Ultrafast spin dynamics
in ferromagnetic metals

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1. INTRODUCTION

1.1 Introduction

In our contemporary society the applications of magnetism are ubiquitous. One of the first magnetic devices ever was the compass needle, allowing for a better navigation over long distances. Today, magnetism is used in many sensors and actuators. As a very visible example, most anti-theft systems in shops and libraries employ thin magnetic strips to mark the products. Their magnetization is changed on the counter to allow one to leave the shop ‘silently’. Modern automobiles contain many magnetic sensors to detect an open trunk, measure the speed of individual wheels for the anti-blocking system, control the motor ignition, etc. Magnetic materials can also be used to hold information. Well-known examples are refrigerator magnets, bank passes and computer hard disks. The latter devices are at this moment the key technology for non-volatile massive data storage in computer systems.

The persistent demand for higher capacity hard drives requires increasing data densities, while also faster read and write speeds are needed to keep data access times reasonable. These demands are fulfilled by rapid developments in the magnetic functional materials research. A convincing example is the discovery of multilayer structures that show a large dependence of their resistance on applied field, e.g. the Giant MagnetoResistance (GMR) effect. In Fig. 1.1(a) such an element is schematically drawn. It consists of two ferromagnetic (FM) layers that are separated by a thin non-magnetic layer (NM), for example a cobalt-copper-cobalt stack. The resistance of this element depends very sensitively on the relative orientation of the magnetization in the FM layers, indicated by arrows in the figure. Since the orientation can be changed by a magnetic field, for example from a magnetic bit on a hard disk, the element can be used as a very sensitive field sensor. Already 10 years after the discovery of the GMR effect in 1988 the first commercial hard disks appeared that employed GMR elements in their read heads, accelerating the already exponential growth of storage density.

GMR elements also play an important role in a new field in magnetism, the so-called spintronics. Spintronic devices are integrated circuits that combine ‘magnetic’ effects with traditional electronics. The name spintronics refers to the spin of electrons that is responsible for the magnetism of materials. Adding the extra magnetic dimension to conventional electronics allows for a completely new functionality. An example is the Magnetic Random Access Memory (MRAM), schematically depicted in Fig. 1.1(b). In this device arrays of GMR elements are combined with traditional semiconductor technology. Every individual element is used to store one bit of data in the form of the relative orientation of its magnetic layers. The data is read from the resistance of the element, and written by current pulses that create a local magnetic field. The latests MRAM devices use Tunnel Magneto Resistance (TMR) elements,
Fig. 1.1: (a) Magneto-resistance structure consisting of a FerroMagnetic/NonMagnetic/FerroMagnetic trilayer. In a Giant Magneto Resistance (GMR) element the non-magnetic layer is metallic, in a Tunnel Magneto Resistance (TMR) element it is a thin insulator. For a parallel alignment of the magnetization, indicated by arrows, the resistance is $\sim 10\%$ lower (GMR) than for the anti-parallel configuration. (b) Impression of a Magnetic Random Access Memory (MRAM). By measuring the resistance through two perpendicular lines the state of the TMR element at their intersection can be measured. Data can be written by sending a current through two perpendicular lines. The total field at their intersection is enough to switch one of the FM layers.

discussed in the caption of Fig. 1.1(a). The advantages of MRAM lie in the non-volatile nature of the stored data, its low power consumption and high speed.

The speed of magnetic devices is eventually limited by the switching characteristics of the magnetic layers. Laboratory demonstrations of hard-disk systems at the end of 2002 featured data densities of 100 giga-bit/inch$^2$ and transfer rates in the order of 0.25 giga-bit/s. With transfer rates approaching the GHz-regime, an intimate knowledge of the magnetization dynamics is needed as precessional phenomena will start to dominate the switching process of both the storage medium and read head.

In this thesis the magnetization dynamics in ferromagnets is studied. Both precessional dynamics, which occur on a typical time scale of hundreds of picoseconds ($10^{-12}$ s), as well as the ultimate time scale at which the magnetization can be influenced by laser heating is investigated. The latter experiments, which probe the dynamics with a sub-picosecond resolution, yield information on the interaction of the electron spins with their environment. Such information is for example needed for a proper understanding of the GMR effect.

