies that amounts to 3.4 THz for bulk and 2.8 THz for the surface mode. We observe a changing in time of the instantaneous frequencies, that shows opposite trends. The bulk frequency decreases i.e. red frequency shift whereas the surface frequency increases i.e. blue frequency shift. This trend reaches a common level around 2 ps. A very interesting fact is that we observe a redshift in the bulk frequency while literature reports [153, 155] regarding bulk coherent phonons, encounter an opposite frequency shift i.e. a blueshift.

5.4.2 Discussion

We start the discussion of the experimental results with the incoherent dynamics presented in upper panel of figure 5.27. Here, the linear reflectivity data could be fitted (solid line) by an exponential increase which gives a time constant of 0.88±0.02 ps. The monotonous increase of the LR and SHG signals reflects the bulk and surface electron dynamics, respectively, after laser excitation. The laser-induced electron dynamics\(^{17}\) is shortly described in the following. Initially the laser energy is deposited in the electronic system which through inelastic \( e-e \) scattering events establishes a hot Fermi-Dirac distribution (here within 100 fs). Subsequently, the energy stored in the electron bath is transferred to the lattice via \( e-p \) scattering, that increase the temperature of the latter one. Within few ps after excitation, the electron and phonon baths reach a common temperature within few ps. The observed saturation of the LR and SHG signal around 3 ps, is thus determined by the equilibration of electrons and phonons temperature. Therefore, for Gd (at the employed laser fluence) the photoexcited hot electrons equilibrate with the lattice at a time constant of 0.88 ps.

At this point, it is worth discussing more detailed the origin of the oscillatory signal measured by linear reflectivity. We have ascribed the LR oscillations to bulk coherent phonons based, first, on the bulk sensitivity considerations of the LR technique. Secondly, the surface coherent mode measured by SHG has a different frequency that excludes measuring of the same phonon mode by both techniques. The coherent phonon excited at the surface represents the modulation of the interlayer distance between two adjacent

\(^{17}\)The reader is referred to chapter 2 for a detailed discussion regarding the laser-induced electron dynamics.
(0001) planes *i.e.* along c-axis. The initial amplitude of the surface mode represents 10% from the total pump-induced dynamics (see fig. 5.21), which means that a considerable amount of excitation energy resides in the surface vibrational mode. Based on this, it is reasonable to assume that the strong surface oscillatory motion couples to the underlaying atomic layers down to a certain depth. Therefore, we ascribe the oscillatory LR signal as arising from the near-surface bulk layers that are set in motion by the strongly excited coherent surface mode. This conclusion is supported by the fact that in bulk, one can photoexcite totally symmetric $A_{1g}$ coherent phonon modes exclusively [158]. For Gd, the predicted [143] frequency of the symmetric $A_1$ mode is 2.3 THz, which is obviously smaller than the measured value of 3.3 THz (deduced from Fourier spectrum). Since the frequency of 3.3 THz observed in LR is close to the value of bulk $\Gamma_{3+}$ mode (asymmetric) of 3.15 THz, we draw the conclusion that the observed bulk phonon mode is excited in the near-surface region by the surface coherent phonon mode.

Regarding the surface and bulk coherent oscillations, we observe initially two different frequencies whose difference amounts to $\approx 18\%$. The higher bulk phonon frequency is explained by the higher atomic coordinate and by the effectively stronger bonding in the bulk with respect to the surface. Breaking of the translation symmetry along z axis (normal to the surface) in the surface region results in different bonding strengths acting on the topmost layer and the atomic layers underneath. Accordingly the interlayer distances are relaxed, their calculated [159] values and signs being: $\approx-3.5\%$ from the bulk equilibrium distance, for the distance between the surface and the subsurface layer and $\approx+1\%$ for the next, subsequent interlayer distance. Hence, the different initial frequencies for the surface and bulk modes are well conceivable from the arguments of different surface and bulk environments and the corresponding bonding strengths.

In the following we address the transient frequency evolution and the opposite frequency shift determined for the coherent surface and bulk phonons. From figure 5.29 we have seen that the bulk mode exhibits a transient blueshift of the frequency of $\approx 9\%$ within the first 3 ps. In the literature [153, 155] the opposite trend *i.e.* redshift in the time evolution of coherent phonons is reported and has been explained by third-order anharmonic effects of the vibrational potential [153]. We have checked if higher order terms of the vibrational potential could account for the observed behavior of bulk and surface phonons. The approximation of a harmonic vibrational potential is valid for small atomic displacements, which in general is not true for the high non-equilibrium conditions produced by femtosecond lasers. Thus, one has to take into account higher order terms in atomic displacements for the potential energy expression: $U(x) = k_2 x^2 + k_3 x^3 + k_4 x^4 + \ldots$ where $k_i$ represent the force constants of the oscillator and $x$ the atomic displacement. Solving the equation of motion for such an anharmonic oscillator one obtains [160] the oscillator frequency:

$$\omega = \omega_0 + \left( \frac{3k_4}{8\omega_0} - \frac{5k_3^2}{12\omega_0^2} \right) \cdot A^2$$

(5.10)

where $\Omega_0$ is the frequency of the harmonic oscillator and $A$ is the amplitude of motion. In the right-hand side of the equation we have the fourth and cubic orders corrections of the frequency that scale with the amplitude in square. According to 5.10 we expect an increase or a decrease of the initial phonon frequency accounting for fourth or cubic
anharmonicities, respectively. In bulk gadolinium, third anharmonic terms are not allowed due to the lattice symmetry\(^\text{18}\) for vibrations along c-axis. According to eq. 5.10 the remaining fourth order would increase the phonon frequency that is the opposite of the encountered trend for bulk phonon mode. At the surface the cubic anharmonic terms are allowed, that would decrease the phonon frequency. Again we observe the reversed behavior for the surface mode. Therefore, we can exclude the anharmonic effects as being the source of the transient frequency shift measured for bulk and surface coherent phonons. As will be shown in the following, we suggest that the transient photoexcited population is responsible for the observed frequency chirp.

As shown in figure 5.29, the initial frequency difference between \(\Omega_s\) and \(\Omega_b\) gradually decreases to zero, where both frequencies reach an asymptotic value of 3.15 THz around a delay time of 2 ps. This frequency reproduces the calculated equilibrium value \(\Omega_0\) \[^{143}\] of the bulk \(\Gamma_3\) mode at \(\Gamma\) point in Gd. Although the error bars increase in \(\Omega_s\) around 2 ps due to the increased damping and it makes difficult to retrieve the bulk frequency at later delays. However, the frequency convergence of the phonon modes is well distinguished. Simultaneously, inelastic electron-phonon scattering transfers the excess energy from the electron to the phonon bath. This process is reflected in the transient incoherent variations of the SH field \(\Delta \omega_{\text{incoh}}\) plotted also in the figure. Interestingly, its time-dependence shows a good agreement with the transient frequency chirp in \(\Omega_s\). This parallelism between \(\Delta \omega_{\text{incoh}}\) and the transient \(\Omega_s\) suggests that the incoherent electron dynamics is responsible for the frequency chirp of the surface mode. Regarding the bulk electron dynamics, we have obtained from the incoherent part of the LR signal an electron-phonon equilibration time of 0.88 ps (see above). The instantaneous amplitudes of the bulk and surface phonons plotted in fig. 5.29, decay exponentially with a time constant of 0.87 ps. Also the decay times for surface and bulk phonons deduced from fitting the oscillatory data with relation 5.8 have comparable values of \(\tau_s=0.86\) ps and \(\tau_b=0.9\) ps, respectively. Based on the good agreement of these values, we can conclude that the transient electron dynamics determines the decay time of both surface and bulk coherent phonon modes. This fact identifies the inelastic electron-phonon scattering as an efficient decay channel for the coherent lattice vibrations in case of Gd(0001).

We have shown above that both, the bulk and surface coherent phonons, live as long as a non-equilibrium exists between electrons and lattice. The question that arises is how can the electron-phonon interaction explain the change in the frequency of the coherent phonon modes. The excitation mechanism of the surface coherent vibration has been attributed (see section 5.3) to an asymmetric photoexcitation of the surface state that leads to an ultrafast charge redistribution at the surface which triggers the initial ion displacement. The changed surface potential on which the atoms start to oscillate thus depends on the photoexcitation strength of the electronic population. The electron-phonon interaction redistribute continuously the excess energy residing in the electronic system and therefore the shape of the surface potential will evolve accordingly. Eventually the electron and phonon baths reach a common temperature \(i.e.\) are in equilibrium, that determines the surface potential to reach its equilibrated state before excitation. This is corroborated

\(^{18}\)The inversion symmetry of the hcp lattice should be fulfilled. Thus, just even order anharmonicities are allowed in the hcp bulk.
by the coherent phonon frequency which reaches the equilibrium frequency of $\Omega_0 = 3.15$ THz when the electrons are in equilibrium with the lattice. The same argument holds also for the bulk phonons dynamics namely the shape of the bulk vibrational potential is determined by the relaxing electron population, that explains the transient frequency shift and eventually levelling to $\Omega_0$. But how the opposite frequency shift for surface and bulk phonons can be explained?

The initially excited electron-hole pairs thermalizes to a hot electron population within 100 fs. Due to the energetic positions of the surface state components with respect to $E_F$, the effect of an excited electron temperature is a stronger decrease of the electron population in the majority state (-0.2 eV binding energy) than the population increase of the minority component (0.4 eV binding energy). Thus, a hot electron temperature results in a lower electron density at the surface with respect to bulk. The excited surface and bulk electron densities are relaxed by incoherent e-p scattering, that changes gradually the shape of the vibrational potential and implicitly the oscillation frequency. Due to the different electron densities in the surface and bulk their behavior is opposite as they relax to the lattice: the bulk electron density gradually decreases while the opposite holds for the surface. This explains the observed opposite frequency shift for bulk and surface phonons.

Summarizing, the observed time-dependent shift in the frequency of the phonon modes could not be explained by anharmonic corrections of the harmonic potential but through the influence of the transient excited electron population on the shape of the vibrational potential. Thus the frequency change of both coherent modes has a pure electronic origin.

### 5.4.3 Conclusions

The coherent optical phonon excited at the Gd(0001) surface couples to the underlying atomic layers which leads to a coherent oscillatory motion of the latter ones. Employing simultaneously surface (SHG) and bulk (LR) sensitive techniques we could distinguish and analyze the dynamics of the coherent phonon modes at the surface and in the bulk. The initial frequencies amount to 3.4 THz and 2.8 THz for the bulk and surface phonon mode, respectively. As a function of pump-probe delay we observe a frequency redshift (decrease) for the bulk mode and a blueshift (increase) for the surface mode that goes in parallel with the incoherent e-p dynamics. The interesting feature of the frequency redshift of the bulk mode, that is opposite trend compared to the results reported in literature, could not be explained by anharmonicity effects. Instead, the transient frequency shift of both coherent modes have been ascribed to the time-evolution of the surface and bulk vibrational potentials under the effect of a relaxing photoexcited electronic population. The electron-phonon scattering has been identified as an efficient decay channel for bulk and surface coherent phonons since they live as long as a non-equilibrium exists between electrons and lattice.
5.5 Coupled coherent phonon-magnon mode: excitation and relaxation

The scope of the present section is to investigate in detail the proposed excitation mechanism of the coherent phonon-magnon mode and to identify the available decay channels. For this purpose, the systematic variation of the laser photon energy and temperature of the sample has been employed. Varying the laser wavelength and accounting for the specific electronic structure of the Gd(0001) surface, different levels of photoexcited carriers are produced in the surface state. Thus, the charge-driven character of the excitation mechanism proposed for the coupled phonon-magnon mode can be tested. Based on the temperature dependence of the surface state exchange splitting, we perform a further check for the excitation of the coupled lattice-spin quasiparticle. Moreover, rising the temperature, the thermal (incoherent) electron, phonon and magnon population is increased that can scatter with the coherent mode and may represent an efficient decay channel of the coherence in the lattice and spin system.

5.5.1 Spectral dependence

First we study the spectral dependence of the transient linear and nonlinear optical response from Gd(0001) surface after laser excitation. For these investigations, the laser photon energy has been varied simultaneously for the pump and probe beams in the available tunability range of the cavity-dumped Ti:Sa oscillator between 1.44 and 1.68 eV. The measured time-resolved dependencies of the SHG signal are plotted in the figure 5.30 together with the transient linear reflectivity (the solid line). The first observation is that despite of the relatively narrow spectral range we see a strong variation of the nonlinear optical response with the laser wavelength. The behavior of the linear reflectivity signal recorded simultaneously with the SHG signal, is wavelength-independent in this spectral range since is not sensitive to the surface state but rather to the bulk states. The showed $\Delta R/R$ data set represents an average over all used wavelengths since no change in the time-dependent profile is observed by varying the laser wavelength, just in the magnitude of the variations. These observations confirm the key role of the exchange-split surface state in the SHG process whose optical transitions evolve resonantly (see figure 5.11) via the surface state.

In order to analyze the rather complex behavior of the even SH field plotted in the upper panel of figure 5.30, its dynamics is separated in coherent and incoherent contributions, that are evaluated here at 80 fs delay time [119]. This delay has been chosen since we are interested on the effect of the excited electron population on the coherent mode. The response at 80 fs pump-probe delay$^{19}$ reflects the initial excitation strength injected into the system upon absorption of the fs laser pulse. At this delay the electronic system is internally thermalized as deduced from the transient energy density obtained in the TRPE measurement (see fig. 5.16) and the 2TM simulation of the electron energy redistribution(see fig. 2.7) on Gd(0001).

$^{19}$The influence of the coherent artifact produced by the cross-correlation of the pump and probe beams, can be safely neglected at 80 fs delay since its effect can be traced up to a delay of maximum 50 fs (see
Figure 5.30: Laser wavelength dependence of the transient SH fields and of LR signal from Gd(0001)/W(110) at T=100 K. **Upper panel:** The transient linear reflectivity (black solid line) does not change with the laser photon energy owing to its bulk sensitivity. The even SH field behavior reveals a competition between coherent and incoherent components as a function of photon energy. The former ones dominate the dynamics for lower photon energies while the latter ones are governing the higher photon energy spectra. **Lower panel:** The time evolution of the odd SH field exhibits a significant spectral dependence for the initial drop in the transient signal and the amplitude of the oscillatory part *i.e.* both quantities increase with increasing the laser photon energy. Adapted from [119].
5.5 Coupled coherent phonon-magnon mode: excitation and relaxation

Figure 5.31: Photon energy dependence of the coherent (squares) and incoherent (empty circles) components of the transient SH even field measured at 80 fs delay time. Both quantities are normalized to the value of even SH field measured at negative delays. Note the clear opposite trend of the coherent and incoherent contributions as a function of photon energy. The solid and the dashed lines are guides for the eye.

Figure 5.30 (upper panel) shows the spectral dependence of the transient even field $\Delta_{\text{even}}$, which exhibits two trends that evolve differently for its coherent and incoherent components. For small photon energies (the 860 and 840 nm data sets) the coherent oscillatory part dominates while for larger photon energies (e.g. 740 nm) the incoherent component prevails. These observations are based on (i) the lack of the incoherent component signature for the measurements at small photon energies, the transient signal having a pure oscillatory character (e.g. 840 nm data set) (ii) the appearance of a pronounced incoherent component for larger photon energies whilst the oscillatory fraction decreases gradually as the photon energy is increased. Such a behavior suggests that for small photon energies the excitation energy goes preponderantly into coherent part whereas the opposite holds for larger photon energies. The possible effect of the probe beam (since the pump and probe beams have the same wavelengths) on the excitation and the subsequent dynamics of the system is discussed later in this section.

The competing behavior of the coherent and incoherent parts of the $\Delta_{\text{even}}$, that is already observable in the raw SHG data of figure 5.30, is much more clearer seen in figure 5.31. Here we plot the coherent phonon amplitude $A_{\text{even}}$ and the incoherent component $\Delta_{\text{incoh}}$ measured at a 80 fs delay in the even SH field for various laser photon energies. Their opposite trend as the laser photon energy increases is clearly distinguishable. For longer wavelengths the incoherent part is close to zero while the coherent one exhibits a maximum and the reversed situation is encountered for smaller wavelengths.
Figure 5.32: Schematic spin-resolved electronic structure for Gd(0001) at Γ point and the main absorption channels for the pump beam at the fundamental frequency depicted by the double-head arrows, that represent the smallest and the largest employed photon energies. The occupied part of the electronic structure is obtained from photoemission measurements [17], the unoccupied surface state component from STS investigations [48] and the unoccupied bulk states from inverse photoemission results [32]. The pump beam excites electrons (filled circle) from bulk to the surface state leaving behind a hole (empty circle), in the minority channel, and majority electrons from surface state to the unoccupied bulk state. Upon increasing the fundamental photon energy (double-head arrows) the absorption in the minority channel is enhanced due to the better energy matching. The optical transitions for the probe SHG process are displayed close to the edges of the diagram. Note that the unoccupied bulk state is measured without spin resolution, but it arises mainly from the unoccupied majority 5d bulk state [32].

The spectral behavior of the transient oscillatory ∆_{even} can be understood by inspecting the schematic spin-resolved electronic structure of Gd(0001) at Γ point, presented in the figure 5.32. Note that in the following we discuss the excitation process i.e. the pump-induced optical transitions depicted in the figure 5.32 by the double-head arrows that represent the lowest and the highest achievable photon energies, respectively. For long wavelengths the laser photon energy does not match the energetic separation in the minority channel i.e. between the occupied bulk state and the unoccupied S↓ surface state. This is not the case for the majority channel where even the smallest photon energy bridges the gap between the S↑ surface state and the unoccupied bulk state. Therefore, for low photon energies the spin-up optical transitions are dominant since the spin-down channel contribution is weak due to the off-resonant spin-down transitions at this photon energy. Consequently, in this energy range the excess charge produced in the surface state...
is dominated by the photoexcited holes. In section 5.3 we have explained the excitation of the coherent phonon as being determined by the initially photoexcited excess charge in the surface state, that requires a transient charge redistribution in the surface region in order to be screened. This ultrafast charge redistribution is considered responsible for the excitation of the coherent mode. Thus, according to the proposed excitation mechanism the amplitude of the coherent lattice mode should reflect the magnitude of the photoexcited excess charge in the surface state. Hence for the low photon energy range a considerable amount of photoholes is generated in the surface state (there are very few photoexcited electrons in the spin-down component) that requires a large transient charge redistribution for screening and therefore producing large amplitude of lattice vibrations. Increasing the photon energy, the optical transitions in the minority channel become active and more electrons are excited in the minority surface state. Thus, a reduced amount of excess charge is produced in the surface state that requires a weaker transient charge redistribution. This results in a decreased coherent phonon amplitude which coincides with the experimental observation for the high energy range. Also with increasing photon energy we notice the appearance of a pronounced incoherent component in the transient SHG response. For the highest achievable photon energy one encounters a decrease in the $A_{\text{even}}$ over one order of magnitude (see fig. 5.31) whereas the drop in the magnitude of the incoherent contribution is almost three times bigger.

The time evolution of the incoherent part of $\Delta_{\text{even}}$ within the first 100 fs is attributed [17, 70, 119] to the relaxation of the highly photoexcited electrons to a thermalized electron bath via inelastic $e-e$ scattering. The electron thermalization is achieved by generating cascades of secondary electron-hole pairs which redistribute the energy of the initially excited electron gas (for details see chapter 2). The thermalized electrons are characterized by a common temperature $T_e$ that determines [44, 56] the excitation energy density $U(t) \propto T_e$ residing in the system. According to eq. 2.18 the pump-induced variations in the SHG response are proportional to $\frac{\partial \chi^{(2)}}{\partial T_e} \Delta T_e$ (also to variations produced by lattice temperature, lattice vibrations etc.) where the $\chi^{(2)}$ is the second-order susceptibility tensor. Thus we can consider the incoherent $\Delta_{\text{even}}$ at 80 fs (when the electron bath is thermalized) to reflect the initial excitation energy deposited into the system.

In order to explain the spectral dependence of the incoherent $\Delta_{\text{even}}$, presented in figure 5.31, we consider the effect of the photoexcited holes and electrons in the surface state components. As mentioned above, at low photon energies the hole generation in the majority surface state dominates over the electron excitation process in the minority channel. The photoexcited holes relax via a symmetric process as for the photoexcited electrons namely hole-hole scattering with generation of secondary hole-electrons pairs close to $E_F$. We can consider that the electrons and holes contribute equally to the energy density term $U(t)$ [56, 13], that is responsible for the induced changes of $\Delta_{\text{even}}$ at early times (see above). Thus for low photon energies we have mainly the contribution from photoexcited holes to the incoherent $\Delta_{\text{even}}$. As long as the amount of photoexcited electrons in the minority channel is reduced, the photoexcited holes contribution to the energy density dominates that is reflected as a relatively constant level in the incoherent $\Delta_{\text{even}}$. Increasing the photon energy, more electrons are excited in the minority surface state and their contribution adds to the energy density term $U(t)$, which decreases the magnitude of the $\Delta_{\text{even}}^{\text{incoh}}$ as can
Figure 5.33: Spectral dependence of the amplitude of the coherent magnons measured by odd SH field at the Gd(0001) surface for T=100 K. The coherent magnon amplitude increases with increasing laser photon energy. The solid line is a guide for the eye.

be observed in fig. 5.31.