To study magnetization dynamics on ultrafast time scales we employ an optical pump-probe scheme that is outlined in the next section. Then the processes occurring upon laser heating of a ferromagnetic material are introduced, followed by a description of the contents of this thesis.

1.2 Optical pump-probe schemes

To gain access to dynamics on ultrafast time scales, i.e. below one picosecond, only a limited number of techniques is available. In this work optical pump-probe techniques are used to study the magnetization dynamics upon laser heating. In a pump-probe experiment the system under study is suddenly brought out of equilibrium by a pump pulse, and after a certain time delay the state of the (spin) system is measured by a
probe pulse.

The basic optical pump-probe scheme is shown in Fig. 1.2. A pulsed laser system provides laser pulses with a sub-picosecond duration. Using a beam splitter they are divided in intense pump and weak probe pulses. The time at which a pump or probe pulse arrives at the sample depends on the distance it has to travel. Using a delay line the optical path of the probe beam can be precisely varied, allowing for an accurate control of the time difference $\Delta t$ between pump and probe. The pump pulse now locally excites the sample and after a time delay $\Delta t$ the probe pulse monitors the result.

It must be noted that this method does not yield the full time-response upon excitation by one pump pulse. Instead, it is a ‘stroboscopic’ method in the sense that it yields for a certain pump-probe delay an average response. Scanning the delay then provides a full view on the evolution of the magnetic state after excitation. A detailed description of the experimental setup and the optical detection of the magnetization will be given in Chap. 2.

1.3 Optically induced magnetization dynamics

In 1996 Beaurepaire et al. were the first to study the magnetization dynamics on a sub-picosecond time scale using an optical pump-probe technique. Their key result, published in Ref. [5], is reproduced in Fig. 1.3. The figure shows the remanent magnetization of a nickel film, i.e. its spontaneous magnetization in absence of an external field, as a function of pump-probe delay $\Delta t$. At $\Delta t = 0$ the magnetization drops sharply, reaching its minimum value already 2 ps after excitation.

To describe the processes following laser excitation one can conceptually separate the material in an electron, spin and lattice system, as is schematically depicted in Fig. 1.4. Upon absorption of a laser pulse electrons are excited to high energy
states, increasing the energy of the electron system and thereby its temperature $T_e$. Interactions between the electron, spin and lattice system will subsequently distribute the additional energy, raising the temperature of the lattice system $T_l$ and the spin system $T_s$ until in equilibrium $T_e = T_s = T_l$. In this three-temperature model the spin temperature $T_s$ is defined by the equilibrium $M(T)$ relation, i.e. $M[T_s(\Delta t)]$ represents the transient magnetization at delay time $\Delta t$. For $T_s$ above the Curie temperature, no net magnetization is left. In optical pump-probe experiments the spin dynamics can be derived from the magneto-optic Kerr effect and the electron dynamics from transient reflectivity measurements.

Up to 1996 it was commonly believed that upon heating the magnetization was reduced by spin-lattice interactions. Theoretical models describing the spin-lattice relaxation and earlier, more indirect experiments were in fair agreement, pointing at a spin relaxation time of tens of picoseconds. Therefore, the ultrafast demagnetization observed in Fig. 1.3 came as a surprise, especially as it was found that the spin temperature increased more rapidly than the lattice temperature. The latter observations pointed at the electron-spin interaction, and not the spin-lattice interaction, as the main route for loss of magnetization. These issues are investigated in detail in Chap. 4.

During this work we found that sub-picosecond laser heating does not only change the magnitude of the magnetization, but also its direction. This way a precession of the magnetization can be started that lasts for hundreds of picoseconds. By measuring the frequency and decay of the precession magnetic properties as anisotropy and damping can be determined. The precessional dynamics is addressed in Chap. 5.
1.4 This thesis

In this thesis the magnetization dynamics of ferromagnets is investigated using optical pump-probe techniques. The optical nature of the experiment requires that the magnetization is measured using laser light. This is possible by using the magneto-optical Kerr effect: when light is reflected from a magnetic material its polarization state will show a magnetization-dependent change. In Chap. 2 the relation between polarization and magnetism is discussed and an experimental setup to measure this magneto-optical effect in a time-resolved manner is presented.