Summarizing this part, the transient behavior of $\Delta_{\text{even}}$ upon laser wavelength variation confirms the charge-driven character of the proposed excitation mechanism showing that the amplitude of the coherent oscillations in $\Delta_{\text{even}}$ (ascribed to coherent phonons) scales with the photoinduced excess charge in the surface state. The incoherent electron and hole dynamics reflected by the $\Delta_{\text{even}}^{\text{incoh}}$ at early times, give a measure of the photo-injected energy density in the surface state, that increases with the efficiency of the spin-selective optical transitions in the surface state components.

Now we address the spectral dependence of the transient odd SH field, that is displayed in the lower panel of the figure 5.30. For clarity reasons we show here three exemplary data sets, the other measurements lying in between and following the trend of the plotted dependencies. We observe that the transient $\Delta_{\text{odd}}$ shows a pronounced dependence on the laser photon energy in the initial drop at early delays and in the amplitude of the oscillatory component. The abrupt drop within laser pulse duration has been discussed in detail in section 5.2.1 and interpreted as the decrease of the spin polarization at the Gd(0001) surface due to spin-flip scattering of hot electrons among spin-mixed states. The oscillatory component of $\Delta_{\text{odd}}$ has been assigned before (section 5.3) to coherent magnons having the same frequency as the coherent phonons measured in $\Delta_{\text{even}}$.

The explanation for the spectral dependence of the initial drop in $\Delta_{\text{odd}}$ is based on the variations of the spin polarization of the surface state as the photon energy is modified. At low photon energy the spin-up channel is active that excites majority electrons from the surface state to the bulk and consequently the spin polarization of the surface state is reduced. In this photon energy range the spin-down transitions are considered to have a weak contribution due to the photon energy mismatch in the spin-down channel (see
Increasing the photon energy, the spin-down channel starts to contribute, due to the better photon energy matching, and minority electrons are photoexcited in the $S^\downarrow$ component. Simultaneously majority electrons are promoted from the surface to the bulk state. Both processes are decreasing further the spin polarization of the surface state that is reflected in the measured $\Delta_{\text{odd}}$ by an increasing drop for higher photon energies.

Simultaneously with the dynamics of the incoherent part an interesting behavior is developed by the coherent contribution of the odd SH field, that has been earlier ascribed to coherent magnons. As depicted in the figure 5.33 the amplitude of the coherent oscillations of $\Delta_{\text{odd}}$ increases with increasing photon energy over one order of magnitude. Such a behavior is intriguing since one expects that the coherent magnon amplitude scales with the amplitude of the coherent phonon which decreases with increasing photon energy (see fig. 5.31). This expectation is based on the proposed excitation mechanism of the coherent phonon-magnon mode, which predicts a coherent magnon amplitude proportional to the magnitude of the lattice displacement via the modulation of the exchange interaction strength $J$ (see fig. 5.24). Thus, according to the excitation model we expect a decreasing amplitude of the coherent magnon with increasing the photon energy, but the opposite trend is observed. One possible explanation is based on the relative phase $\phi$ (see section 5.1) between the even and odd SH fields, whose spectral dependence is displayed in the figure 5.9. In the photon energy range between 1.63 eV and 1.68 eV, the relative phase shows an oscillatory variation from -60 to 80 degrees complemented by a decrease of the magnetic contrast to zero value. The phase variation affects drastically the relative weight of the even and odd SH field contributions to the total SHG response (see fig. 5.6), and implicitly their oscillatory components. Thus, the observed relative phase variations can change also for the oscillatory fractions of the SH fields, that might lead to a significant increase in the coherent magnon amplitude as has been observed.

The spectral region in which the relative phase exhibits sharp modifications covers the last three points in the dependence of the oscillatory $\Delta_{\text{odd}}$ amplitude displayed in figure 5.33. Neglecting these data points we still encounter, for lower photon energy, an increasing trend in the amplitude of the coherent magnons by a factor of two. Thus one can suggest that in the high energy spectral range the three points follow the increasing behavior observed for at low energies but their magnitude is enhanced by a ”spectroscopic factor” determined by the value of the relative phase $\phi$.

One check for this tentatively explanation of the oscillatory $\Delta_{\text{odd}}$ behavior is to measure the pump-induced variations in the relative phase $\phi$. Unfortunately, with the present experimental setup such a measurement is not possible. However, the spectral dependence of the coherent magnon mode is not completely understood, and for the moment is still an open question that requires further investigations.

Until now we have obtained a general picture describing the encountered dynamics (coherent and incoherent SHG components) based on the photoexcitation effect of the pump pulse only. Since the probe beam has the same wavelength as the pump, it is worthwhile discussing its possible effects on the detected SHG response. One extreme case would be the bleaching of the probe optical transition after a strong pump beam excitation (see section 2.5 for details regarding bleaching). That means that the probe transition is blocked (the material becomes transparent for this optical transition), due to
the occupation by the excited population of the final states for the probe transition, that before excitation were available. This will be reflected in the transient signal as a sharp decrease that would be maintained as long as the electronic population is in a highly excited state i.e. within the first hundreds fs [85]. Such a behavior is not observed in the spectral dependence of the nonlinear optical response from Gd(0001) surface: $\Delta_{\text{odd}}$ decrease holds for several tens of ps whereas $\Delta_{\text{even}}$ exhibits the effect of the cross-correlation in the first 50 fs and starting with 80 fs reflects the pure electron dynamics (see fig. 5.16).

An intermediate situation would be when the probe optical transition can evolve but is contributing weakly to the initial excitation of the system. This last situation might be our case and we are aware of its potential implications e.g. the probe can contribute to the excitation of additional carriers in the surface state and thus influence the coherent mode and the initial dynamics in the incoherent SH fields. In order to evaluate the presumably effect of the probe beam on the excitation and the subsequent dynamics encountered on Gd(0001), a two-color experiment (different wavelengths for the pump and probe beams) would be required.

**Conclusion**

Pronounced changes in the time-resolved MSHG response from the Gd(0001) surface have been measured upon changing the laser wavelength between 740 nm and 860 nm. The coherent and incoherent components of $\Delta_{\text{even}}$ (that reflect the lattice and electron dynamics, respectively) show a competing behavior as the laser photon energy is varied. The coherent part of $\Delta_{\text{even}}$ dominates the low energy range whilst at higher photon energies the incoherent $\Delta_{\text{even}}$ part prevails. This behavior has been assigned to the relative weight of the spin selective optical transitions via the surface state contributing to the total MSHG signal. The amplitude of the coherent phonons varies over one order of magnitude in the investigated photon energy interval, which is attributed to the different degrees of charge asymmetry excited in the surface state as the laser wavelength is varied. Therefore this result provides a strong support for the proposed excitation mechanism of the coherent phonon-magnon mode as being a charge-driven mechanism. The incoherent part of $\Delta_{\text{even}}$ measured at 80 fs pump-probe delay reflects the photo-injected energy density, that increases with increasing photon energy. The behavior of the SH odd field is consistent with the variation of the spin polarization in the surface state that occurs simultaneously with the photoexcited charge redistribution i.e. at small photon energies a reduction of the spin polarization is encountered that continuously decreases as the photon energy increases.

**5.5.2 Temperature dependence**

In this part we study the temperature dependence of the time-resolved linear and SHG response from the Gd(0001)/W(110) sample. The idea is (i) to check how the temperature-dependent variation of the exchange splitting of the surface state can affect the coherent and incoherent SHG dynamics since this will lead to changes in the resonance condition of the SHG process via the surface state (ii) to investigate the possible relaxation pathways of the coherent mode, since elevating the temperature results in an increased electron, phonon and magnon thermal population, which can scatter with the coherent mode and
might modify the relaxation/damping of the coherent excitation.

The temperature dependent study has been performed between 40-400 K at a laser wavelength of 800 nm. The temperature range below the Curie point (293 K for bulk Gd) has been covered in 20 K steps whereas above \( T_C \) a lower density data points have been measured. This was due to the much longer measurement times required to resolve the small oscillatory components (one order of magnitude smaller in comparison to low temperature data) of the transient signal. The dependence of the transient SH even \( \Delta_{\text{even}} \) and odd \( \Delta_{\text{odd}} \) fields on the temperature are presented in figure 5.34 and 5.35, respectively. For clarity, in figure 5.35, a few representative SH odd field dependencies have been chosen, the other measurements following the observed trend.

We observe pronounced changes in both the coherent and the incoherent components of the MSHG response as the temperature is varied. In \( \Delta_{\text{even}} \), shown in fig. 5.34, the oscillation amplitude decreases gradually with temperature and simultaneously the pump-induced variations in the incoherent background decrease with increasing temperature. As an exemplary data set for temperatures above the Curie point we have selected the measurement performed at 400 K, that is magnified by a factor of two in figure 5.34. The oscillatory feature, although reduced in amplitude, can be clearly distinguished even at this elevated temperature. Regarding the \( \Delta_{\text{odd}} \) dependence, shown in figure 5.35, the magnitude of the oscillatory component is decreasing with increased temperature and can be resolved (with a reasonable statistics) up to 200 K. For higher temperatures the noise in \( \Delta_{\text{odd}} \) increases above the oscillatory amplitude, that hinder an exact determination of the temperature at which the coherent magnon vanishes. In this context we note that an oscillatory pattern is present (one period) for the 240 K data set, but is in the noise level of the transient signal. For the incoherent \( \Delta_{\text{odd}} \) we observe a temperature-dependent drop at early delay times (from 40\% at 40 K to 80\% at 240 K), displayed in the inset of the figure 5.35, followed by a levelling to a constant value. Increasing further the temperature the magnetic contrast \( \rho \) decreases to zero (see fig. 5.12) and the drop in \( \Delta_{\text{odd}} \) is approaching -1 value, that is equivalent with a total loss of magnetic ordering. This produces also a higher level of noise and because of this reason the curves for higher temperatures in the vicinity of \( T_C \) are left out.

**Incoherent behavior**

In the interpretation of the experimental data we start with the incoherent behavior of the \( \Delta_{\text{even}} \) and \( \Delta_{\text{odd}} \) transients. The time evolution (within 0-3 ps interval) of the incoherent part of \( \Delta_{\text{even}} \) (denoted \( \Delta_{\text{even}}^{\text{incoh}} \)) reflects [17, 70] the formation of a hot electron distribution via e-e scattering and the subsequent energy transfer to the lattice via e-p scattering, that leads eventually to a common temperature for the electrons and lattice subsystems. These events correspond to the rapid modifications of \( \Delta_{\text{even}} \) within the first\(^{20} \) 100 fs and its monotonous increase and equilibration around 2 ps, respectively. This behavior, presented in sections 5.3 and 5.4 at \( T = 90 \) K, is observed also here as plotted in the figure 5.34. Elevating the temperature, the absolute value of the pump-induced change in \( \Delta_{\text{even}}^{\text{incoh}} \)

\(^{20}\)As pointed out in the preceding section, the pump and probe cross-correlation pattern extends up to 50 fs (see figure 4.9), and thus the later time delays reflect the real dynamical behavior of the system.
Figure 5.34: The pump-induced variations in even SH field for various temperatures from a 20 nm Gd(0001) film. The measurements covered the 40–400 K temperature range and representative data sets are presented. As an example for the measured scans above Curie point (293 K), the measurement performed at 400 K is displayed (for clarity magnified by a factor of two).

shows a gradual decrease, which are quantified at 3 ps pump-probe delay. We will come back to these results further below.

The incoherent part of the $\Delta_{\text{odd}}$ depicted in the figure 5.35, shows also significant changes with temperature. In the low temperature range the temporal evolution of $\Delta_{\text{odd}}$ is rather monotonous, with the initial drop and the levelling off to a constant value (around 1.5 ps). At $T=100$ K, the equilibrium spin polarization is recovered on a hundreds of picosecond time scale due to spin-lattice relaxation, as has been shown in section 5.2.2. The magnitude of the initial decrease in $\Delta_{\text{odd}}$ as a function of temperature, plotted in the inset of fig. 5.35, shows a gradual decrease with elevating temperature. As suggested by the solid line, the drop in $\Delta_{\text{odd}}$ seems to follow a $M(T)$ behavior, reaching a -1 value (total loss of magnetic ordering) around 290 K (extrapolating the $M(T)$ curve), that is close to Curie point of 293 K. The initial drop observed in $\Delta_{\text{odd}}$ has been attributed (see section 5.2.1) to the spin-flip scattering of the hot electrons among spin-mixed states. Increasing the temperature
the amount of spin-mixed states is enhanced [36]. Thus, the increased drop in $\Delta_{\text{odd}}$ at early times, as the temperature is elevated, is explained by the increased phase space for spin-flip scattering provided by the higher density of spin-mixed states.

Coming back to the transient even SH field behavior, we have considered the saturation of $\Delta_{\text{incoh}}$ to a maximum level around 2 ps delay, as reflecting the $e$-$p$ equilibration. Since here we are interested in the effect of $e$-$p$ equilibration on the SHG dynamics we monitor the temperature-dependent behavior of the maximum value of $\Delta_{\text{incoh}}$ at a pump-probe delay of 3 ps. Hence, this is our criterion in interpreting the temperature-dependent profile of the incoherent $\Delta_{\text{even}}$. This is displayed in the left panel of the figure 5.36. Here we observe up to 100 K a constant level followed by a major decrease to 280 K and a relatively constant value (within the error bars) at $T_C$ and higher. In the same figure (right panel) we plot the variation of the surface state exchange splitting as a function of

Figure 5.35: The pump-induced variations in odd SH field for several selected temperatures measured simultaneously with the data presented in figure 5.34. In the inset the measured drop in $\Delta_{\text{odd}}$ close to zero delay is plotted versus temperature. The solid line in the inset is a guide for the eye.
temperature, as was measured with scanning tunnelling spectroscopy (STS) by Bode et al. [33]. As noticed, the temperature dependence of $\Delta_{\text{max, even}}$ and of the surface state $\Delta_{\text{ex}}$ exhibit a few similarities. We observe nearly constant levels in both dependencies covering the same temperature intervals i.e. from low temperature to 100 K and from $T_C$ to higher temperatures (360 K for $\Delta_{\text{ex}}$ and 400 K for $\Delta_{\text{max, even}}$). Also we know that the SHG process evolves resonantly enhanced via the surface state, and thus any change (binding energy, broadening etc.) of the latter one will affect sensitively the SHG response. Hence, these facts suggest that the $\Delta_{\text{ex}}$ of the surface state might be related to the observed dynamics of $\Delta_{\text{max, even}}$.

Considering the electronic structure of Gd(0001) surface plotted in fig. 5.32, we see that a decreased $\Delta_{\text{ex}}$ due to temperature increase affects mainly the efficiency of the optical transitions in the minority channel. The transitions in the majority channel are less affected due to the energetically broad final state of the optical transition and due to smaller change in binding energy of the majority surface state [34, 33]. At low temperature and for the employed photon energy of 1.55 eV, the transitions in both majority and minority channels contribute, and photoexcited electrons and holes are excited in the surface state whose thermalization (and subsequent cooling to the lattice) produce the observed changes in $\Delta_{\text{even}}$ (see the preceding section). Increasing the temperature to 100 K the exchange splitting remains nearly constant [30] and thus a constant level of $\Delta_{\text{max, even}}$ is observed (see fig. 5.36). Above 100 K the $\Delta_{\text{ex}}$ gradually decreases i.e. $S^\downarrow$ shifts to lower binding energies, which means that the laser photon energy matches better the energetic separation in the minority channel, that enhances the excitation probability of the minority electrons in the surface state.

As pointed out in the previous section, an increased population of electrons (and holes) increases the energy density into the system that decreases the magnitude of $\Delta_{\text{even}}$. The same interpretation holds also here, but now the increased electron population is determined by the shift of the spin-down surface state and not because of the increased photon energy. The decrease of $\Delta_{\text{max, even}}$ continues as long as the $\Delta_{\text{ex}}$ decreases i.e. up to the Curie
point. Above $T_C$, $\Delta_{ex}$ is constant [33] (up to the highest investigated temperature of 360 K) and is reflected as a constant level of the $\Delta_{max}^{even}$. However, their absolute changes upon temperature increasing are different with $\Delta_{ex}$ that reduces by roughly 50% while $\Delta_{max}^{even}$ decreases by more than one order of magnitude. That means there is no linear relationship between these quantities, which suggests either a nonlinearity between $\Delta_{ex}$ and the carriers excitation probability or there is another process that contributes to the $\Delta_{max}^{even}$ behavior.

Summarizing, by considering the qualitative similarities of the $\Delta_{max}^{even}$ and the $\Delta_{ex}$ of the surface state and accounting for the resonance enhancement of the SHG process via the surface state, we could explain the temperature-dependent variation of $\Delta_{max}^{even}$ as a changing carriers excitation probability in the surface state due to the temperature-dependent shift of the surface state components i.e. a decreasing exchange splitting of the surface state.

Coherent behavior

In the following we continue with the presentation of the behavior of the coherent phonon-magnon mode upon temperature variation. The oscillatory component of the transient SH fields has been obtained after removing the incoherent background in an identical manner with the procedure presented in section 5.3. The resulting amplitudes of the oscillatory $\Delta_{even}$ and $\Delta_{odd}$ are plotted in the figure 5.37. We observe that the phonon and magnon amplitudes exhibit a rather similar trend versus temperature, although the coherent magnon data shows a higher scattering due to lower signal to noise ratio of the $\Delta_{odd}$. The oscillatory feature of the magnon could be resolved up to a temperature of 200 K. The equivalent temperature behavior of the phonons and magnons gives us an indication about the coupling strength of these quasiparticles. The measured amplitude of the coherent phonon mode is decreasing with increasing temperature over one order of magnitude and, remarkably we could resolve it even above Curie point up to 400 K. The latter observation demonstrates the presence of a residual exchange splitting of the surface state above $T_C$ since the excitation of the coherent phonon-magnon mode is intrinsically connected with the presence of an exchange-split surface state (see Y overlayer experiment in section 5.3).

The overall decrease of the amplitude of the coherent phonons and magnons as the temperature is elevated is ascribed to a variation of their excitation probability with the temperature. Since the excitation of the phonon-magnon mode is connected with the presence of the exchange-split surface state (see section 5.3), a variation of the exchange splitting will influence the excitation and the subsequent dynamics of the coupled quasiparticles. Upon temperature increase the exchange splitting of the surface state decreases from 0.7 eV at 20 K to roughly 0.4 eV at the Curie point and remains constant at this value above $T_C$ up to 360 K (the highest investigated temperature) [33].

The excitation of the phonon-magnon mode depends on the amount of photoexcited electrons and holes produced in the surface state (see the wavelength dependence in the preceding section) by the pump pulse optical transitions, which evolve via the surface

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21 As mentioned in section 5.3 when refer to the coherent phonon and magnon amplitudes we meant the amplitude of the oscillatory features in the transient SH fields and not the real e.g. amplitude of lattice vibrations produced by the coherent phonon motion that can be measured only in time-resolved X-ray experiments.
Referring now to the spin-resolved DOS at the Gd(0001) surface showed in fig. 5.32 we can explain the temperature dependence as follows. At low temperatures and a laser photon energy of 1.55 eV the optical transitions in both channels are active but are dominated by the majority transitions, as has been explained in the previous section. Thus, a selective hole creation in the surface state that is not balanced by the photoexcited electrons, requires a transient charge redistribution for screening in the surface region, that displaces the surface layer from equilibrium position and produces the observed oscillation amplitude. As the temperature increases, both surface state components shift towards $E_F$ i.e. the exchange splitting decreases. Having in mind that the optical transitions in the majority channel have a weak spectral dependence due to the energetically broad final state (see preceding section), the temperature increase will produce, gradually, a better fulfillment of the SHG resonance condition in the minority channel i.e. a better laser photon energy matching between the spin-down bulk and surface state. Thus, as the temperature is varied, the majority channel gives a rather constant\textsuperscript{22} contribution

\textsuperscript{22}As shown in section 5.1, modelling the SHG response with a double resonance scheme the contribution from majority channel has been found to be small in comparison to the contribution of the minority channel to the total resonance condition. Thus the overall temperature induced variations of the weak contribution of the majority channel can be considered constant with regard to the minority channel contribution to the excitation process.

Figure 5.37: The amplitude of the coherent phonons (filled circles) and the scaled amplitude of magnons (empty circles) as a function of temperature increase. Note the variation over one order of magnitude of the phonon amplitude and its finite values above $T_C$. 
5.5 Coupled coherent phonon-magnon mode: excitation and relaxation

5.5.1 Excitation

To the excitation process while the contribution from minority channel increases as the photon energy matches better the energetic separation between the bulk and the surface state. Increasing contribution of the minority channel results in an increasing amount of photoexcited electrons in the $S^{\downarrow}$ surface state that balances the photo-generated holes in the surface state. Thus a weaker charge redistribution is necessary, that produces a smaller lattice displacement and therefore a smaller coherent phonon and magnon (up to the temperature where can be resolved) amplitude. According to our explanation the excitation probability and consequently the phonon amplitude is varying with the decreasing exchange-splitting of the surface state. Above $T_C$ the $\Delta_{ex}$ is constant up to the highest studied temperature of 360 K [33] and we can use this fact to check our explanation. Indeed we observe a constant coherent phonon amplitude (see fig. 5.37) that confirms the availability of the proposed explanation.

Another experimental support for this interpretation is provided by the dependence of the total SHG yield versus temperature. As shown in figure 5.38, the SHG intensity increases in two times as the temperature is elevated showing the typical behavior of the SHG resonance enhancement (see fig. 3.2) as suggested also by the lorentzian fit of the measured data. Assuming that, mainly, the shift of the $S^{\downarrow}$ surface state is responsible for the SHG enhancement (majority channel has been considered to have a weaker contribution), than the above proposed picture is confirmed. The figure 5.38 shows that the resonance maximum is achieved in the range 220 K to 260 K followed by a signal decrease to the initial level, which indicates less fulfillment of the SHG resonance condition. Hence, above 260 K the amount of unbalanced charge starts to increase again which according to the excitation mechanism will increase the coherent mode amplitude. We do not observe this feature and it is most likely due to the increased thermal population that scatters with the coherent mode, that will be in detail discussed later in this section. Thus the above results support the proposed model of a transient excitation probability with the temperature-dependent shift of the surface state, the latter one being reflected in the resonance enhancement of the SHG process.

Summarizing this part, upon temperature increase the amplitude of the coherent phonons and magnons decreases, that is ascribed to a temperature-dependent excitation probability of the surface state population. The latter one is determined by the initial amount of photoexcited electrons and holes in the surface state, that varies with the exchange splitting of the surface state for a constant laser photon energy.

5.5.2 Relaxation of the coherent phonon-magnon mode

Regarding the damping of the coherent phonon-magnon mode various scattering processes might contribute. As has been shown in chapter 2, elastic and inelastic scattering events are responsible for the decay of a coherent mode. Elastic scattering leads to a loss of the coherence with no energy transfer, as is the case for scattering with defects [75]. Inelastic scattering determines changes in the momentum and energy of the involved scattering partners, this process being known as decay or energy relaxation (see chapter 2 for details).

Evaluation of the relaxation time of the coherent phonon-magnon mode can be done according to Matthiessen’s rule [135] as the sum of the scattering rates determined by the
total inelastic and elastic scattering events that contribute:

\[ \frac{1}{\tau} = \frac{1}{\tau_e} + \frac{1}{\tau_i} \]  

where the \( \tau^{-1} = \Gamma \) defines the scattering rate. In time-domain measurements one can determine \( \tau \) as the decay time of the oscillatory components of the time-resolved signal.

For the case of coherent phonons on semimetals and semiconductors [76, 77] the dominant decay mechanism has been identified to be the phonon-phonon scattering or the \textit{anharmonic decay} (see chapter 2 and figure 2.10). This decay process, that accounts for the anharmonic corrections of the vibrational potential, describes (in the first order) the decay of an optical phonon of energy \( \hbar \Omega \) decays in two acoustical phonons with opposite wavevectors and energy \( \hbar \Omega / 2 \). In the case of metals, has been shown by Hase et al. [64] that the same phonon-phonon scattering mechanism plays also the major role in the coherent phonon decay with a weak influence of the coherent phonon-electron scattering.

The case of the coupled phonon-magnon mode on Gd(0001) is more complex in terms of the decay process since we have an additional degree of freedom namely the magnon subsystem. Moreover, Gd is a metal that implies an efficient scattering of the coherent mode with electrons. The latter process might be enhanced at the surface due to the laser resonant absorption in the surface state. Thus, several processes might contribute to the decay of the coherent phonon-magnon mode, and presumably with different relative weights. Therefore, identification and quantification of their contribution in not a trivial task. However, the present temperature-dependent study could demonstrate the presence of a few relaxation channels that are described in the following.

It is worthwhile mentioning the possible scattering events that might influence the decay of the coherent mode for Gd case. The coherent phonons and magnons might scatter with thermal phonons and magnons as well as with defects. Also, the coherent phonon-magnon mode can decay through excitation of an electron-hole pair via phonon-electron
5.5 Coupled coherent phonon-magnon mode: excitation and relaxation

Figure 5.39: Temperature-dependent evolution of the decay rate for the coherent phonons (filled circles) and magnons (empty diamonds). Note the non-monotonous behavior of the coherent phonon decay rate, that changes its tendency around 220 K. A fit (the solid line) according to eq. 5.12 which accounts for the scattering of the coherent phonons with electrons and thermal phonons describes well the data at lower temperatures but gives a monotonous increase of the scattering rate over the whole temperature range.

The behavior of the decay rate of the coherent phonon-magnon mode versus temperature is presented in figure 5.39. The decay rate $\Gamma$ is deduced from the damping time $\tau$ obtained by fitting the oscillatory SH fields with the expression 5.8. Upon elevating the temperature, the decay rate for phonons monotonously increases up to 220 K where a turning point in its behavior is encountered. The decay rate for magnons has a significantly increased error bars due to the lower signal to noise ratio of the odd SH field. Within the error bars of the magnon data we can say that we observe a constant decay rate over the temperature interval where the coherent magnons contribution can be resolved. Owing to the better signal to noise ratio detected for coherent lattice mode, we focus in the following on the coherent phonon behavior.

The decay rate of the coherent phonon shows a linear increase with temperature up to 220 K where an interesting feature is observed namely the decay rate starts to decrease i.e. the decay time increases although the amount of scattering partners (phonons, magnons, electrons) increase. Accounting for the scattering with thermal phonons the decay rate should exhibit a linear behavior [76] with increasing the temperature. Since the excitation of the coherent mode is due to a resonant absorption in the surface state, which means a significant amount of photoexcited carriers in the surface region are involved, we consider also
the scattering events of the coherent phonon with electrons. The temperature-dependent distribution functions of electrons and phonons render the scattering probability with the coherent phonon because they account for the increased electron and phonon population with temperature. Thus we can evaluate the contribution of the electrons and thermal phonons to the total scattering rate of the coherent phonon as [64, 76]:

$$\Gamma = \Gamma_{cp-p} \cdot \left( 1 + \frac{2}{e^{\frac{\hbar \Omega}{k_B T}} - 1} \right) + \Gamma_{cp-e} \cdot \left( 1 + \frac{2}{e^{\frac{\hbar \Omega}{e^{2k_B T}}} + 1} \right)$$  \hspace{1cm} (5.13)

where the terms on the right-hand side denote the decay rate of an optical phonon of energy $\hbar \Omega$ into two acoustic phonons of energy $\hbar \Omega / 2$ and into an electron-hole pair, respectively. In the last term of eq. 5.13 the effect of a hot electron distribution is not included for simplicity. The terms $\Gamma_{cp-p}$ and $\Gamma_{cp-e}$ in the above equation account for the scattering probability of the coherent phonon with thermal phonons and electrons, respectively. Fitting the measured decay rate of the coherent phonon with the above expression up to a temperature of 220 K one obtains a good description of experimental data (the solid line in fig. 5.39). Using a coherent phonon frequency of 2.9 THz in expression 5.13 the scattering rates $\Gamma_{cp-p}=0.17$ ps$^{-1}$ and $\Gamma_{cp-e}=0.35$ ps$^{-1}$ (that are the only fitting parameters) are obtained. As deduced from the values of the scattering rates the electron-coherent phonon collision events are more frequent than phonon-phonon scattering. Considering only these two scattering channels the decay rate would continue to increase with increasing temperature, as can be noticed in figure 5.39. Instead, we observe a decreasing of the scattering rate which is tentatively assigned to the effect of the coherent magnon decoupling. We shall explain the decay scenario in the following.

As the temperature of the system is elevated the scattering of the coherent mode with electrons, phonons and magnons increases. Analogous to the coupled oscillators system

\textbf{Figure 5.40:} The dependence of the coherent phonons (filled circles) and magnons (empty circles) frequency versus temperature. Note the drop in the coherent phonon frequency as the temperature approaches the Curie point.
the coupled phonon-magnon mode oscillates with a common (normal) frequency of 2.9 THz until one oscillator is decoupled (the magnon). The excitation energy residing initially in the coupled system is conducted now to the coherent phonon only. Moreover, the additional decay channels active for the coherent magnon (thermal magnon, phonon, electron), that were acting on the coupled mode as a whole, are now silent. A release of one oscillator should be accompanied by non-monotonous changes in frequency and energy of the remaining oscillator. We observe such a frequency modification in the temperature range where the magnon signature in the transient signal vanishes (see left panel of figure 5.40). At the same temperature of 260 K we notice a change in the energy of the coherent phonon oscillator \( E \propto A^2 \) [160] (see eq. 5.10), as can be seen in right panel of figure 5.40. Note, that above 260 K the energy is not zero but is finite small due to the reduced amplitude in this temperature range (see fig. 5.37).

These two observation might explain the observed decreasing of the decay rate. However, in order to confirm these proposals, higher density of data points in the vicinity of \( T_C \) are required and measured with a better statistics. For a thorough understanding of the decay rate of the coherent mode also a theoretical input would be valuable.

**Conclusion**

Temperature-dependent measurements of the MSHG signal from the Gd(0001) surface have been performed between 40 and 400 K. The incoherent and coherent components of the MSHG response revealed the existence of various decay channels that exhibit a complex interplay and affect the dynamics of the electron, lattice and spin subsystems. The observed changes with temperature in the incoherent \( \Delta_{\text{even}} \), evaluated at electron-phonon equilibration time of 3 ps, resemble qualitatively the temperature-dependent variation of the exchange splitting of the surface state. Based on this observation, a model has been proposed in which the temperature-dependent shift of the \( S^\downarrow \) surface state results in a various levels of photoexcited electron densities, that are responsible for the variation of the incoherent \( \Delta_{\text{even}} \). The incoherent \( \Delta_{\text{odd}} \) is mainly affected by the temperature increase in the sudden drop exhibited at early delay times. Its increasing value with the temperature increase has been attributed to higher density of spin-mixed states available for electronic spin-flip scattering. Regarding the dynamics of the coherent phonon-magnon mode, the coherent magnon could be resolved up to 200 K while the coherent phonon has been measured over the entire investigated temperature range. The coherent phonon amplitude varies over one order of magnitude as the temperature is increased that is explain by a changing excitation probability with reducing the exchange splitting of the surface state. We observe the coherent phonons also above \( T_C \) that proves the existence of an exchange-split surface state despite the loss of long-range magnetic ordering. The decay rate of the coherent phonon exhibits a non-monotonous behavior with temperature, that is ascribed to the combined effect of scattering with thermal phonons and electrons and presumably to the coherent magnon decoupling.
5.5.3 Conclusions

Systematic study of the incoherent and coherent MSHG response from the Gd(0001) surface has been performed by varying the laser wavelength and the static temperature of the system. Investigating the photon energy range between 1.44 and 1.68 eV, we observe significant changes of the MSHG response. A complex spectral behavior of the even SH field is observed, that is determined by the competition between the coherent and incoherent SHG components as the photon energy is varied. This behavior has been ascribed to the various levels of photoexcited carriers in the surface state, that produces (i) the spectral behavior of the coherent phonon mode and (ii) their thermalization (of the initially excited electrons and holes) is reflected in the incoherent part. Thus, the wavelength-dependent measurements gives evidence for a charge-driven excitation mechanism of the lattice and spin coherence. These results emphasize the central role of the exchange-split surface state in the SHG process from Gd(0001) surface, that causes the high spectral sensitivity due to the spin selective optical transitions via the surface state components. Measurements within the temperature interval 40 K to 400 K show gives a further support for a charge-driven excitation mechanism of the coherent phonon-magnon mode. The amplitude of the coherent phonon could be traced well above Curie point, that indicate the presence of a residual exchange-split surface state above $T_C$ in agreement with the literature [33, 36], and confirming the spin-mixing behavior of Gd(0001) on ultrafast time scales (see section 5.2.1). At low temperatures the main decay channels of the coherent phonon-magnon mode are the scattering with the electrons and thermal phonons. The scattering with electrons gives the major contribution to the total decay rate. In the high temperature range ($T > 200K$) the total decay rate decreases, which is tentatively ascribed to the effect of the coherent magnon decoupling.

5.6 Coupled coherent phonon-magnon mode: the effect of film thickness and morphology changes

Here we investigate the effects of the reduced film thickness and of morphological modifications of the Gd(0001)/W(110) films on the dynamics of the linear and nonlinear optical response. Lowering the film thickness, of particular interest is the possibility of excitation and detection of interface phonon modes. Also a reduced thickness lowers the phase space for the relaxation of the photoexcited electrons, that results in higher energy densities residing into the system$^{23}$, which can influence both the incoherent and coherent SHG components. The second part of the present section is devoted to the results obtained upon modification of film morphology i.e. from a layer-by-layer mode to three-dimensional islands and its effect on the coherent and incoherent dynamics of the SHG response.

$^{23}$ Assuming a negligible energy transport out of the excited region by non-equilibrium electrons i.e. ballistic transport (see chapter 2).
5.6 Coupled coherent phonon-magnon mode: the effect of film thickness and morphology changes

5.6.1 Film thickness effects

Nominal film thicknesses between 15Å (≈5 ML) and 200Å (≈67 ML) have been studied with the laser tuned at a wavelength of 800 nm and at a sample temperature of 30 K. Lower thicknesses are not investigated due to the vanishing magnetic contrast (e.g. for the 15Å film the contrast is 0.5%) and the lack of a well developed surface state. The preparation of films with lower thickness has been done following our standard procedure (see chapter 4) used for growing epitaxially thin Gd(0001) films on the W(110) substrate. This consists in depositing gadolinium at room temperature on the W(110) substrate followed by annealing to a temperature situated below the threshold temperature at which the film splits into islands [121]. The structural ordering of the films has been checked by LEED. The film thickness has been monitored by a quartz microbalance and additionally we have used the reduced Curie temperature [136] of the lower thickness films as a criterion for the thickness calibration. The resulting error in the thickness reading is evaluated at ≈10%. The finite-size scaling law [25], that quantifies the change in the Curie temperature with thickness variation reads [136]:

\[
\frac{T_C(\infty) - T_C(d)}{T_C(\infty)} = c \cdot d^{-\lambda}
\]

where \(T_C(\infty)\) and \(T_C(d)\) the bulk and the reduced Curie temperature, respectively, \(d\) is the film thickness, \(\lambda\) is the critical exponent related with the range of magnetic ordering, \(c\) is a phenomenological constant. For Gd the bulk Curie temperature is \(T_C(\infty) = 293\) K and for Gd(0001) film thicknesses in the range of 60–70 ML (≈200 Å) the reduced Curie temperature \(T_C(d)\) tends asymptotically to \(T_C(\infty)\) [136].

First results showing the transient behavior of the even and odd SH fields for various thicknesses are displayed in figure 5.41 and 5.42, respectively. Regarding the \(\Delta_{\text{odd}}\) behavior, we show the measurements for thicknesses above 50Å since below this thickness the magnetic contrast is reduced close to zero value (see figure 5.43) and consequently a high level of noise is present, that hinders any attempt to retrieve the coherent and incoherent components of the signal. As the thickness is varied we observe in both transient SH fields a rich dynamics that involves the incoherent and coherent fractions of the SHG response.

Referring to the transient even SH field displayed in fig. 5.41, we notice the presence of an oscillatory component even for the lowest thickness i.e. 15Å, with the amplitude increasing with increasing thickness. The pump-induced variations in the incoherent \(\Delta_{\text{even}}\) increase their absolute value with thickness, seems to saturate around 100Å and simultaneously change their time-dependent profile. The behavior of \(\Delta_{\text{odd}}\) plotted in figure 5.42 shows also interesting features upon changing the thickness. The initial drop at early times reaches the -1 value for the 50Å film, that reflects a total loss of spin polarization, and is followed by a rapid relaxation to an intermediate constant level. Such behavior is not observed for larger thicknesses, for which the initial drop scales inverse proportionally with the thickness and the time-dependent profile is the usual one, as observed earlier (see fig. 5.21).

According to STS measurements [33] on Gd(0001), a well developed exchange split surface state is present for film thickness bigger than 4 ML ≈ 12Å.

The finite-size scaling law is determined by the different exchange coupling acting on the surface and bulk atoms due to their different coordination number. As a function of thickness their ratio is changing and consequently the \(T_C\).
Figure 5.41: Pump-induced variations in the even SH field measured at $T=30$ K on epitaxially grown Gd(0001)/W(110) films with various thicknesses. Notice the presence of oscillatory component even for the lowest investigated thickness of $\approx 5$ ML Gd.

The oscillatory component of $\Delta_{odd}$ resembles the opposite trend of that encountered in $\Delta_{even}$ namely amplitude is larger for low thickness and decreases with increasing the film dimensions.

Another important piece of information regarding the system modification with thickness is provided by the SHG signal and the magnetic contrast. Their behavior versus film thickness is displayed in the figure 5.43. Within the scattering of the data points we observe a rather constant SHG yield and simultaneously an increase by more than one order of magnitude for the magnetic contrast. The constant level of the SHG signal, that is resonantly enhanced via the surface state (see the preceding sections), can be related to the exchange splitting of the surface state, which remains constant as the Gd(0001) film thickness increases [33]. The behavior of the magnetic contrast indicates a better magnetic ordering at the surface as the thickness increases or reflects the effect of an increased bulk magnetization on the surface magnetic ordering. An additional explanation is that the MSHG response is sensitive to the bulk magnetization, which increases with the film
5.6 Coupled coherent phonon-magnon mode: the effect of film thickness and morphology changes

Figure 5.42: Pump-induced variations in the odd SH field measured at T=30 K on epitaxially grown Gd(0001)/W(110) films with various thicknesses. We do not show here the measured data for 15Å and 25Å because of the high level of noise (due to the vanishing magnetic contrast).

In order to get quantitative information about the oscillatory component of the SHG signal, we have separated the coherent and incoherent fractions of the signal using the procedure presented in section 5.3. The resulting variations in the amplitude, frequency and decay time of the coherent lattice and spin excitations with the film thickness are displayed in figure 5.44. One of the first observations is the opposite trend of the coherent phonons and magnons amplitude i.e. upon increasing the film thickness the phonon amplitude increases in approximately five times while the magnon amplitude decreases in roughly three times. The second observation is the appearance of a saturation behavior in the amplitudes of lattice vibrations around 100Å film thickness, as suggested by the dashed line in the top panel of fig. 5.44. A similar saturation behavior is observed for this thickness also in the pump-induced variations of the incoherent $\Delta_{\text{even}}$ (see fig. 5.41). Regarding the frequency of the coupled quasiparticles (plotted in the central panel of fig. 5.44), no major changes (within the error bars) of the 2.9 THz frequency value measured
on 20 nm films are observed upon varying the film thickness. Also no other frequencies have been observed that would indicate the presence of phonon (magnon) modes located at the interface. The decay time (bottom panel of fig. 5.44) shows a slight increase with increasing thickness (from 1 ps to 1.4 ps) for the phonon mode while for the magnon is centered around a value of 1.2 ps (within the error bars).

**Discussion**

Before we start any discussion regarding the experimental results, we point out that owing to the preliminary character of these measurements we cannot formulate strong conclusions and rather we indicate some possible interpretations that are subject of future investigations. However, although the presented data are first measurements, the main trends in their dynamics are already discernible.