For both the demagnetization experiments and the precessional experiments the same samples are used. The structural description and magnetic characterization of the samples is therefore given separately in Chap. 3. In this chapter also results of optical absorption and thermal diffusion calculations are presented. The calculations give information on the amount of optical heating and the dynamics of the heat transport in the different layers.

Chapter 4 explores the ultrafast demagnetization dynamics of ferromagnetic materials upon laser heating. Important issues here are the identification of the mechanisms that are important for the loss of magnetization and the interpretation of the magneto-optical data, as it is found that optical techniques may not be able to probe the magnetization directly after laser excitation.

In Chap. 5 a novel application of the laser-heating scheme is investigated: the excitation of a coherent precession of the magnetization. It is shown that the all-optical technique can locally launch a spin precession and even spin waves in thin films. This allows one to optically measure the anisotropy, damping parameter and spin wave stiffness of magnetic materials. The spatial resolution and the time-domain character make this an interesting technique for the characterization of microstructured...
magnetic devices, as for example MRAMs.
2. MAGNETO-OPTICAL PUMP-PROBE TECHNIQUES

2.1 Introduction

In this work the response of the magnetization upon sudden laser heating is studied on a sub-picosecond time scale. To gain access to this ultrafast dynamics a magneto-optical pump-probe technique is applied, employing an intense laser pulse to excite the material and a weak probe pulse to measure its response.

To optically detect the magnetization of a material the polarization of the reflected probe is measured. In the first section of this chapter the relationship between magnetism and the polarization of light, i.e. the magneto-optical Kerr effect, is explained. Next, the experimental method to measure the generally small polarization changes is introduced. Since we are interested in the ultrafast dynamics this method has to be used in a pump-probe scheme. In Sect. 2.4 the time-resolved magneto-optical Kerr technique is explained, analyzing the different modulation schemes used to sensitively measure the pump-induced changes of the magnetization. In the final section issues concerning measurements with short laser pulses and Gaussian spot profiles are discussed.

2.2 Magneto-optic Kerr effect

The Magneto-Optic Kerr Effect (MOKE) is the optical phenomenon by which the polarization of light changes in a magnetization-dependent way when reflected from a magnetic material. By measuring the polarization of a reflected laser beam one can therefore obtain information on the magnetic state of a material. In this section the relation between polarization and magnetism is formalized and its microscopic origin is discussed.

2.2.1 Phenomenological description

The optical response of materials that are isotropic or have a high enough symmetry (e.g. cubic) can be described by a single wavelength dependent parameter, the dielectric constant \( \varepsilon \). The dielectric constant links the displacement \( \vec{D} \) to the electric field \( \vec{E} \) according to \( \vec{D} = \varepsilon \vec{E} \). However, if the symmetry is lowered this simple description fails and a tensor formulation should be used.

In a ferromagnetic material the symmetry is broken due to its finite magnetization \( \vec{M} \). For a cubic, ferromagnetic material the dielectric tensor \( \varepsilon \) can be written as

\[
\varepsilon = \begin{bmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\
-\varepsilon_{xy} & \varepsilon_{xx} & \varepsilon_{yx} \\
-\varepsilon_{xz} & -\varepsilon_{yx} & \varepsilon_{xx}
\end{bmatrix},
\] (2.1)
where the limited number of free variables follows from symmetry considerations. Additionally, the Onsager relation demands \( \varepsilon_{nn}(\vec{M}) = \varepsilon_{nn}(-\vec{M}) \) and \( \varepsilon_{nm}(\vec{M}) = -\varepsilon_{nm}(-\vec{M}) \), i.e. the diagonal elements are even and the off-diagonal elements are odd in the magnetization. Considering only effects to first order in \( \vec{M} \), the diagonal elements are independent of the magnetization. In the absence of a magnetization the off-diagonal elements are zero.