We address in the first place the oscillatory components of the transient even and odd SH fields. As pointed out earlier, the signature of the coherent phonon can be resolved down to a thickness of 5 ML, as can be seen from the top panel of figure 5.44. Increasing the thickness the coherent lattice amplitude increases in five times up to a rather constant\textsuperscript{26} value that is maintained for thicknesses above 100Å. Simultaneously the coherent phonon decay time increases slightly with thickness to a value of 1.4 ps (see bottom panel of fig. 5.44). These observations suggest that the decay process of the coherent lattice motion becomes weaker as the thickness grows. In a simple picture, no change in the oscillatory behavior of the coherent mode is expected by changing the film thickness due to its localization at the surface. In reality, the underlying bulk of the film can exhibit

\textsuperscript{26}Here a higher density of measured data points would be helpful in order to check the constant level.
5.6 Coupled coherent phonon-magnon mode: the effect of film thickness and morphology changes

Figure 5.44: The amplitude, frequency and the decay time of the oscillatory component of the MSHG transients (from fig. 5.41 and 5.42), measured for various Gd(0001) film thicknesses at \( T = 30 \) K. The dashed line in the top panel is a guide for the eye indicating a saturating behavior exhibited by the coherent phonon amplitude.

Various degrees of defects that affect the long-range crystalline ordering and consequently the film surface also. Thus a possible explanation of the phonon mode behavior relies on the strain that is build-up in the film due to the film-substrate lattice mismatch. It has been shown \([146, 147]\) that the presence of strain can change the binding energies of surface states. In our case this will affect the excitation probability of the coherent mode (see the preceding section) and the SHG resonance condition. However, STS measurements \([33, 34]\) reveal a well developed surface state starting with 4 ML Gd(0001) film and no changes in its binding energies for bigger thicknesses. Also we do not observe significant changes in the SHG yield as a function of thickness, that would indicate a modification of the SHG resonance due to a change in the energetic positions of the surface state. Thus we can neglect in this context the effect of strain on the Gd(0001) surface electronic structure.

On the other hand, an earlier work shows \([24]\) that starting with 4 ML the induced strain in the Gd(0001) film is reduced to \( \approx 75\% \) of its initial value and is totally released after
The pump-induced changes in the linear reflectivity measured from Gd(0001) films with different thicknesses and from the clean W(110) substrate, at T= 30 K. Note the radical change in the time-dependent profile in ∆R/R for the 100 Å data set with respect to lower thicknesses. The transient linear reflectivity is measured simultaneously with the SHG response.

≈30 ML. This thickness fits well with the observed thickness interval in the figure 5.44 where the amplitude of the coherent phonon becomes constant. Thus one can consider the structural defects or dislocations produced by the strain presence and strain release in the Gd(0001) film, to explain the lower amplitude and decay time of the phonon mode at low thicknesses via the elastic scattering of the coherent mode with defects.

Another potential candidate is the Gd-W interface contribution to the total SHG response, that can interfere constructively or destructively with the surface part of the nonlinear polarization, according to their mutual phase relationship. As mentioned in chapter 4, we have selected the 20 nm film thickness as the typical thickness for our experiments, since for this film dimension the interface should have no or a negligible contribution to the SHG response based on the optical penetration depth \( \delta \approx 20 \text{ nm} \). Thus for lower thicknesses the film-substrate interface should contribute. One experimental indication that the interface plays a role in the SHG process comes from the pump-induced variations in linear reflectivity plotted in figure 5.45. In the same figure we have plotted for comparison also the transient linear reflectivity measured on clean W(110) substrate. Since LR is bulk sensitive within the optical penetration depth, it is probing the whole Gd film, and for thicknesses smaller than the skin depth is sensitive also to the tungsten substrate. This is apparent for film thicknesses up to 50 Å for which the signature of the substrate
5.6 Coupled coherent phonon-magnon mode: the effect of film thickness and morphology changes

can be clearly distinguished \(i.e\). similar shapes of the transient profiles. For the 100Å film we observe a totally changed time-dependent profile, that closely resembles the one of the 200Å film thickness. Fitting the LR measurements (not shown for clarity) with a model function accounting for the relative contributions of the substrate and Gd film to the transient LR, we obtained a W:Gd ratio ranging from \(\approx 1:10\) to \(\approx 1:40\) for the thickness range from 50Å to 100Å, respectively. Thus we can say that in the thickness range 50Å to 100Å the substrate contribution to the LR signal is strongly reduced and above 100Å is very small\(^{27}\). For thicknesses ranging from 50Å to 15Å, for which the substrate is contributing to the transient LR, we observe a gradual decrease in the oscillatory and incoherent SHG components as the thickness decreases (see fig. 5.44 and fig. 5.41). Thus one can consider a Gd-W interface contribution to the SHG response that might interfere (partial) destructively with the surface contribution (coherent and incoherent) to explain the observed decreasing in the coherent and incoherent SHG fractions.

Regarding the transient \(\Delta_{\text{odd}}\) behavior, plotted in fig. 5.42, we observe an interesting feature for the 50Å film thickness. At early delay time the initial drop in \(\Delta_{\text{odd}}\) reaches\(^{28}\) -1 value, that is equivalent to a total loss of spin polarization of the surface state. We have explained in section 5.2.1 the initial drop of \(\Delta_{\text{odd}}\) as being determined by the hot electrons spin-flip scattering among spin-mixed states. This proposed demagnetization mechanism describes very well the encountered \(\Delta_{\text{odd}}\) behavior for the wavelength- and temperature-dependent data in the preceding sections. Here we cannot use it to explain the measured data since decreasing the thickness neither the density of spin-mixed states nor the population of hot electrons increases. In principle one can utilize the same argument of interface contributions, that are active up to 50Å and diminish as the thickness grows. This point is supported also by the different time-dependent profiles of \(\Delta_{\text{odd}}\) for the 50Å thickness in comparison with the 100Å and 200Å measurements. Also we cannot exclude the effect of the relative phase between the SH fields (see section 5.1), that has been shown to change with the film thickness \([127, 132]\). However, based on the actual experimental input we cannot make any statements and this point requires further investigations.

Finally we discuss the possibility that the SHG technique might be sensitive to the bulk magnetization. This possibility arises from the measured behavior of the magnetic contrast \(\rho\) versus thickness (see fig. 5.43) \(i.e\). a monotonous increase of \(\rho\) with increasing thickness. Increasing the thickness of a ferromagnetic film results in an increased value of the total magnetic moment of the specimen. But how can a bulk property can be detected by the SHG, which is considered to be a surface sensitive technique?

As shown in chapter 3, for centrosymmetric media and within electric-dipole approximation the nonlinear source of the SHG signal is constrained at surfaces and interfaces where the inversion symmetry is broken. In the nonlinear polarization expression (see eq. 3.19 and 3.20) one can account for higher order terms describing electric quadrupole and magnetic dipole contributions, that are bulk sensitive. These are usually small, but when large bulk volumes are involved their contribution can be of comparable magnitude with the surface contribution. If this is also the case for the higher thicknesses Gd(0001) films,

\(^{27}\)For the 200Å Gd film the W:Gd ratio is \(\approx 1:80\)

\(^{28}\)Actually, there are two data points below -1 value, which are explained by the increased noise level due to the low magnetic contrast of \(\approx 2\%\).
at this point, is difficult to judge, since separating the surface and bulk contributions to the SHG response is a complex task \[100, 117\]. Nevertheless, measurements of the polarization dependence from the Gd(0001) sample for various MSHG geometries might help in this respect \[117\]. In short, the bulk magnetization can be in principle reflected in the SHG response but further measurements are necessary in order to clarify this issue.

### 5.6.2 Morphology effects

In this part we present the effect of a changed Gd(0001) film morphology on the time-resolved nonlinear optical response. Morphology changes refer to the transformation of a smooth film to a three-dimensional (3D) islands structure, upon annealing to high temperatures \[121\]. Of special interest here is the evolution of the coherent phonon-magnon mode on the 3D Gd islands.

As mentioned in chapter 4, the morphology of the Gd(0001) film can be modified by employing annealing temperatures above a certain threshold limit, for which the film is transformed from the initial layer-by-layer growth mode to a 3D islands film. The critical temperature at which the transition flat film-3D island takes place, has been investigated by Aspelmaier et al. \[121\] for various Gd(0001) film thicknesses. Their results are summarized in the figure 4.3, where the critical annealing temperature is displayed for Gd(0001) film thicknesses ranging from 5 ML to 100 ML. For the preparation of the Gd(0001) islands structure we followed the threshold temperature diagram reported in this work.

For illustration of this structural transformation, STM pictures from literature are reproduced in figure 5.46. Here the effect of different annealing temperatures on a 11 ML Gd(0001)/W(110) film is showed. We see that annealing to a temperature (here 530 K) below the threshold limit of reference \[121\], a smooth film is obtained showing monoatomic steps whereas annealing to 710 K (above the threshold limit), the film breaks up in 3D islands of quasi-hexagonal shape sitting on top of 1 ML Gd, that covers the substrate. Thus the morphology of the Gd(0001) film changes upon annealing to temperatures above the critical limit, from a smooth film to 3D islands lying on one Gd layer (Stranki-Krasnolov-like mode).

As a representative example for the transition from a layer-by-layer to a islands film upon annealing to higher temperatures, we have selected a 50Å (≈ 16 ML) thick Gd(0001) film. According to the critical temperature diagram (see fig. 4.3), the flat Gd(0001) film is obtained after annealing to 550 K while for temperatures higher than 750 K the film is transforming to islands. For this film dimension, and upon annealing to 800 K, we encounter the most pronounced changes in the oscillatory part of $\Delta_{\text{even}}$. Also starting with this thickness the interface contribution to the SHG response becomes weaker (see previous subsection). Moreover, STM measurements covering this thickness range are available in literature \[33, 34, 123\], that render useful information regarding the islands size and shape.

First results showing the time-resolved nonlinear magneto-optical response from a smooth Gd(0001) film and from a three-dimensional islands film, are displayed in the upper and the lower panel of figure 5.47, respectively. The measurements are performed on a 50Å Gd(0001) film at a sample temperature of 30 K and with the laser tuned to 800 nm. The changed morphology affects the SHG response in two ways. First, the period of oscilla-
5.6 Coupled coherent phonon-magnon mode: the effect of film thickness and morphology changes

Figure 5.46: STM (scanning tunnelling microscopy) measurements of a 11 ML Gd(0001)/W(110) film. **Left:** A smooth and flat gadolinium film obtained after annealing to 530 K. **Right:** Different morphology is obtained upon annealing to 710 K: one can observe 3D islands on top of a completely closed Gd monolayer. From [123].

Oppositions in $\Delta_{\text{even}}$ becomes smaller *i.e.* higher frequency, whilst the oscillatory component of the transient odd SH field is not observable anymore. Also the oscillations in $\Delta_{\text{even}}$ are much longer lived in comparison with the flat film, with a very clear oscillatory pattern even at 5 ps pump-probe delay. Second, the incoherent part of the transient $\Delta_{\text{even}}$ and $\Delta_{\text{odd}}$ is changing its time-dependent profile and simultaneously showing considerably lower pump-induced variations.

Since an interesting change in the measured frequency of the coherent phonon mode is encountered, we focus on the oscillatory behavior of the SH response. The coherent and incoherent parts of $\Delta_{\text{even}}$ have been separated utilizing the procedure presented in the section 5.3. The resulting oscillatory fraction $\Delta_{\text{osc}}^{\text{even}}$ is displayed in figure 5.48. Here we observe an oscillatory period of 220 fs, that corresponds to a frequency of 4.5 THz, and simultaneously the presence of a weak beating pattern. The latter observation suggests that more oscillatory modes are involved. In order to obtain the values of the involved frequencies we have Fourier transformed the oscillatory data from fig. 5.48 with the result plotted in figure 5.49. The Fourier transformation reveals the presence of three frequency modes in the oscillatory part of $\Delta_{\text{even}}$. There is a high amplitude mode centered at 4.5 THz that dominates the frequency spectrum, together with smaller amplitude peaks at 3 THz and 10 THz. The 3 THz mode represents the coherent phonon measured on the flat film, that is accompanied by two unknown frequency modes. The 4.5 THz mode is very long lived as can be seen in fig. 5.48, while the 10 THz mode has a short lifetime accounting for its broad width in the frequency spectrum. For a quantitative evaluation of the parameters (amplitude, frequency, decay time) of the oscillatory $\Delta_{\text{even}}$, we have utilized an extended version of the fit function 5.8, that consists of three exponentially damped oscillatory modes. The obtained fit (the solid line in the figure 5.48) shows a good
Figure 5.47: The pump-induced variations in the SH fields, for a 50Å Gd(0001) film, measured for two different annealing temperatures. Annealing to 800 K produces a change in the period of the oscillatory component of $\Delta_{\text{even}}$ while the oscillations in $\Delta_{\text{odd}}$ cannot be resolved anymore. Also the time-dependent profile of the incoherent components of the SH fields is changed.
reproducibility of the measured oscillatory data. The extracted fit parameters are listed in the table 5.1.

As already discernable from the raw data, the 4.5 THz mode is the longest lived mode with $\approx 8$ ps decay time, followed by the 3 THz mode with $\approx 2.5$ ps lifetime and the short lived 10 THz mode with $\approx 0.5$ ps. For a clearer picture of the time evolution of the encountered frequency modes we have performed, in addition, a time-frequency analysis of the oscillatory $\Delta_{\text{even}}$ data. For this a Wigner transformation [161, 162] of the time-domain os-

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (THz)</th>
<th>Decay time (ps)</th>
<th>Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3±0.01</td>
<td>2.48±0.6</td>
<td>0.0013±0.0002</td>
</tr>
<tr>
<td>Mode 2</td>
<td>4.47±0.002</td>
<td>7.8±1.4</td>
<td>0.0027±0.00015</td>
</tr>
<tr>
<td>Mode 3</td>
<td>10±0.036</td>
<td>0.46±0.08</td>
<td>0.0011±0.0006</td>
</tr>
</tbody>
</table>

Table 5.1: The parameters of the oscillatory fraction of $\Delta_{\text{even}}$ displayed in the figure 5.48 deduced by fitting the data with a model accounting for three oscillatory damped motions (extension of eq. 5.8).
oscillatory signal has been performed resulting in a 2D time-frequency representation plotted in figure 5.50. The Wigner transformation is similar with the short-time Fourier transform in the sense that the time-domain signal is frequency-analyzed within an adjustable temporal window (here a Gaussian) that is sliding along the time scale. This method renders the instantaneous frequency value and its modifications in the time. Now one can distinguish very clearly (see fig. 5.50) the short lived 10 THz mode and the beating pattern having the frequency of \(\approx 1.45\) THz, that corresponds to the frequency difference between the 4.5 THz and 3 THz modes. Also the dominating oscillatory mode \(4.5\) THz, exhibits an interesting feature of increasing amplitude along the pump-probe delay with the maximum level achieved after the other two modes have decayed.

**Discussion**

Again we have to mention that the above presented measurements (as well as the thickness-dependent study from preceding subsection) are in an incipient stage and more detailed investigation are required. Therefore, based on the actual experimental input, we present our actual understanding and no strong conclusions can be drawn.

As we have seen above, changing the morphology of the Gd(0001) film to 3D islands, results in the appearance of two additional frequencies, besides the 3 THz mode, in the oscillatory even SH field. The question that arises is how the changed morphology can explain the presence of these higher frequency modes. STM pictures of the Gd(0001) film after annealing above the the critical temperature, show 3D islands of (quasi)hexagonal shape (see fig. 5.46) with lateral dimensions in the range of hundreds of nm sitting on top of 1 ML gadolinium that fully covers the W(110) substrate [123, 33].

The appearance of the 3 THz mode, although with one order of magnitude smaller amplitude compared to the flat film, is attributed to the excitation of the surface coherent phonon mode on top of the 3D islands in an identical manner as for the layer-by-layer films. This interpretation is based on the well-developed surface state present at the islands surface that resembles the same characteristics as for the flat film [33]. Also the
5.6 Coupled coherent phonon-magnon mode: the effect of film thickness and morphology changes

Figure 5.50: Wigner transformation of the oscillatory $\Delta_{\text{even}}$ signal (see fig. 5.48) measured on the Gd(0001) islands film. The short lived mode at 10 THz and the beating pattern at 1.45 THz are well discernable. Also a gradual increase of the amplitude of the 4.5 THz mode along pump-probe delay is observed.
islands size can sustain collective lattice motion without producing the confinement of the phonon mode that would change its frequency. The lower amplitude of the phonon mode might originate from the increased roughness present on top of the Gd islands and thus an enhanced coherent phonon-defect scattering can take place. The presence of the coherent phonon mode should be accompanied by a coherent spin excitation (see section 5.3), but no oscillatory pattern could be resolved in the transient $\Delta_{\text{odd}}$. This is most likely due to the reduced excitation probability of the coupled quasiparticle (one order lower amplitude of the phonon mode) and due to the relatively low signal to noise ratio of the odd SH field (see fig. 5.47).

One possible explanation of the 4.5 THz mode is related with the presence of the above mentioned gadolinium monolayer among the 3D islands. One can suggest that the Gd atoms forming the single monolayer situated among the islands are vibrationally excited that results in a coherent vibration of the Gd-W bond. There are a few experimental observations that point to this interpretation. First of all, based on the surface/interface sensitivity of the SHG process, this oscillatory mode should be constrained to spatial regions where the inversion symmetry is broken. For the 5 ML Gd(0001) film (the lowest investigated thickness in the present work) prepared in a layer-by-layer growth mode we measure the oscillatory feature at 3 THz but no other modes are observed (see fig. 5.41). Investigating the bare W(110) substrate with time-resolved SHG no oscillatory feature could be observed. Moreover, the SHG measurement geometry is p-P (p-polarized input fundamental and output second-harmonic, respectively), which means that the infrared-active vibrational modes can be excited and detected with the dipole moments oriented
5.6 Coupled coherent phonon-magnon mode: the effect of film thickness and morphology changes

along the $x$ and $z$ axes (see figure 3.4), where $z$ is normal to the surface.

Inspecting the phonon density of states for tungsten, displayed in the figure 5.51, we notice the presence of two peaks concentrated around 4.5 THz and 6 THz in the phonon DOS spectrum. The pronounced peaks in the phonon DOS correspond to the measured [163, 164] phonon frequencies at N point in the tungsten Brillouin zone with 4.40(5) THz frequency for a transversal phonon and 6.75(1) THz frequency for the longitudinal branch. As noticed, the frequency of the transversal mode exhibits a very good agreement with the measured frequency of the oscillatory $\Delta_{\text{even}}$ of 4.5 THz. This intriguing observation give rise to several questions. How a transversal bulk phonon mode that belongs to tungsten can explain the oscillatory feature measured on Gd(0001)/W(110) system by a surface sensitive technique? And why the 4.5 THz mode could not be detected on the bare tungsten, if it has a surface character? Moreover, why a phonon mode that is at edge of the Brillouin zone $q=0.5 \ \text{Å}^{-1}$ can be measured since with optical techniques is well known that only phonon modes with $q \leq 0$ can be detected? All these questions are to be investigated in detail by more systematic studies that beside time-resolved SHG should involve also surface sensitive techniques like Auger spectroscopy and/or surface imaging like STM. Regarding the origin of the short lived 10 THz mode is, as well as the 4.5 THz mode, for the moment an open question that requires further studies.

As an outlook to future work regarding these interesting higher frequency phonon modes observed for the modified Gd(0001) film morphology, polarization dependent measurements i.e. for both pump and probe beams, are necessary in order to investigate the excitation mechanism and the symmetry of the coherent phonon motion. Also the bare substrate should be subject to a polarization-dependent study in order to check for a potential tungsten surface mode. An important verification of the above proposed model for the 4.5 THz mode would be the preparation [166] and investigation of a single monolayer of Gd on the W(110) substrate.

5.6.3 Conclusions

First results regarding the effect of the film thickness and the changed morphology on the electron, lattice and spin dynamics of the Gd(0001) system, have been presented. Varying the film thickness between 15Å and 200Å the frequency of the coherent phonon-magnon mode remains unchanged at a value of ≈ 2.9 THz, which emphasizes the surface character of the coherent mode. An increased amplitude and decay time of the coherent phonon is observed by increasing the film thickness up to 100Å followed by a levelling to a constant value. Two possibilities have been discussed: the scattering of the phonon mode with defects produced by the Gd-W lattice mismatch induced strain and the destructive interference between surface and interface contributions to the SHG response. For the 50Å film thickness a total loss of spin polarization is encountered at early delay time followed by a rapid relaxation within 1.5 ps to a constant level. The origin of this interesting observation is unclear for the moment and necessitates further investigations. Upon changing the morphology of the smooth Gd(0001) films to 3D islands by annealing to higher temperatures, two higher frequency modes at 4.5 THz and 10 THz have been detected in the oscillatory part of $\Delta_{\text{even}}$. Simultaneously no oscillatory feature in the transient odd SH field could be resolved, presumably due to the lower amplitude of the coherent phonon mode at 3 THz.
(there is a coupled phonon-magnon mode at 3 THz) and the lower statistics of the $\Delta_{\text{odd}}$.
Also there is no magnon at a frequency of 4.5 THz in the magnon dispersion curves at $\Gamma$ point (see fig. 5.20). The origin of the higher frequency modes is unclear and further studies are necessary. On a speculative level the coherent vibration of the Gd-W bond has been discussed as a potential explanation of the 4.5 THz mode.

5.7 Conclusions and outlook

In this chapter the laser-induced dynamics of the ferromagnetic thin films of Gd(0001)/W(110) under an UHV environment has been investigated by means of time-resolved linear optical and nonlinear magneto-optical techniques.

Before the investigation of the dynamic properties of the system, a detailed study of the static response has been performed. A major result has been obtained from the spectral dependence of the SHG yield, magnetic contrast and of the relative phase between the even and odd second-harmonic fields. Their spectral evolution give evidence for the resonance enhancement of the SHG process via the exchange-split surface state of Gd(0001).

One of the first question we have addressed is the laser-induced magnetization dynamics on Gd(0001) by measuring the time evolution of the spin polarization and the exchange-splitting of the exchange-split surface state. Upon laser excitation the spin polarization of the surface state drops to 50% of the equilibrium value within the first 100 fs after excitation. Simultaneously the exchange splitting remains constant despite of the highly excited electron population in the sample. The latter observation shows that the surface magnetization of Gd(0001) does not follow the electronic temperature as was the case for the itinerant ferromagnetic systems [84, 82]. The combined observation of a decreasing spin polarization and a constant exchange splitting, lead us to the conclusion that, in Gd(0001), on the ultrafast time scale the spin-mixing behavior prevails over the Stoner behavior. The latter conclusions helps us to identify the elementary spin-scattering mechanism responsible for the optically-induced magnetization reduction in Gd(0001) namely the spin-flip scattering of hot electrons among spin-mixed states. In order to fulfill the angular momentum conservation the spin-flip events are accompanied by emission/absorption of magnons that involve the 5$d$ magnetic moments and presumably also the 4$f$ moments. The proposed demagnetization mechanism is particularly efficient in the case of Gd due to the strong electron-magnon coupling. The magnetization is recovered on a longer time-scale with a time constant of $\approx 150$ ps, that has been ascribed to the effect of spin-lattice interaction.

In this context, a useful check of the suggested demagnetization model can be made by employing photon energies that can excite and probe the 4$f$ electrons, that have a binding energy around -9 eV. As an example are the UV and XUV light sources provided by free-electron laser or the high-harmonics generated in the rare gas cells. Also a time-resolved x-ray circular magnetic dichroism (XMCD) experiment would provide information about the dynamics of the orbital (5$d$) and spin magnetic (4$f$) moments. Another issue that should be investigated is whether the observed ultrafast demagnetization is surface specific or it evolves also in the bulk of the ferromagnetic Gd(0001). For this purpose a time-resolved MOKE experiment would help to settle this issue.
The next investigated subject has been the new and exciting phenomenon of coupled coherent phonon and magnon on the Gd(0001) surface, that evolves at a frequency of 2.9 THz. The excitation of this coupled quasiparticle is attributed to the asymmetric excitation of the surface state components which results in an ultrafast transient charge redistribution at the surface that sets the surface ions in an oscillatory motion. The lattice vibration modulate the exchange interaction strength $J$ between nearest neighbors and consequently the magnetic moments oscillate at the same frequency as the lattice. The observed coherent phonon-magnon mode on the Gd(0001) surface represents a novel phonon-magnon interaction that relies not on the spin-orbit coupling (it is very weak in Gd) but on the dynamical variation of the exchange interaction. The proposed excitation mechanism of the phonon-magnon mode has been verified by measuring the binding energy of the occupied surface state that oscillates with the same frequency as the coupled quasiparticle. As a remark, the present study of the coherent optical phonon encountered on the metal surface of Gd(0001) represents the first time measurements of a coherent optical lattice mode on a metal.

Further insight in the physics of the coupled phonon-magnon mode has been acquired by studying its dependence on the laser wavelength and the temperature of the system. Upon changing the laser photon energy between 1.48 eV and 1.68 eV, we assist at a competition between the electron and coherent lattice dynamics that is ascribed to the relative weight of the optical transitions via the surface state components. These measurements confirm and emphasize the central role played by the exchange-split surface state in the excitation of the coherent-phonon mode. The temperature dependent study shows that the excitation probability of the coupled mode depends on the exchange splitting of the surface state. The major decay channels of the coupled coherent phonon-magnon mode have been identified as the scattering with electrons and with the thermal phonons (anharmonic decay). Decreasing of the total scattering rate of the coherent phonon starting with 200 K remains an open question that requires further studies. As potential candidate in explaining this behavior the decoupling of the coherent magnon at elevated temperatures has been discussed.

As an additional check of the surface character of the coherent mode we have performed a thickness dependent study and the effect of a changed film morphology has been investigated. Down to 5 ML of Gd(0001) film thickness the coherent oscillations are resolvable with no change in the oscillatory frequency, which confirms the surface localization of the coherent phonon mode. Modifying the morphology of the smooth film to three-dimensional islands on top of 1 ML of Gd(0001), we notice the presence of two additional oscillatory modes at a frequency of 4.5 THz and 10 THz. The former one is tentatively assigned to the Gd-W bond vibration and the latter one is of an unclear origin. Further measurements are necessary in order to clarify the origin of the higher frequency modes, that should be accompanied by STM measurements performed on a film prepared in identical conditions, which would give exact information about the morphology of the investigated film.
5 Electron, lattice and spin dynamics on Gd(0001)/W(110)
6 Acoustic phonons on Y(0001)/W(110)

This chapter presents the laser-induced electron and lattice dynamics on the Y(0001)/W(110) system, investigated with time-resolved linear reflectivity and second-harmonic generation techniques. Of central importance here is the encountered phenomenon of travelling acoustic phonons within the Y(0001) thin film, the so-called phonon echo. The chapter is structured as follows. After a brief presentation of the characteristic properties of the investigated system Y(0001)/W(110), the physics of phonon echo and its vast area of applications are introduced. The theoretical model used to describe the phonon echo dynamics is detailed in the following section. In the next step we present the measured phonon echo dynamics on the Y(0001) films and the way is reflected in the transient linear reflectivity. More insight in the physics of the phonon echo is gained by varying the temperature of the system and the laser wavelength. Concluding remarks and an outlook to the future work are closing the chapter.

6.1 Introduction

The motivation that triggers the investigation of the second rare-earth system in this work is to test the accumulated knowledge in the case of gadolinium regarding the excitation of coherent lattice motion and presumably to get more insight into the physics of quasiparticle excitations and interactions. From the previous chapter we have seen that the main ingredients in excitation and detection of coherent lattice vibrations at the surface are: a crystalline structure that can support optical branch phonons, an electronic configuration resembling an exchange-split surface state through which an efficient excitation of the surface lattice motion can be achieved and a surface sensitive tool that can detect these coherent lattice vibrations. In this context yttrium is a good candidate since it is a rare-earth metal [18, 19] that crystallizes in a hcp structure with two atoms per unit cell, having the values of the lattice constants close to Gd metal. Thus the first condition is fulfilled, the measured phonon dispersion curves [167] for yttrium showing at Γ point a frequency of 4.6 THz for the longitudinal optical phonons. Similar to gadolinium, yttrium is a trivalent metal (4d5s)\(^3\) i.e. has the same valence electronic structure and exhibiting a surface state which is now positioned at the E\(_F\) (see figure 6.6). Unlike Gd, the surface state is not exchange-split since Y is a paramagnet i.e. shows no long-range magnetic ordering. As investigation tools we employ here the time-resolved second-harmonic generation together with linear reflectivity. Hence, we can check wheatear on yttrium one can initiate coherent lattice vibrations in the THz frequency range.
Phonon echo

The concept of phonon echo denotes a propagating acoustic phonon wavepacket through a medium, being reflected at the buried (medium/substrate) interface or at any discontinuity in the material and at the free surface. As it travels, the acoustic pulse modulates locally the optical properties of the system, which can be monitored with e.g. time-resolved linear optical techniques as a change in the reflectivity or transmission measured in the transient signal. The back and forth travelling within the sample (see fig. 6.1) of the acoustic pulse is reflected in the transient signal as sharp peaks (see fig. 6.7), which appear at regular time intervals accounting for the propagating time through the sample. Because these peaks represent replica of the initially generated acoustic pulse, this phenomenon is known as phonon echo by analogy to the spin-echo process.

The propagating acoustic pulse or sound wave can be excited mechanically by a piezoelectric transducer attached to the investigated specimen or optically by absorption of ultrashort laser pulses that heats up the lattice which expands and thus generating a strain pulse. The latter method allows generation of acoustic pulses in the GHz frequency range whereas with the former one MHz frequencies (the practical limit of driving electronics is below 1 GHz) can be obtained. The technique of the laser-induced propagating acoustic pulses is known as picosecond ultrasonics or laser ultrasonics [168, 169] due to the ability to generate acoustic pulses with temporal extents in the picosecond time scale.

A schematic picture of the laser-induced strain pulses is presented in the figure 6.1. Initially the pump pulse is absorbed within a distance given by the optical penetration depth. The photoexcited electrons will transfer their energy to the lattice which will be heated up and expand. Thermal expansion of the lattice produces the strain pulse (its shape will be discussed later in this section) that travels through the sample being partially reflected and transmitted at the buried interface and totally reflected with a sign change at the free surface. Its presence is detected by the time-delayed probe pulse as a temporally change (see fig. 6.7) in the relative variations of the measured signal (reflectivity, transmission etc.).

A big advantage of the optically generated acoustic pulses represents the capability of performing non-contact, non-invasive and non-destructive measurements, which with the conventional ultrasonic techniques is impossible. Because of these characteristics the laser ultrasonics is widely use in industry in general [170] and is particularly useful in the semiconductor industry [171] for measurements and quality characterization of multilayered thin films and microstructures. Also this technique can investigate specimens held at elevated temperatures, located in corrosive and hostile environments etc. Moreover, the phonon echo effect exhibits a large variety of applications ranging from medical investigation to determination of thin film thickness and mechanical properties (sound velocity, bulk modulus) [172] and from diagnostics of various materials [173] to imaging nano-objects in embedded structures [174]. These are just a few areas where the laser ultrasonics is applied and the extensive literature covering these fields can not be cited here. The interested reader is referred to the work of Scruby [168] and Gusev [169], that give a wider overview of the research field.

In general, for the generation of the high frequency acoustic pulses metallic films are used due to the relatively short optical penetration depth and the rapid response of the
6.1 Introduction

Figure 6.1: Schematic illustration of the laser-induced generation and propagation of the strain pulse within a film/substrate system. At \( t=0 \) the laser pulse is absorbed in the limit of the optical penetration depth that produces a temperature increase having the distribution of the absorption profile. At a later time the generated strain pulse travels to the buried interface where is partially reflected and transmitted. Arriving at the free surface the strain pulse is reflected with a sign change. The arrows indicate the propagating direction of the strain pulse.

The phenomenon of propagating strain pulse should not be mixed with the acoustic shock wave. The latter one is also a travelling strain pulse but with different characteristics namely high amplitude and very short durations. Due to the high amplitudes of the strain the deformation of the lattice is so large that the travelling velocity \( i.e. \) sound velocity starts to depend on the local pressure within the pulse. As a result we assist at a self-steepening of the strain pulse since the sound velocity increases with the increase of the locally applied pressure. Consequently the peak of the strain pulse travels faster and even overtakes the leading trail of the pulse and thus creating a shock wave.

The most use investigation technique for the measurement of the propagating strain pulse is the time-resolved linear reflectivity. Here the changes produced in the optical constants of the material by the strain pulse upon pump pulse absorption are detected in the near-surface region by the time-delayed probe pulse. In the present thesis we employ
this technique for the detection of the phonon echo on Y(0001). Another technique that measures actually the change in the geometry of the surface created by the strain pulse arriving at the surface is the beam deflection technique [44, 177]. With this technique one measures beside the changes in the reflectivity also the deflection of the probe beam produced by the local tilting of the surface plane produced by the strain pulse. A more advanced interferometric technique has been recently introduced [176], that renders simultaneously information about the magnitude and phase of the modulations produced in the linear reflectivity by the propagating acoustic pulse.

6.2 Thermoelastic model

In this section the theoretical model accounting for the optical excitation, propagation and detection of the strain pulse is described. This model has been proposed for the first time by Thomsen et al. [178], the description presented here following in some parts the original work of Thomsen. The thermoelastic model is presented in detail here since it provides a thorough understanding of the laser excitation, propagation and detection of the phonon echo process.

6.2.1 Acoustic pulse generation and propagation

In the following the absorption of an ultrafast laser pulse at the surface of a metal film and the subsequent excitation and propagation of the strain pulse is modelled.

The absorption of the laser pulse in the material take place within the optical penetration depth $\delta$ defined in eq. 2.3. The variation of the laser intensity along $z$ direction, where $z$ is along the surface normal, has an exponential profile with the characteristic length of the penetration depth (see figure 6.1):

$$ I(z) = I_0 (1 - R) \exp \left( -\frac{z}{\delta} \right) $$ (6.1)

Here $R$ denotes the reflectivity and $I_0$ is the incident laser intensity. The absorbed energy from the pump pulse per unit volume at a distance $z$ for an uniformly irradiated area $A$ reads [178]:

$$ E(z) = (1 - R) \frac{E_p}{A \delta} \exp \left( -\frac{z}{\delta} \right) $$ (6.2)

with $E_p$ being the energy per laser pulse. Accounting for the expression of the energy per pulse $E_p = I \cdot A \cdot \tau_p$ one can write eq. 6.2 in terms of laser pulse duration $\tau_p$ as:

$$ E(z) = (1 - R) \frac{I_0 \tau_p}{\delta} \exp \left( -\frac{z}{\delta} \right) $$ (6.3)

The absorbed energy produces a temperature increase of the lattice, which resembles the gradient of the absorption profile, and can be written as:

$$ \Delta T(z) = \frac{E(z)}{C} = (1 - R) \frac{I_0 \tau_p}{\delta \rho c} \exp \left( -\frac{z}{\delta} \right) $$ (6.4)
6.2 Thermoelastic model

![Graph showing the temperature gradient along film thickness upon laser pulse absorption using eq. 6.4 for the case of a yttrium thin film.](image)

**Figure 6.2:** Calculated temperature gradient along film thickness upon laser pulse absorption using eq. 6.4 for the case of a yttrium thin film.

<table>
<thead>
<tr>
<th>Property</th>
<th>Yttrium</th>
<th>Tungsten</th>
</tr>
</thead>
<tbody>
<tr>
<td>density [kg/m³]</td>
<td>4472</td>
<td>19250</td>
</tr>
<tr>
<td>sound velocity [m/s]</td>
<td>3300</td>
<td>5174</td>
</tr>
<tr>
<td>reflectivity (775 nm)</td>
<td>0.19</td>
<td>–</td>
</tr>
<tr>
<td>penetration depth [nm] (775 nm)</td>
<td>28.7</td>
<td>23</td>
</tr>
<tr>
<td>linear expansion coefficient [K⁻¹] (100 K)</td>
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<td>2.6e-6</td>
</tr>
<tr>
<td>Poisson ratio</td>
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<td>0.28</td>
</tr>
<tr>
<td>bulk modulus [GPa]</td>
<td>41</td>
<td>310</td>
</tr>
<tr>
<td>specific heat [J/m³K]</td>
<td>300</td>
<td>–</td>
</tr>
<tr>
<td>thermal conductivity [W/mK]</td>
<td>17.2</td>
<td>170</td>
</tr>
</tbody>
</table>

**Table 6.1:** The physical properties used in the simulation of the propagating strain pulse within the framework of the thermoelastic model.

where \( C = \rho \cdot c \) is the specific heat per unit volume determined by the density \( \rho \) and the specific heat capacity \( c \) of the material.

In the figure 6.2 we show the calculated temperature increase with the expression 6.4 in the case of a yttrium film. We have used a pulse duration \( \tau_p = 35 \) fs and a fluence of \( 1 \text{mJ/cm}^2 \). The other values of the parameters involved in the calculation are listed in table 6.1. We observe a relatively high temperature increase of 160 K which is mainly determined by the high optical absorption (\( R = 0.19 \) at 775 nm laser wavelength) of the yttrium film. Also we notice that the temperature gradient is extended on a spatial extent covering approximately three times the penetration depth \( \delta = 28.68 \) nm.

The increased temperature of the material results in a thermal expansion of the lattice and consequently to the appearance of a thermal stress \( \sigma_{\text{therm}} \) that will set up a lattice strain \( \eta \). The relationship between stress and strain is similar to applied force-resulting effect connection since the stress is defined as force per area and the strain is the resulting lattice displacement \( \frac{\partial u}{\partial z} \) [135], with \( u \) the equilibrium lattice coordinate.
Before we proceed with the description of the thermoelastic model is worthwhile to make some remarks. In metals the penetration depth is in order of 10–30 nm, that is much smaller than the laser spot diameter, usually in the µm range. Thus the lateral extension of the thermoelastic source is much bigger than its spatial extent along z axis. Accounting for the diffusive heat transport out of the irradiated region during the laser pulse duration one obtains a travel distance \( l_{\text{diff}} \approx \sqrt{D\tau_p} \) [175], where \( D = K/C \) is thermal diffusivity and \( K \) is thermal conductivity. For yttrium \( l_{\text{diff}} \) amounts to \( \approx 0.66 \) nm which much smaller than skin depth. Also during the laser pulse the produced strain can travel over a distance \( l_{\text{ap}} = v\tau_p \) (\( v \) is the sound velocity), that for yttrium amounts to 0.115 nm again much smaller than \( \delta \). Based on these observations we can consider the initial temperature distribution as being homogeneously distributed in the plane of the sample and exponentially decaying along z. Consequently the resulting strain tensor \( \eta \) has only one component that should be considered namely along z direction, \( \eta_z \), and thus the thermoelastic model has an one-dimensional character. In our further deductions we consider the stress and strain with components just along z direction.

The expression of the induced stress, for an elastically isotropic medium, consists of two components that denote the normal mechanical stress and a component induced by the lattice heating:

\[
\sigma_z = \sigma_{\text{mech}} + \sigma_{\text{therm}} = 3\frac{1-\nu}{1+\nu}B\eta_z - 3B\alpha \Delta T(z) \tag{6.5}
\]

with \( \nu, B \) and \( \alpha \) representing the Poisson ratio, bulk modulus and the linear expansion coefficient, respectively.

Solving eq. 6.5 together with the equation of motion along z direction

\[
\rho \frac{\partial^2 u_z}{\partial t^2} = \frac{\partial \sigma_z}{\partial z} \tag{6.6}
\]

and with the expression of the strain tensor

\[
\eta_z = \frac{\partial u_z}{\partial z} \tag{6.7}
\]

the spatial and temporal profile of the propagating strain pulse is obtained [178]:

\[
\eta_z(z,t) = (1 - R) I_0 \tau_p \alpha \frac{1-\nu}{1+\nu} \left[ e^{-\frac{z}{\delta}} \left( 1 - \frac{1}{2} e^{-\frac{z}{\delta}} \right) - \frac{1}{2} e^{-\frac{|z-vt|}{\delta}} \text{sgn}(z-vt) \right] \tag{6.8}
\]

The strain pulse travels with the longitudinal sound velocity \( v \) of the material, that is defined as:

\[
v = \sqrt{\frac{3(1-\nu)B}{1+\nu\rho}} \tag{6.9}
\]

The above obtained strain expression is plotted in the figure 6.3 for the yttrium case at different instances in time. We see that the strain contains a time-dependent part denoting the propagating acoustic pulse that is described by the second term in eq. 6.11, and a time-independent component located in the near-surface region caused by the initial laser-induced thermal expansion. The propagating part of the strain pulse consists of two
components of equal magnitude and opposite sign. During the laser pulse absorption one part is travelling along positive direction of \( z \) axis (the component with negative strain) while the other part goes to the negative direction \((-z)\) being instantaneously reflected at the free surface with a sign change.

As it travels through the sample the strain pulse is partially reflected and partially transmitted at the film/substrate interface with a certain factor \( r_{fs} \) while at the free surface it will be totally reflected with a change in polarity. The factor \( r_{fs} \) denotes the acoustic reflection coefficient that is defined as:

\[
r_{fs} = \frac{Z_s - Z_f}{Z_s + Z_f}
\]  

(6.10)

where \( Z_i = \rho \cdot v \) represents the acoustic impedance for the film and the underlying substrate. The magnitude of \( r_{fs} \) gives how much from the travelling acoustic pulse is reflected at the film-substrate interface and its sign giving the polarity of the strain pulse.

Accounting just for the propagating part of the strain pulse one can write expression 6.11 as:

\[
\eta_z(z,t) = (1 - R) \frac{I_0 \tau \alpha}{\delta \rho c} \frac{1 - \nu}{1 + \nu} r_{fs} \left[ \frac{1}{2} e^{-\frac{|z + vt|}{\delta}} \text{sgn}(z + vt) + \frac{1}{2} e^{-\frac{|z - vt|}{\delta}} \text{sgn}(z - vt) \right]
\]

(6.11)

with the first term describing the strain component with negative sign and the second term the positive strain component.
6.2.2 Acoustic pulse detection

The laser-induced variations in the linear reflectivity of the system will consist in this case of a temperature (electron and lattice) induced component and changes produced by the travelling strain pulse that modulates locally the optical properties of the system. In the following we focus on the detection of the strain-induced changes in the optical reflectivity. Generally, one can write both effects as giving a change in the linear reflectivity as:

\[ \Delta R = |r + \Delta r|^2 - |r|^2 \]  

(6.12)

with \( r \) being the reflectivity of the system in equilibrium and \( \Delta r \) the modulation of the LR due to the presence of strain. The dielectric constant is given by \( \epsilon = (n + ik)^2 \) where \( n \) and \( k \) represent the real and the imaginary part of the refractive index. The produced changes of the optical constant by the propagating acoustic pulse are given by:

\[ \Delta n(z, t) = \frac{\partial n}{\partial \eta_z} \eta_z(z, t) \]  

(6.13)

\[ \Delta k(z, t) = \frac{\partial k}{\partial \eta_z} \eta_z(z, t) \]  

(6.14)

where \( \frac{\partial n}{\partial \eta_z} \) and \( \frac{\partial k}{\partial \eta_z} \) represent the photoelastic constants. These values are very rare in the literature (no reports for yttrium) and are also wavelength dependent [179] and might change the polarity of the phonon echo pulse. Thus we can write the variation of the dielectric constant due to the presence of strain as:

\[ \Delta \epsilon(z, t) = 2(n + ik) \left[ \frac{\partial n}{\partial \eta_z} \sin \left( \frac{4\pi nz}{\lambda} - \phi \right) + i \frac{\partial k}{\partial \eta_z} \cos \left( \frac{4\pi nz}{\lambda} - \phi \right) \right] \eta_z(z, t) \]  

(6.16)

The final expression of the strain-induced changes in the linear reflectivity is given by [178]:

\[ \Delta R = \int_0^\infty f(z) \eta_z(z, t) dz \]  

(6.17)

Here \( f(z) \) is the so-called sensitivity function that quantifies the contribution of the strain being situated at different depths below the surface to the detected linear reflectivity:

\[ f(z) = f_0 \left[ \frac{\partial n}{\partial \eta_z} \sin \left( \frac{4\pi nz}{\lambda} - \phi \right) + i \frac{\partial k}{\partial \eta_z} \cos \left( \frac{4\pi nz}{\lambda} - \phi \right) \right] e^{-\frac{z}{\delta}} \]  

(6.18)

with:

\[ f_0 = \frac{16\pi}{\lambda} \left[ \frac{n^2(n^2 + k^2 - 1)^2 + k^2(n^2 + k^2 + 1)^2}{[(n + 1)^2 + k^2]^2} \right]^{1/2} \]  

(6.19)

and

\[ \tan \phi = \frac{k(n^2 + k^2 + 1)}{n(n^2 + k^2 - 1)} \]  

(6.20)

The spatial shape of the sensitivity function is plotted in figure 6.4 using the values of the photoelastic constants as deduced from the fit of the first acoustic phonon echo in the
6.3 Acoustic phonons in yttrium

The phenomenon of travelling acoustic phonons has been studied for various Y(0001) film thicknesses employing the time-resolved linear reflectivity and second-harmonic generation. The measurements have been performed at a sample temperature of 90 K. The preparation of the thin Y(0001) films has been done in a similar manner as for Gd(0001) films namely deposition on the W(110) substrate held at room temperature and a subsequent annealing to 680 K for 10 minutes. The crystalline quality of the film has been checked with LEED.

A typical measurement showing the linear and nonlinear optical response from a 10 nm Y(0001) film with the laser tuned to 775 nm (for reasons that are apparent later) and at T=90 K is displayed in the figure 6.5. In the first place we notice the conspicuous peaks with alternating polarity in the linear reflectivity signal that are the signature of the travelling acoustic pulse. These are superimposed on a slowly decaying background that reflects (on this time scale) the cooling of the laser spot via thermal diffusion. The time evolution of the second-harmonic field resembles a comparable behavior as the linear reflectivity, with a sharp increase at early delays reflecting the increased temperature of the electronic bath and the subsequent relaxation to the lattice via e-p coupling (ps time...
Figure 6.5: The time-resolved linear reflectivity (dotted line) and the second-harmonic (solid line) response from a 10 nm Y(0001) film, at a laser wavelength of 775 nm and T=90 K. Note the pronounced spikes in the linear reflectivity transient signal that reflect the phonon echo dynamics. The SHG signal lacks the phonon echo signature and shows a low signal to noise ratio due to the reduced efficiency of the SHG process on the Y(0001) surface (for details see text)

As noticed from the raw data presented in figure 6.5, a lower signal to noise ratio is encountered in the transient SH field in comparison to the SHG response from Gd(0001) surface (see for example fig. 5.18). At the employed laser wavelength of 775 nm the probe beam SHG signal reaches ≈11 KHz (compared to typically 60–100 KHz from Gd(0001)),

scale) as well as the cooling of the heated region via heat diffusion on a hundreds of ps time scale. Here we do not investigate in detail the behavior of the incoherent components of the time-resolved LR and SHG but we focus on the phonon echo dynamics. Regarding the excitation of coherent optical phonons on the Y(0001) surface, the transient SHG signal does not show the oscillatory signature of coherent lattice vibrations as was the case for Gd(0001). Also we could not resolve the phonon echoes in the SHG signal, although at the first glance one expects to observe such an effect due to the surface sensitivity of the SHG technique. We will come to these points later in this section.
Figure 6.6: The valence electronic structure at Γ point for a 10 nm Y(0001) film at a temperature of 90 K. The arrows represent the pump-induced optical transitions (bottom) and the SHG probing mechanism (top). The occupied part of the electronic structure has been measured by O. Krupin (within the collaboration with our group) with photoemission at BESSY with synchrotron radiation of 36 eV beam energy at normal incidence. Note the position of the surface state that is positioned exactly at the $E_F$. The peak above Fermi level is a replica of the occupied bulk state centered at an energy of 2 eV, as reported in the literature [180].

that is the highest achievable SHG yield from the Y(0001) surface in the tunability range of the oscillator\(^1\): here 740 nm to 830 nm. The low SHG efficiency is determined by the the evolution of the SHG optical transitions via the electronic structure of Y(0001) presented in the figure 6.6.

Similar to gadolinium, Y(0001) exhibits a surface state that is now energetically located exactly at the Fermi level and is not exchange-split due to lack of ferromagnetic ordering of Y(0001) system. As shown in figure 6.6, the unoccupied (half) of the surface state acts as an intermediate level for the SHG optical transitions starting from the occupied bulk state centered at $\approx 1.65$ eV below $E_F$. At 90 K the measured FWHM of the surface state amounts to $\approx 280$ meV. Since at finite temperatures the unoccupied half of the surface state is partially populated by thermally excited electrons near $E_F$, the optical transition probability at the fundamental wavelength via the surface state is low and consequently the efficiency of the SHG process is weak. Above Fermi level, inverse photoemission

\(^1\)These measurements have been performed before mounting in the laser oscillator mirrors with a broader bandwidth (see chapter 4).
Figure 6.7: The time-resolved linear reflectivity measured on a 50 nm Y(0001) film at a laser wavelength of 775 nm and at a temperature of 90 K. Note the conspicuous peaks in the transient LR that reflect the propagating strain pulse within the film, that can be resolved up to the eighth echo. For clarity, the arrows are pointing the positions of the weaker intensity echoes.

measurements [180] performed at room temperature, show the existence of two features at $0.5 \pm 0.2$ eV and $2 \pm 0.2$ eV which have been ascribed to a surface state and unoccupied bulk state, respectively. The latter feature supports band structure calculations [181] of yttrium that at Γ point that give a value of 1.8 eV for the energetic position of the bulk state. From these results it is clear that the employed phonon energy in our experiment, between 1.5 eV to 1.65 eV, does not match the energetic separation between the measured surface state and the unoccupied bulk state, and thus the second optical transition involved in the SHG process evolves via a virtual state. Therefore the low SHG signal arising from the Y(0001) surface is explained by the low transition probability between the occupied bulk state and the half unoccupied surface state at the fundamental photon energy and the photon energy mismatch between the surface state and the unoccupied bulk state.

In the figure 6.7 the transient linear reflectivity measured from a 50 nm Y(0001) film is displayed. Here we can see clearly the dynamics of the propagating acoustic pulse with an alternating polarity, with the phonon echo signature resolved up to the eighth echo. The measured phonon echo is relatively long lived this fact being attributed to the special characteristics of the Y(0001)/W(110) system. First of all the acoustic reflection coefficient at the film/substrate interface $r_{fs}$ amounts to 0.76 as deduced from eq. 6.10 using the
acoustic impedances of bulk Y and W (see table 6.1). Secondly the optical absorption of the incident laser light is relatively high ($R \approx 0.19$ at $\lambda = 775$ nm), that increases significantly the temperature of the irradiated region (see fig. 6.2) and consequently a high value of the initial strain that is launched into the film. Moreover, it seems that the film/substrate interface is smooth on the wavelength scale of the acoustic pulse, which prevents the distortion or deterioration of the propagating acoustic pulse. The good quality of the interface can be inferred from the UHV preparation conditions of the Y(0001) thin film.

Similar phonon echo transients are obtained for lower film thicknesses as can be seen in the figure 6.8. Here the measured LR dependencies for 10 nm and 20 nm film thickness are plotted together with the data for the 50 nm film, but on a shorter time scale (for clarity). A first information that can be deduced from the measured data of the figure 6.8 is either the thickness of the film or the sound velocity by measuring the time intervals between the echoes. A round trip that takes 36.5 ps within the 50 nm yttrium film while for the 20 nm and 10 nm it takes like 14 ps and 7 ps, respectively. From these data one obtains a sound velocity $s=2816 \pm 55$ m/s or accounting for the bulk sound velocity [182] $s_{th}=3300$ m/s one deduces a film thickness of 59.4 nm, 23.1 nm and 11.5 nm. Accounting

Figure 6.8: The dynamics of the phonon echo for various Y(0001) film thicknesses measured at 90 K. For clarity the transient LR for the 50 nm film is plotted with a positive offset along y axis.
Figure 6.9: The frequency content obtained by Fourier transforming the first echoes measured on various Y(0001) film thicknesses. Note the higher frequencies 156 GHz and 111 GHz of the pulses obtained for lower thicknesses 10 nm and 20 nm, respectively, that are smaller than the penetration depth.

Another important piece of information that can be retrieved from the data is the value of the optical penetration depth $\delta$. Taking into account the scattering of the optical constants data reported in literature, this is an useful insight from the experiment. The penetration depth can be deduced from the temporal extent of the acoustic pulses for different thicknesses. As long as the investigated thicknesses are smaller than $\delta$, the shape and the temporal extent of the phonon echo is determined just by the film thickness (see eq. 6.4). Thus, smaller the thickness narrower is the pulse width in time and broader is the frequency content of the propagating strain pulse. The latter feature can be seen in the figure 6.9 where the Fourier transform of the first phonon echoes measured on different film thicknesses is displayed. For the 10 nm and 20 nm film thicknesses, that are lower than the penetration depth, higher frequency pulses are launched with central frequencies around 156 GHz and 111 GHz, respectively.

The skin depth can be deduced since together with the sound velocity of the material are the only quantities (in a first approximation) that limit the rise time of the lattice thermal expansion and implicitly the strain pulse duration. Accounting for the literature data [183] of the refractive index for bulk Y at 775 nm the calculated value of $\delta$ is 28.7 nm. Assuming this value to be close to the real one we should see no change in the duration of the acoustic pulse starting to this film thickness. Unfortunately no measured data is available for thicknesses between 20 nm and 50 nm, and thus we take the acoustic pulse duration value of the 50 nm measurement that amounts to 14 ps (for 10 nm and 20 nm the pulse duration is 6.4 ps and 9 ps respectively). This value together with the measured sound velocity of $\approx 2816$ m/s results in an optical penetration depth $\delta \approx 39$ nm. One can
take this value as the optical penetration depth if, within the rise time of the strain pulse, 
the spatial extent of the energy transport (ballistic, electron diffusion, heat diffusion) is 
smaller than the obtained value of $\delta$. Otherwise one obtains the depth that contributes 
to the generation of the strain pulse. For yttrium using the strain rise time $\tau$ of 14 ps 
and the defined diffusion length $l_{\text{diff}} = \sqrt{D\tau}$ from section 6.2 one obtains $l_{\text{diff}}=13.3$ nm, 
which is smaller than $\delta$.

From the thickness-dependent data we can evaluate the value of the acoustic reflection 
coefficient from the magnitude ratio of subsequent phonon echo peaks. For an accurate 
determination of the reflection coefficient, the incoherent background has been removed 
from the raw data and the remaining part, reflecting the propagating strain pulse, is 
squared. From the ratios of subsequent peaks magnitude we get a value of $r_{fs} = 0.69\pm0.061$ 
for the acoustic reflection coefficient of the Y(0001)/W(110) system, that agrees with the 
calculated one of 0.76. We have to keep in mind that the decrease of the phonon echo 
magnitude is partially determined also by the acoustic attenuation of the strain pulse in 
the film, which is not included in the definition of $r_{fs}$. By comparing the calculated and 
measured values of $r_{fs}$ one can infer a good crystalline quality of the film with less defects.

In the figure 6.10 the first phonon echo measured on a 50 nm Y(0001) film is plotted 
together with the simulated one based on the thermoelastic model presented in section
6.2. We notice a general good agreement between the measured and the simulated phonon echo but the latter one cannot account for the entire measured pulse width. This is due to the fact that the thermoelastic model assumes an instantaneous temperature increase upon laser pulse absorption neglecting any energy transport (ballistic, electronic diffusion or heat diffusion) out of the irradiated region as well as the heat diffusion. As a result, the spatial extent over which the energy is distributed can be larger than the optical penetration depth and consequently the phonon echo pulse width is broader than initially estimated by the thermoelastic model. This might be also our case since the estimated temperature increase according to thermoelastic model is 160 K while calculated with the two-temperature model, that accounts for electronic diffusion, is just \( \approx 80 \) K at the electron-phonon equilibration time. The computed\(^2\) electronic and lattice temperatures according to 2TM are plotted in the figure 6.11. However, for an accurate theoretical description of the photo-generated strain pulse in metals and semiconductors the energy transport effects out of the irradiated region during the rise time of the strain pulse should be included in the framework of the thermoelastic model.

Finally we address the lack of the coherent optical phonons and of the phonon echoes in the transient SHG signal. As showed earlier in this section the efficiency of the pump-induced optical transitions over the partially empty surface state of Y(0001) is small. As a result the excited electron population at the surface cannot trigger coherent lattice

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\(^2\)The used parameters in the computation using 2TM are \( \Theta_{D}=256 \) K, electron heat capacity \( \gamma=300 \) \( J/m^3K^2 \) [53] and the electron-phonon coupling constant \( g=1\cdot10^{17}W/m^3K \) [58].
6.4 Influence of the laser wavelength and temperature

This section addresses the effect of the laser wavelength and the temperature variation of the sample on the phonon echo dynamics on Y(0001)/W(110). A wavelength-dependent study of the phonon echo is always required taking into account the dependence of the sensitivity function (see eq. 6.18) on the probing laser wavelength and the fact that the photoelastic constants might change with the wavelength. As for the temperature dependence, upon increasing the temperature the lattice expands and simultaneously the thermal phonons population is increased, both affecting the sound velocity of the material and implicitly the propagating strain pulse.

Wavelength dependence

Here we investigate the effect of the laser wavelength on the phonon echo dynamics measured from Y(0001)/W(110). For this purpose the wavelength of the laser is varied between 750 nm to 825 nm with the sample held at 90 K. As mentioned above, the laser wavelength determines the magnitude and the spatial profile of the sensitivity function through equation 6.18, that influence the detection of the strain pulse (see section 6.2). Simultaneously the photoelastic constants can vary with the laser photon energy and thus affecting the amplitude of the detected change in the linear reflectivity caused by the presence of travelling strain pulse (see eq. 6.13). Moreover the optical penetration depth changes with the wavelength, that results in different spatial extents of the generated strain pulse.

The wavelength dependence measured from a 20 nm Y(0001) film is shown in the figure 6.12. We notice that varying the laser wavelength no change in the shape of the phonon echoes is produced, contrary to what has been reported in literature [179, 184, 185] for various systems. We have to mention here that larger wavelength ranges have been employed
Figure 6.12: The pump-induced variations in the linear reflectivity for various laser wavelengths measured from a 20 nm Y(0001)/W(110) film at $T=90$ K. The transient LR measured at $\lambda=800$ nm is recorded with a higher density of data points on a shorter delay time scale.

in the above cited works. However, a wavelength-dependent variation in the magnitude of the phonon echo peaks is encountered. This can be clearly observed in the figure 6.13, where the LR signal arising from the propagating strain pulse is plotted after removing of the incoherent background. From here we see a variation of $\approx 50\%$ in the phonon echo magnitude upon changing the laser wavelength. Also the change in magnitude of the phonon echoes with wavelength exhibits a non-monotonous behavior: the peak amplitude is higher for the central wavelengths (800 nm and 775 nm) and decreases for the limit wavelengths (750 nm and 825 nm).

As for the magnitude of the phonon echoes, a non-monotonous wavelength-dependent change appears in the absolute values of the pump-induced variations of the incoherent background. Inspecting the raw data in the figure 6.12, we notice a similar value for the incoherent background of the LR transients measured for 825 nm and 750 nm, while larger values are measured for 775 nm and 800 nm data sets. The incoherent part of the linear reflectivity reflects the initial photoexcited electron population that transfers energy to the lattice via $e$-$ph$ coupling (sub-picosecond time scale) and the subsequent cooling of the lattice through heat diffusion. Thus for the 775 nm and 800 nm measurements the the absorbed energy density is higher than for the limit wavelengths 750 nm and 825 nm. The source term that describes the absorbed energy density (eq. 6.2) becomes dependent only on the reflectivity value $R$ when the penetration depth is smaller than the film thickness, which is our case. Calculating the reflectivity values based on literature values for the
6.4 Influence of the laser wavelength and temperature

refractive index [183], one obtains a monotonous decreasing of the reflectivity from \( \approx 0.24 \) to \( \approx 0.17 \) by increasing the wavelength from 750 nm to 825 nm, respectively. Hence the highest absorption value would be for a laser wavelength of 825 nm and thus the highest pump-induced variations of the incoherent LR are expected for this laser wavelength. Instead we observe a similar incoherent background level as for the 750 nm data set. This behavior suggests that an additional mechanism should be involved in the initial optical absorption and implicitly excitation of the system. It might be that the unoccupied part of the surface state present on Y(0001) (see fig. 6.6) is responsible for this non-monotonous behavior observed in the phonon echo and the incoherent LR dynamics. It seems that for the lowest and the highest laser wavelengths used here (750 nm and 825 nm) the photon energy does not match the unoccupied part of the surface state, whereas for the central wavelengths a better photon energy matching takes place. Hence an additional absorption process of the fundamental photon might take place via the surface state. As an experimental input that supports this allegation is the wavelength-dependent SHG (a process sensitive to surface electronic structure see the previous chapter) signal displayed in figure 6.14, that increases for these central wavelengths. However, in order to check this proposal further measurements are needed with a smaller step variation in the laser wavelength and covering a broader wavelength range.

Summarizing, within the investigated laser wavelength range between 750 nm and 825 nm we do not observe major changes in the phonon echo dynamics. Beside a variation in the magnitude of the detected echoes that depends on the laser photon energy being more pronounced for central wavelengths (775 nm and 800 nm), no change in their shape is noticed. The same trend with the change of the laser photon energy is encountered in
the pump-induced variations of the incoherent background, that points to a more efficient optical excitation for the 775 nm and 800 nm wavelengths. Since the encountered behavior is non-monotonous i.e. for the highest and lowest photon energies the transient LR are similar (see fig. 6.12), this suggests that the surface state might play a role in the optical excitation of the system and the generation of the strain pulse.

Temperature effects

The effect of the temperature variation on the phonon echo dynamics measured on 10 nm Y(0001) film is presented in the figure 6.15. Here the measured time-evolution of the linear reflectivity is shown for three representative temperatures. We notice that the LR transients exhibit a qualitatively similar behavior upon temperature increase, with the absolute level of pump-induced variations of the incoherent background decreasing with increasing temperature. Simultaneously the magnitude of the phonon echoes peak is slightly decreasing by elevating the temperature. The latter behavior is better seen in the figure 6.16, where the contribution to the LR arising from the propagating acoustic pulse, obtained after background subtraction, is plotted for the employed temperatures. Within the investigated temperature range the decrease of the phonon echo peak is linear with the temperature increase. This can be seen from the figure 6.17, where the magnitude of the phonon echoes is displayed versus temperature for the first three echoes of the strain pulse (due to their better statistics).

Another feature that can be observed upon temperature increase is the fact that the phonon echoes arrive at the surface temporally delayed with respect to the detected echoes measured at low temperature. This can be clearly seen for all five echoes in figure 6.16. By evaluating the difference in the arrival time of the strain pulse for different temperatures one can calculate the variation of the sound velocity as a function of temperature. We measure a positive delay in the arrival time of the phonon echoes around 0.2 ps for each step in the temperature increase, that results in a decrease of the sound velocity of \( \approx 6\% \) at 400 K in comparison with the low temperature data. In order to have a complete picture about the temperature-dependent sound velocity and acoustic attenuation, the investigated temperature interval should be extended up to temperatures at which the phonon echoes can not be detected anymore. Also a higher density of data points in the

![Figure 6.14: The variation of the SHG signal with the wavelength of the fundamental laser beam. The data points are fitted with a lorentzian centered around 780 nm.](image)
6.4 Influence of the laser wavelength and temperature

Temperature dependence are needed. Therefore more detailed measurements would be useful in this context.

The temperature-dependent variation of the sound velocity is determined by two factors: the thermal expansion of the material and the increased thermal phonon population. The effect of the first factor is straightforward since an increased thermal expansion produces an additional strain of the lattice and thus affecting the sound velocity of the specimen. Regarding the second factor the increased phonon population affects the travelling sound wave by anharmonic interactions where a longitudinal acoustic phonon i.e. the propagating strain pulse scatters into two transversal (thermal) phonons with the conservation of energy and momentum. In principle more phonons can be involved in the decay of the longitudinal acoustic phonon but these are higher order effects and usually appearing with a lower probability. One way to disentangle between the anharmonic decay and the thermal expansion contribution to the temperature-dependent decrease of the sound velocity relies on the fact that the first contribution depends on the frequency of the acoustic pulse while the other not. Moreover the thermal expansion gives a linear dependence of the sound velocity on the temperature. Unfortunately, due to the lack of higher density of data points we could not perform a detailed analysis in order to identify the source of the sound velocity variation with temperature.

Summarizing, upon increasing the temperature the phonon echo magnitude decreases
linearly and simultaneously the sound velocity decreases by \(\approx 6\%\) in comparison to the low temperature value. The processes responsible for the temperature-dependent sound velocity behavior have been discussed but due to the lack of higher density of measured data points their contribution could not be separated.

### 6.5 Conclusions and outlook

In this chapter preliminary results regarding the laser-induced dynamics on the Y(0001) thin films have been presented, employing as investigation tools time-resolved linear reflectivity and second-harmonic generation. Upon laser excitation the time-resolved linear reflectivity shows pronounced "spikes" with alternating polarity which appear at constant time intervals in the transient signal, that have been interpreted as propagating acoustic phonons in the Y(0001) film. These phonon echoes are relatively long lived due to the high
optical absorption of the material, the high value of the acoustic reflection coefficient of the Y/W interface and presumably due to the smoothness of the buried interface region. The frequency content of the acoustic pulses is ranging from 70 GHz to 156 GHz (central frequency), that can be varied by employing different film thicknesses smaller than the optical penetration depth. From the phonon echo dynamics measured on various Y(0001) film thicknesses we could accurately measure the sound velocity, the optical penetration depth and the actual film thickness. Moreover we could determine the photoelastic constants for yttrium by fitting the first phonon echo peak using the phenomenological thermoelastic model. In this context an extension of the thermoelastic model using a transfer matrix method for the simulation of the entire travelling path of the strain pulse would be useful. Although a good reproducibility of the first phonon echo with the actual model could be obtained, the integration of the electronic energy transport into the model would account for the additional broadening of the pulse determined by the heat diffusion. Upon varying the laser wavelength the magnitude of the phonon echoes changes with no modification in the shape of the travelling strain pulse, which means that the photoelastic constants do not change significantly within the employed wavelength range. Increasing the temperature of the sample the sound velocity of the propagating acoustic pulse changes due to the combined effect of the thermal expansion and increased thermal phonon population. We could not resolved the phonon echo signature in the second-harmonic signal arising from the Y(0001) surface presumably due to small changes of the photoelastic constants in the SH frequency range, the restricted probing depth to the surface region and the symmetry of the strain. This is described by a second rank tensor and thus can not be detected with second-harmonic or any nonlinear tool sensitive to odd rank tensors. In this context the third-harmonic generation would be able to detect the changes in the optical susceptibility of the sample by the propagating strain pulse. Also the excitation of the coherent optical phonons on the Y(0001) surface could not done due to the specificity of the surface state positioned at $E_F$, that does not allow an efficient excitation of the system.
6 Acoustic phonons on Y(0001)/W(110)
7 Summary

This thesis presents the femtosecond laser-induced electron, lattice and spin dynamics measured on two representative rare-earth systems: the ferromagnetic Gd(0001) and the paramagnetic Y(0001) metals. The main issues addressed in this work are:

- the investigation of the excitation mechanism, the interaction and the relaxation of the coupled coherent lattice and spin excitations that evolve at THz frequencies on the Gd(0001) surface.

- identification and separation of the elementary spin scattering processes that are responsible for the ultrafast demagnetization dynamics, following the excitation with a femtosecond laser pulse, on the localized magnetic moment ferromagnet Gadolinium.

- study of the physics of the propagating acoustic phonons in Y(0001) thin films and retrieval of the elastic and photoelastic characteristics of the system.

The employed investigation tools are the time-resolved linear reflectivity and second-harmonic generation, which offer simultaneously complementary information about the bulk and surface/interface dynamics, respectively. In the following the obtained results are detailed.

Coherent lattice and spin dynamics

The optical excitation of the exchange-split surface state of Gd(0001) triggers simultaneously the coherent vibrational dynamics of the lattice and spin subsystem in the surface region at a frequency of 3 THz. The electron/lattice and spin dynamics could be separated owing to the symmetry of the even and odd SH fields with respect to magnetization reversal. The coherent optical phonon measured by the even SH field represents the vibration of the topmost atomic layer against the underlying bulk along the normal direction to the surface. This periodic variation of the interlayer distance between two adjacent hcp planes modulates the exchange interaction $J$ between neighbor atoms that gives rise to an oscillatory motion of the magnetic moments at the same frequency with the lattice vibration. Thus, we show the possibility of the spin system to follow the lattice coherently at THz frequencies. The coupled coherent phonon-magnon mode represents a new type of magneto-elastic interaction, that is mediated not by the spin-orbit coupling but by the dynamical variation of the exchange interaction. The excitation mechanism of the lattice vibration has been identified as being DECP (displacive excitation of coherent phonons)-like from the initial cosine phase of the oscillations. The charge-driven character of the excitation mechanism has been proved in wavelength-dependent measurements. Independent support comes from the time-resolved photoemission measurements that show an oscillatory motion of the majority surface state binding energy with the same frequency.

183
as the lattice vibration. Upon elevating the temperature of the system we could identify the scattering with electrons as the dominant relaxation pathway of the coherent phonon. Contributions coming from the phonon-phonon and phonon-magnon scattering, are also considered.

**Femtosecond demagnetization dynamics**

Another goal of this project is to study the femtosecond laser-induced demagnetization on the local magnetic moment ferromagnet gadolinium, and to identify and disentangle the elementary processes responsible for the ultrafast loss of magnetization. For this purpose the dynamics of the spin polarization and of the exchange splitting of the Gd(0001) surface state following the excitation with a femtosecond laser pulse have been studied. Employing pump-probe MSHG the spin polarization of the Gd(0001) surface state is measured, which exhibits a sudden drop within the laser pulse duration of 50 fs. An independent time-resolved photoemission study [13], performed under similar conditions, shows a constant exchange splitting of the surface state. From these observations has been concluded that on Gd(0001) the spin polarization does not follow the exchange splitting dynamics and that on ultrafast time scales the spin-mixing behavior dominates. The time scale on which the demagnetization occurs is at least comparable if not smaller than observed for the itinerant ferromagnets. The ultrafast decrease of spin polarization can be explained by the quasi-elastic spin-flip scattering of the hot electrons among spin-mixed states. The angular momentum conservation is fulfilled by emission or absorption of magnons, that can involve also the 4\(f\) moments.

**Phonon echo dynamics**

Epitaxially grown thin films of Y(0001) on W(110) substrate have been investigated with time-resolved linear reflectivity and second-harmonic generation. Upon pump pulse excitation, in the transient LR signal sharp peaks with alternating polarity have been observed, that appear at regular time intervals. This has been interpreted as the signature of propagating acoustic phonons at sound velocities within the film, the so called phonon echo phenomenon. The phonon echo signature is long lived on Y(0001)/W(110) system due to the high optical absorption at 800 nm, the high acoustic impedance of the film/substrate interface and due to a presumably smooth film/substrate interface. The phonon echo is excited by the sudden temperature increase produced by the absorption of the femtosecond laser pulse, which leads to a lattice expansion that launches a strain pulse. The values for the film thickness, sound velocity and optical penetration depth could be retrieved from the phonon echo data. The central frequencies of the travelling strain pulse ranges from 70 GHz to 200 GHz, that can be varied as a function of the film thickness. Using the thermoelastic model we could compute the shape of the first phonon echo, and from here we deduced the values of the photoelastic constants of the Y(0001) thin film.
Spin-polarized adsorbates investigated with magnetization induced sum-frequency generation

Furthermore a pilot experiment has been developed within the framework of this thesis, in which the CO molecules adsorbed on the ferromagnetic thin films of Ni on Cu(100) substrate are investigated. The goal of this project is to explore the capabilities of the new technique of magnetization-induced sum-frequency generation (MSFG) on a model system characterized by a spin reorientation transition Ni/Cu(100). For this purpose a new UHV system has been constructed and the magnetic characterization of Ni/Cu(100) films as well as the TDS (thermal desorption spectroscopy) measurements of CO on Ni/Cu(100) have been performed.

Future developments

Based on the insight developed in the present study there are several points that can be investigated in the future. With regard to the coherent lattice and spin dynamics, two similar rare-earth systems Tb(0001) and Dy(0001) are very interesting candidates since exhibit an exchange-split surface state and the same valence electronic structure. Also they have a similar phonon spectrum but with a higher magnetic anisotropy and implicitly an active spin-orbit coupling. Moreover, the phonon and magnon dispersion curves do not overlap anymore, the magnons having lower energies. Thus, the excitation and the coupling mechanism of the coherent phonons and magnons can be tested. Also these two systems are suitable to investigate how the spin-orbit coupling and the higher magnetic anisotropy influence the femtosecond magnetization dynamics observed on Gd(0001). For both the coherent and the incoherent spin dynamics, time-resolved investigation with femtosecond light sources that can reach the localized 4f moments (9 eV binding energy), like UV and XUV free-electron laser or the generation of higher-harmonics in gas cells, would be very valuable. Also a time-resolved XMCD experiment, that could disentangle the orbital and spin contribution to the total magnetic moment, might clarify whether the 4f are involved in the coherent and incoherent spin phenomena encountered on the Gd(0001) surface.
Ziel dieser Arbeit ist die Untersuchung von laserinduzierter Elektronen-, Gitter- und Spin-
dynamik. Hierfür wurden zwei repräsentative Seltenerd-systeme untersucht: das ferro-
magnetische Gd(0001) und das paramagnetische Y(0001). Die wichtigsten Punkte dieser
Arbeit sind:

- die Untersuchung des Anregungmechanismus, der Kopplung einer kohärenten Gitter-
und Spinanregung an der Gd(0001) Oberfläche

- die Detektion elementarer spinabhängiger Streuprozesse, die im Fall von Gd mit
seinen lokализierten magnetischen Momenten, verantwortlich sind für ultraschnelle,
optisch induzierte Entmagnetisierung.

- die physikalischen Grundlagen propagierender akustischer Phononen in dünnen
Y(0001) Filmen und die Auswertung von elastischen und photoelastischen Eigen-
schaften des Systems.

Die benutzten Untersuchungsmethoden sind zeitaufgelöste lineare Reflektivität und Erzeu-
gung der zweiten Harmonischen (SHG), die eine simultane komplementäre Information
über die Volumen und Oberfläche/Grenzfläche Dynamik ermöglichen. Die wichtigsten
Ergebnisse sind:

### Kohärente Gitter- und Spindynamik

Die optische Anregung des austauschaufgespaltenen Oberflächenzustand von Gd(0001)
lässt simultan eine kohärente Schwingungsdynamik des Gitter- und Spin-Subsystems an
der Oberfläche bei einer Frequenz von 3 THz aus. Die Gitter und Spindynamik kon-
mnte man trennen dank der Symmetrie von geraden und ungeraden SH Feldern bezüglich
der Magnetisierungs Umkehrung. Das kohärente optische Phonon, gemessen mit dem
geraden SH Feld, repräsentiert die Schwingung der obersten Atomlage in Bezug auf tiefer-
liegende Schichten entlang der Oberfläche. Die periodische Modulation des Zwischenla-
genabstands zwischen zwei benachbarten Ebenen senkrecht zur Oberfläche moduliert die
Austauschwechselwirkung $J$ zwischen benachbarten Atomen. Dadurch entsteht eine oszil-
latorische Variation des magnetischen Moments bei der Frequenz der Gitter-Schwingung.
Wir zeigen damit eine Möglichkeit, wie das Spinsystem mit THz Frequenzen kohärent
dem Gitter folgen kann. Die kohärente Phonon-Magnon-Mode stellt für Gd einen neuen
Typ von magnetooelastischer Wechselwirkung dar, die nicht von der Spinbahnkopplung,
sondern von der dynamischen Modulation der Austauschwechselwirkung vermittelt wird.
Aus der kosinusartigen Phase der Oszillationen bei $t=0$ schließen wir auf einen DECP
(displacive excitation of coherent phonons) Anregungmechanismus der Gitter-Schwingung.
Zusammenfassung


Femtosekunden Entmagnetisierungs Dynamik


Phonon-Echo Dynamik

Y(0001) Film angeben.

Spin-polarisierte Adsorbate untersucht mit der magnetisierungsinduzierten Summenfrequenz-Erzeugung


Zukünftige Entwicklungen

8 Zusammenfassung
A Sum-frequency generation from CO on the Ni/Cu(100) system

In parallel with the measurements performed on the Gd(0001) and Y(0001) systems I have developed a pilot experiment in which the CO molecules adsorbed on top a thin ferromagnetic films of Ni/Cu(100) are studied by means of sum-frequency generation technique. For this purpose I have build up a new UHV system devoted to thin films preparation and characterization as well as optical spectroscopy, and designed the optical scheme for the nonlinear optical measurements. The tool of choice in this experiment is the infrared visible sum-frequency generation, that is a widely used investigation technique for vibrational dynamics of the molecular adsorbates [97].

Unfortunately due to the unavailability of the laser system which provides laser pulses with wavelengths in the far-infrared region, the SFG measurements have been postponed until the end phase of this thesis. However, the magnetic characterization of the Ni/Cu(100) thin films with the help of MOKE as well as the study of the adsorption energetics of the CO on the epitaxial Ni films employing TDS, have been performed. Also, preliminary SFG measurements of CO/Cu(100) and CO/Ni/Cu(100) have been made, the whole work being in progress. The shown SFG spectra have been measured by my colleagues H. Öström and M. Krenz, that have joined lately this project.

The appendix is structured as follows. The UHV chamber and the laser system are briefly described followed by the Ni films preparation procedure and their magneto-optical characterization. Next the TDS measurements on the Ni thin films are showed and compared to the available data for bulk Ni crystals. In the remainder of the appendix the first SFG results are shown.

The basic idea of the experiment is to use the underlying ferromagnetic thin film in order to magnetically polarize the molecular adsorbate, here the CO molecules, and to measure the SFG signal coming from the CO stretching vibration for opposite magnetization directions. In other words, to investigate the existence of a magnetic contrast in the SFG intensity and presumably for a change of the energetic position of the SFG resonance upon magnetization reversal. As a model system for the ferromagnetic support of the adsorbate, thin films of Ni on a Cu(100) substrate have been chosen. This system provides the freedom of choosing the direction of magnetization according to the spin reorientation transition (SRT) [186], that takes place as a function of the Ni film thickness. According to literature [186, 187], below \( \approx 7 \) ML Ni/Cu(100) the magnetization direction lies in the plane of the film whereas for higher thicknesses is oriented to an out-of-plane direction. The magnetization reorientation to an in-plane direction takes place above \( \approx 35 \) ML [188]. Details about the origin of the SRT in Ni/Cu(100) are given latter in the Appendix.

A schematic illustration of the experiment is shown in the figure A.1. On the left side of the figure the studied system and the investigation technique are sketched. Varying the Ni
A Sum-frequency generation from CO on the Ni/Cu(100) system

Figure A.1: Left: Schematic illustration of the SFG process and the investigated system CO adsorbed on Ni thin films on a Cu(100) substrate. As a function of Ni film thickness the magnetization reorients from in-plane to out-of-plane direction that can affect the vibrational dynamics and the adsorption geometry of the CO molecules. Right: The generation of the resonant SFG process in the case of CO molecule with the IR photon energy matching the energy difference between two vibrational levels of the molecule.

film thickness the orientation of magnetization M can be changed which might affect the vibrational dynamics and the geometry of the adsorbed CO molecule. The SFG process is used to detect the vibrational dynamics of the adsorbate with the infrared beam photon energy matching the intramolecular vibrational transition of the adsorbed molecule. As a result the SFG process is resonantly enhanced. This is illustrated on the right side of the figure A.1, where the vibrational potential of the CO molecule and the optical transitions of the three photons involved in the SFG process are shown.

The CO molecule chemisorbed on the Ni surface, and in general on metals, with the C atom pointing downwards. Bonding is determined by the hybridization of the 3d levels of the Ni metal with the CO 5σ and 2π* orbitals. In the gas phase CO is diamagnetic, but upon chemisorption on the ferromagnetic Ni(100) surface, magnetic signals arising from the CO molecule could be detected by XMCD [189, 190]. The magnetic XMCD measured on 10 ML Ni/Cu(100) (out-of-plane magnetization) at the O 1s→ CO 2π* transition revealed the parallel alignment of an CO 2π* orbital moment with the Ni film magnetization [190]. For a Ni film (6 ML) with in-plane magnetization the CO 2π* orbital moment is interpreted to be antiparallel relative to film magnetization. For the latter case, in order to maintain the hybridization with Ni atom, the CO should tilt with an angle of ≈30° with respect to surface normal [189].

The goal of this project is to detect by means of SFG the effect of the induced magnetization in CO molecule, and if successful to proceed to time-resolved measurements.

UHV chamber and the laser system

The UHV chamber is pumped by a turbomolecular pump (PFEIFFER) together with a pumping stage (PFEIFFER) consisting of a turbomolecular and a membrane pump acting
Figure A.2: Overview of the SFG optical scheme and the UHV chamber. The IR and the VIS are guided to the UHV chamber by gold-coated and dielectric mirrors, respectively, and focused to the sample (S) at \( \approx 78^\circ \) angle of incidence. The spatial and temporal overlap of the IR and VIS pulses on the sample is checked by mimicking the sample with a LiIO\(_3\) nonlinear crystal that generates a SFG reference signal. The SFG signal generated on the Ni surface and by the reference crystal are directed to the detector stage formed by a monochromator and a CCD camera. A notch filter is used in order to filter-out the VIS beam. The SFG signal is measured for opposite directions of the external magnetic field H. The sample is positioned between the magnetic poles MP.

as a pre-vacuum pump. After a careful baking of the chamber the achievable base pressure is in the upper \( 10^{-11} \) mbar range.

The UHV chamber is structured on two levels: one for preparation and characterization of the thin films and a specially designed one for the optical measurements. In the preparation level an electron-beam evaporator with a quartz microbalance for thickness measurements, an electron gun together with an Ar dosing valve for sputtering, a LEED device, a quadrupole-mass spectrometer and a dosing gas system are mounted. The optical level has a special off-axis construction that allows a sample positioning close to the entrance window used for guiding the laser beams to the sample. Employing short focal distance optics a better focusing can be achieved and thus a considerable increase of the incident laser fluence. Such a chamber design is useful for the nonlinear optical measurements where the laser focus is a parameter that can increase the efficiency.
The LEED patterns obtained from a clean Cu(100) substrate (left) and a 7 ML Ni film (right) at 153 eV and 140 eV beam energy, respectively. Both spectra are recorded at room temperature.

of the nonlinear process (see eq....). In the optical level a home-made electromagnet is installed. This is specially designed with the poles situated in vacuum, mounted uninterruptedly through the chamber flanges and closing the loop outside the chamber where the coils are installed. By this construction, high currents can be used for producing the magnetic field with no risk of contaminating the vacuum by outgassing. The maximum obtainable magnetic field is \( \approx 250 \) gauss measured in the middle of the electromagnet gap, which has a 36 mm length. The strength of the external magnetic field is sufficient in order to magnetize the Ni films in saturation along the magnetization easy axis. This electromagnet design allows magneto-optical measurements in the polar and longitudinal configurations (see figure 3.5).

For the magnetic characterization of the grown Ni films I have constructed a MOKE polarimeter designed in the balanced detection configuration [113]. This construction is particularly useful for detecting ultrathin ferromagnetic films since the possible laser fluctuations are single out. The sensitivity of the MOKE detector is in the atomic monolayer range.

At the preparation level a home-made evaporator is installed, with the evaporation material under the form of Ni wires (99.99% purity) mounted in a W crucible. The crucible has been extensively outgassed before using. The evaporation is realized by electron-beam heating with the crucible and the filament mounted in a water-cooled Cu shroud. The QMS is used for TDS measurements and residual-gas analysis. The CO is dosed on the sample using a gas dosing system consisting of leak valve and a metallic tube extended into the chamber. The sample can be positioned very close to the dosing tube and thus avoiding to expose other parts of the sample holder to the dosed adsorbate. A rough estimation of the dosed adsorbate quantity is made by reading the ion gauge pressure and the time of dosing.

The laser system used for the SFG measurements consists of an Ti:Sa oscillator (Coherent Vitesse) that seeds an regenerative amplifier (Quantronix Titan II). The amplified laser pulses are used in the generation of the far infrared pulses by employing a commercial system (TOPAS) in which several nonlinear processes (optical parametric generation and amplification, difference frequency generation) are involved. The output IR pulses are
Figure A.4: The MOKE spectra measured on 8 ML and 3 ML Ni film thickness at a sample temperature of 300 K and 200 K, respectively, in the polar configuration with a s-polarized laser beam.

tunable between 2.4 and 10 µm, ≈150 fs in duration, with a pulse energy of 15 µJ. The VIS laser beam used for SFG up-conversion process is centered at 800 nm wavelength, a pulse duration of 5 ps and energy per pulse around 15 µJ. For more details about the laser system the reader is referred to the Daniel Denzler’s thesis [191].

**Ni thin films preparation and characterization**

The Cu(100) substrate is cleaned by repeated cycles of Ar⁺ sputtering at 1 KeV energy and subsequent annealing to 850 K for 5 minutes. The cleanliness and the crystalline quality of the substrate has been checked by LEED. The LEED picture obtained for a clean Cu(100) substrate at a beam energy of 153 eV is displayed in the left part of the figure A.3.

Epitaxial Ni thin films with thicknesses ranging from 3 ML (1 ML=1.7 Å) to 30 ML have been prepared using a similar method as reported by Shen et al. [192]. This consists in depositing the Ni on the Cu(100) substrate held at room temperature at a ≈1 Å/min deposition rate followed by annealing to 420 K for 5 minutes. By this method smooth Ni films have been obtained as can be judged from the LEED picture displayed on the right part of the figure A.3. Higher annealing temperatures (above 450 K) are not recommended since for this system significant atomic inter-diffusion from the substrate to the film surface can occur.

**MOKE measurements**

The film growth of Ni on the Cu(100) substrate is pseudomorph with a face-centered tetragonal (fct) Ni lattice, up to ≈11 ML [187] film thickness. This is due to the film/substrate lattice mismatch that amounts to 2.5%, the Ni layers becoming strained in order to match the Cu(100) lattice. For higher thicknesses the strain induced by the lattice mismatch is released by defects (misfit dislocations) and the lattice symmetry is relaxed to the normal face-centered cube (fcc) type. This tetragonal distortion of the lattice is the origin of the spin-reorientation transition that take place on the Ni/Cu(100) system in the low thickness
A Sum-frequency generation from CO on the Ni/Cu(100) system

range [186]. More detailed, in ferromagnetic thin films the orientation of magnetization is determined by the interplay among different magnetic anisotropy terms, whose magnitude can change with temperature, film thickness etc. In general, an out-of-plane magnetization orientation is favored when the following condition is fulfilled [188]:

\[ K_V + \frac{K_S + K_i}{d} > 2\pi M^2 \]  

(A.1)

where \( d \) is the film thickness, \( M \) the saturation magnetization and \( K_V \), \( K_S \) and \( K_i \) represent the second-order magnetization anisotropy energy terms of bulk (volume), surface and interface regions, respectively. The right-hand term denotes the shape anisotropy energy of magnetic dipolar origin. The tetragonal distortion produces a uniaxial anisotropy that increases the value of the volume \( K_V \) anisotropy term [186] and thus overcoming the the negative value of \( K_S \) and shape anisotropy, the latter one being favorable to an in-plane magnetization orientation. As a result the magnetization orients from in-plane to out-of-plane direction.

In the figure A.4 the MOKE measurements for two different Ni film thicknesses are displayed. The MOKE hysteresis are measured in polar configuration (magnetization in the plane of incidence and normal to the surface) with a s-polarized laser beam. In the polar configuration one thus detects the out-of-plane component of the magnetization \( M_z \). We observe a square shape of the hysteresis for the 8 ML Ni film whereas for the 3 ML we notice a hysteresis with no coercivity. The former one indicates a measurement along easy axis whereas the latter one shows a shape that is typical for measurements performed along hard-axis of magnetization. From here one can conclude that for the 8 ML Ni film the magnetization orientation is out-of-plane while for the 3 ML thickness is having an in-plane direction. Higher Ni film thicknesses (up to 30 ML) have been investigated (not shown) showing larger coercivity but no significant change in the shape of the hysteresis loop \( i.e. \) square-like, indicating an out-of-plane magnetization direction.

TDS CO on Ni(100) thin films

The next step was to investigate the adsorption energetics of the CO molecules on the Ni thin films and to study which is the optimal film thickness in terms of adsorption sites occupation. No TDS measurement are reported in literature for CO adsorbed on epitaxial Ni films just on Ni bulk single crystals [193, 194]. For bulk crystals the CO TDS measurements reveal [193] three desorption sites at 450 K, 350 K and 280 K labelled as \( \beta_2 \), \( \beta_1 \) and \( \alpha \), respectively. In the same study the adsorption sites of the CO molecules have been identified employing Fourier transform infrared adsorption spectroscopy (FTIRA): at low temperatures (around 200 K) the bridge sites adsorption is favored while for temperatures above 300 K the terminal (on-top) sites are preferred. The high temperature desorption peak is considered [194] to arise from the on-top adsorbed CO while the other peaks are attributed to bridge and hollow sites. For our experiment is important to prepare samples with an ordered adsorbate structure in order to have a narrow signature in the vibrational spectra. For the case of CO on Ni(100) a c(2x2) structure is obtained upon dosing the CO saturation coverage followed by a short annealing to 330 K. The same procedure is used for the clean Cu(100) substrate in obtaining the c(2x2) structure, but for a short annealing to 140 K.
Figure A.5: TDS measurements of the CO adsorbed on a 15 ML Ni film at 100 K, performed at various CO coverages and a heating rate of 1.67 K/sec. The coverages are indicated by the exposure time in seconds at a background pressure of 2x10^{-10} mbar. In the inset the TDS spectrum measured on the Cu(100) substrate for the saturation coverage of CO.

In the figure A.5 the TDS spectra measured on a 15 ML Ni/Cu(100) film are displayed. The CO is dosed at 100 K by monitoring the background pressure and the time of dosing. We observe three peaks that can be attributed to the desorbed species from Ni: the 400 K, 290 K and the weak one at 210 K. The lower temperature desorption peaks are from the Cu sample as can be deduced by comparing them with the TDS data measured on the clean Cu(100) substrate (see the inset of the figure A.5). Comparing the measured TDS spectra on the Ni thin films to the corresponding data on the bulk Ni crystal [193, 194], we notice a shift to lower temperatures of the desorption peaks. On a speculative level one can ascribe this behavior to the presence of higher density of defects induced by strain release, that could reduce the adsorption energy of the CO on the Ni film. We have investigated also Ni films of higher thicknesses in order to check the influence of the increased roughness on the CO adsorption. The measured TDS spectra for various Ni film thicknesses are displayed in the figure A.6. The plotted spectra correspond to the CO saturation coverage of the on-top site i.e. the 400 K desorption peak in the figure A.5. By increasing the thickness from 15 ML to 30 ML we observe a gradual intensity increase of the TDS $\beta_1$ peak (presumably bridge sites) at the extent of $\beta_2$ peak (presumably on top sites), and for the 30 ML Ni film becomes dominant adsorption site. This is an interesting observation that requires further investigations.

Based on these measurements and literature data, that report the strain release starting...
A Sum-frequency generation from CO on the Ni/Cu(100) system

with the 11 ML Ni film thickness, we decided that the thickness around 10-11 ML to be the optimal one for the SFG measurements.

SFG theory and experiment

As detailed in chapter 3, sum-frequency generation is a second-order nonlinear optical process, in which, unlike SHG, the involved photons have different frequencies. Thus one can write the nonlinear optical polarization responsible for the SFG process as:

\[ P^{(2)}(\omega_{SFG}) = \chi^{(2)}_{SFG} E(\omega_1) E(\omega_2) \]  

(A.2)

with the \( \omega_{SFG} = \omega_1 + \omega_2 \) representing the outgoing sum-frequency photon as a sum of the two input photons frequencies. Similar to the SHG the SFG process is forbidden (within electric-dipole approximation) in the centrosymmetric media and thus allowed only in spatial regions with broken inversion symmetry e.g. surfaces, interfaces etc. For the investigation of the molecular vibrations the broadband infrared (IR) visible (VIS) sum-frequency generation technique is widely employed [195, 196], with a tunable IR beam through vibrational resonances of the adsorbed species and with the VIS beam used for up-converting the resulting SFG signal to visible range. Thus one can write the second-order susceptibility as the sum of a resonant and non-resonant term [196]:

\[ \chi^{(2)}_{SFG} = \chi^{(2)}_R + \chi^{(2)}_{NR} = \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q} + A_0 e^{i\phi} \]  

(A.3)
Figure A.7: The SFG spectra measured at T=100 K arising from the CO resonance adsorbed on Cu(100) and from the non-resonant background generated by the clean Cu(100) substrate.

where the $A_q$, $\omega_q$, $\omega_{IR}$, $\Gamma_q$ denote the amplitude and the resonant frequency of the $q$-th vibrational mode, the infrared laser frequency, the damping constant of the vibrational mode ($2\Gamma_q$ is the linewidth), respectively. $A_0$ is the amplitude of the non-resonant susceptibility and $\phi$ is its phase with respect to the resonant susceptibility. The amplitude of the vibrational mode is defined as: $A_q = (2\omega_q)^{-1} \frac{\partial \mu}{\partial q} \frac{\partial \alpha}{\partial q}$ where $\mu$ and $\alpha$ represent the dipole moment and the linear polarizability. This relation shows that a vibrational mode can be measured by SFG when is simultaneously infrared and Raman active.

As for the SHG case the susceptibility tensor has 27 components that can by reduced by applying the symmetry operations of the particular system. For the case of fcc Ni(100) the symmetry ($C_{4v}$) is identical to an isotropic surface and the resulting non-vanishing tensor components are:

\[
\chi_{xzx} = \chi_{gyz}; \quad \chi_{xxz} = \chi_{gyz}; \quad \chi_{zxx} = \chi_{zyy}; \quad \chi_{zzz}
\]

The presence of the magnetization lowers the symmetry of the system and the number of non-vanishing tensor components is increased, with the tensor components behaving even and odd with respect to magnetization reversal (see chapter 3). For the case of polar geometry, with $M \parallel z$ and the plane of incidence in the $(xz)$ plane, the SFG susceptibility
tensor takes the following form:

\[
\begin{pmatrix}
0 & 0 & \chi_{xx}^{\text{even}} & 0 & 0 & \chi_{yy}^{\text{odd}} & 0 & 0 & \chi_{zz}^{\text{even}} & 0 \\
0 & 0 & \chi_{xy}^{\text{odd}} & 0 & 0 & \chi_{yz}^{\text{even}} & 0 & 0 & \chi_{xz}^{\text{odd}} & 0 \\
\chi_{xz}^{\text{even}} & \chi_{xy}^{\text{odd}} & 0 & \chi_{yz}^{\text{odd}} & 0 & \chi_{zz}^{\text{even}} & 0 & 0 & \chi_{yz}^{\text{even}} & 0 \\
\chi_{yy}^{\text{even}} & \chi_{yz}^{\text{odd}} & 0 & \chi_{zz}^{\text{odd}} & 0 & \chi_{xx}^{\text{even}} & 0 & 0 & \chi_{xx}^{\text{odd}} & 0 \\
0 & 0 & \chi_{zz}^{\text{odd}} & 0 & 0 & \chi_{xx}^{\text{even}} & 0 & 0 & \chi_{yy}^{\text{odd}} & 0 \\
0 & 0 & \chi_{hh}^{\text{odd}} & 0 & 0 & \chi_{hh}^{\text{even}} & 0 & 0 & \chi_{hh}^{\text{odd}} & 0 \\
0 & 0 & \chi_{hh}^{\text{even}} & 0 & 0 & \chi_{hh}^{\text{odd}} & 0 & 0 & \chi_{hh}^{\text{even}} & 0
\end{pmatrix}
\]  \quad (A.4)

In order to have a magnetic induced SFG signal one has to look for the proper magneto-optical geometry and polarization combinations. Sine we are interested in the \(M_z\) component of the magnetization, we stay in the polar geometry and choose the polarization configuration with the highest number of even and odd tensor components. This experimental geometry is (P45°P) or (total45°P), where the letters represent the polarization of the SFG, VIS and the IR beam, respectively. The ”total” denotes the SFG signal detection without analyzing its output polarization.

Before measuring the SFG signal from the Ni film a test measurement has been performed on the clean Cu(100) substrate. The wavelength of the VIS and IR beams were 790 nm and 5 \(\mu m\), respectively. The result is plotted in the figure A.7, showing the resonant and the non-resonant SFG signals arising from the on top CO stretching vibration and the free electrons response, respectively. As expected, the CO resonance is energetically positioned at 2035 cm\(^{-1}\) and has a FWHM of 11 cm\(^{-1}\).
Only recently, the very first SFG measurements of CO adsorbed on the Ni thin films have started, showing a magnetic contrast of \( \approx 1\% \) in the MSFG signal arising from the CO stretching vibration. Such a measurement is displayed in figure A.8, where we observe the vibrational signature of the on top and bridge species at \( \approx 2000 \text{ cm}^{-1} \) and \( \approx 1894 \text{ cm}^{-1} \), respectively. These values are slightly lower than the reported (coverage dependent) data in literature for bulk Ni [193]; between 2010-2050 cm\(^{-1}\) for the on top and 1910-1970 cm\(^{-1}\) for the bridge sites. These measurements are in progress and upon improving the experimental parameters better results are expected. These results show the potential of this technique that can be applied to other magnetic systems. A very interesting fact will be to investigate in a time-resolved manner the spin-polarization of the CO molecules on Ni films employing the MSFG.
A Sum-frequency generation from CO on the Ni/Cu(100) system
B Fitting procedure

In the following, the procedure used for data analysis of the time-resolved linear reflectivity and second-harmonic generation transients is presented in detail. The main purpose of this procedure is to extract the oscillatory component of the transient signal in a correct manner out of the raw data. This could not be achieved by simply fitting the incoherent background with a pre-defined function like exponential or low order polynomial since the former one could not well reproduced the non-oscillatory background and the latter one introduces fitting artifacts at the limits of the fitted data range. Also one needs a criterion to judge if the separation of the oscillatory and non-oscillatory components is correct and eventually the data analysis is reliable. This procedure has been developed by Alexey Melnikov for a quantitative evaluation of the oscillatory component encountered in the time-resolved LR and SHG signals.

The expression of the oscillatory component of the signal has been defined in eq. 5.8, which describes an exponentially damped cosine function. For a better understanding of the data analysis procedure this expression is reproduce here once again:

\[ f(t) = A e^{-t/\tau} \cdot \cos[2\pi(\Omega \cdot t + c \cdot t^2 + \varphi)] \] (B.1)

with \( A, \tau, \Omega \) and \( \varphi \) being the amplitude, decay time, frequency and the phase, respectively.

The first step in the data analysis is smoothing the original data \( E_d \). This step is necessary especially for the data sets with a low signal to noise ratio obtained e.g. at high temperatures (see fig B.2). Smoothing is carried out by fitting the original data with a polynomial function in a certain time window i.e. each data point is replaced by the value of the polynomial fitted to the data. The order of the polynomial function \( i \) and the number of points \( j \) within the time window (pump-probe delay steps) are optimized by an autocorrelation criterion, that optimizes the non-randomness in the resulting smoothed data set. That means the noise is filtered while keeping the correct representation of the oscillatory part of the signal. The time window is shifted along the time axis of the original data set and a subsequent averaging over the window position is performed, that results in the smoothed curve \( E_s \). The noise level \( E_n \) is obtained straightforward making the difference between \( E_d \) and \( E_s \).

In the next step the incoherent part of the transient data is evaluated. For this, the expression B.1 is subtracted from the smoothed data by optimizing the parameters \( A, \tau, \Omega \) and \( \varphi \) in order to get a minimum of the mean square of the second derivative of the resulting expression: \( E_{\text{sub}} = E_s - A e^{-t/\tau} \cdot \cos[2\pi(\Omega \cdot t + c \cdot t^2 + \varphi)] \) with \( \langle \left( \frac{\partial^2 E_{\text{sub}}}{\partial t^2} \right) \rangle \rightarrow \text{min.} \)

Here we have to mention that we made an a-priori assumption regarding the oscillatory profile of the expression B.1, that reproduces the original oscillatory signal. The incoherent background \( E_b \) is obtained using the same autocorrelation criterion applied now to \( E_{\text{sub}} \).
Figure B.1: Exemplary data set showing the pump-induced variations in the even SH field measured at 90 K as well as the relevant quantities involved in the data analysis procedure. In the upper panel the $E_d$, $E_s$, $E_b$ denote the original data, the smoothed curve and the non-oscillatory background, respectively. In the lower panel $E_o$, $E_n$, $E_f$ describe the resulting oscillatory data, the noise and the fit according to B.1, respectively.
Figure B.2: The same as in figure B.1 but for a measurement performed at 300 K. Note the different time-evolution of the incoherent background and the higher level of noise.
but inverted using a low polynomial degree and a larger time-window \textit{i.e.} having the optimal window size condition fulfilled:

\[
\frac{\langle (E_b - E_{\text{sub}})^2 \rangle}{\langle (P - E_{\text{sub}})^2 \rangle} + \frac{\langle (\dot{E}_b - \dot{P})^2 \rangle}{\langle (\dot{E}_{\text{sub}} - \dot{P})^2 \rangle} \sqrt{\frac{\langle E_{\text{sub}}^2 \rangle}{\langle \dot{P}^2 \rangle}} \rightarrow \text{min} \tag{B.2}
\]

where \(P(t)\) is the polynomial fit to \(E_{\text{sub}}(t)\).

The final stage is to obtain the oscillatory component \(E_o\) of the data. \(E_o\) is retrieved by subtracting the incoherent background \(E_b\) from the smoothed original data \(E_s\). Now one can fit the oscillatory data \(E_o\) with the expression B.1 in order to get the values of the parameters \(A, \tau, \Omega\) and \(\varphi\).

In order to show how the fitting procedure works two exemplary data sets have been chosen, measured at low and elevated temperatures \textit{i.e.} a lower and higher level of noise, respectively. The displayed measurements are performed under identical conditions: incident laser beams parameters, film thickness etc.
Bibliography


[45] The two-temperature model code has been developed within our research group by Stefan Funk, Mischa Bonn and Daniel Denzler.


210


Bibliography


213


[125] Kai Starke. private communications.


[150] P.A. Loukakos et al.; to be published.


Publications


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Akademischer Lebenslauf

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