The effect of the off-diagonal elements on the optical properties of the material is made most clear by considering the case where both the incident light and magnetization are parallel to the \( z \)-axis. For this field configuration Eq. 2.1 simplifies to

\[
\bar{\varepsilon} = \begin{bmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & 0 \\
-\varepsilon_{xy} & \varepsilon_{xx} & 0 \\
0 & 0 & \varepsilon_{xx}
\end{bmatrix},
\]

(2.2)

Due to off-diagonal elements \( \varepsilon_{xy} \) an electric field along \( \hat{x} \) will induce a finite polarization in the \( \hat{y} \) direction. Since \( \varepsilon_{xy} \) depends on \( M \) this will cause a magnetization-dependent polarization change. This can readily be seen by using cylindrical coordinates, defined by

\[
\hat{e}_- = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{y}),
\]

\[
\hat{e}_+ = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{y}),
\]

\[
\hat{e}_z = \hat{z}.
\]

(2.3)

In this new coordinate system \( \hat{e}_- \) describes a left-handed and \( \hat{e}_+ \) a right-handed circularly polarized electric field. Transforming Eq. 2.2 to cylindrical coordinates one finds

\[
\bar{\varepsilon}' = \begin{bmatrix}
\varepsilon_{xx} - i\varepsilon_{xy} & 0 & 0 \\
0 & \varepsilon_{xx} + i\varepsilon_{xy} & 0 \\
0 & 0 & \varepsilon_{xx}
\end{bmatrix},
\]

(2.4)

i.e. in this new coordinate system the dielectric tensor is diagonalized. This allows us to define (different) dielectric constants for the two circular polarization states:

\[
\varepsilon_\pm = \varepsilon_{xx} \pm i\varepsilon_{xy}.
\]

(2.5)

Thus, by recording the difference between the reflection or transmission of left- and right-handed polarized light one is sensitive to the magnetization of a material through the magnetization-dependence of \( \varepsilon_{xy} \).

Linearly polarized light is a combination of left- and right-handed circularly polarized light, e.g. \( \hat{x} = 1/\sqrt{2}(\hat{e}_+ + \hat{e}_-) \). Upon reflection from a magnetic material the polarization of originally linearly polarized light will change due to the different reflection of its circular components. In the present case of perpendicular incidence, the polarization state of the reflected light is given by

\[
\psi' = \frac{\varepsilon_{xy}}{\sqrt{\varepsilon_{xx}(\varepsilon_{xx} - 1)}},
\]

(2.6)
with $\psi = \psi' + i\psi''$ the complex rotation of the polarization vector. Note that $\varepsilon_{xx}$ and $\varepsilon_{xy}$ are, in general, complex. In this notation $\psi'$ is the rotation of the polarization, while $\psi''$ represents its ellipticity.

Equation 2.6 is only valid when the magnetization and the incident light are parallel to the $z$ axis. When $\vec{M}$ is rotated in-plane $\varepsilon_{xy}$ vanishes and $xz$ an $yz$ elements appear in the dielectric tensor. It can be shown that in this configuration no polarization change occurs. In fact, at perpendicular incidence $\psi$ can be written as

$$\psi = F \cdot M_z,$$

(2.7)

with $F$ a complex constant. A measuring of the polarization at perpendicular incidence thus yields a value proportional to the out-of-plane component of the magnetization, $M_z$. For an arbitrary angle of incidence and orientation of $\vec{M}$, $\psi$ is given by [83]

$$\psi = \sum_{i=x}^z F_i \cdot M_i,$$

(2.8)

with $F_i$ complex constants. In the derivation of Eq. 2.8 the generally small transverse Kerr effect is neglected.

### 2.2.2 Microscopic origin

So far the treatment of the MO-effect was only macroscopic and based on symmetry arguments. Its microscopic origin lies in the spin-orbit (SO) coupling and the optical selection rules. For circularly polarized light, the dipole selection rules only allow transitions with $\Delta l = \pm 1$ and $\Delta m_l = \pm 1$. The SO coupling induces a correlation between the orbital momentum $\vec{L}$ and the spin momentum $\vec{S}$, which allows one to probe the spin system by the optical selection rules on orbital momentum.

The transitions that are probed using optical techniques depend on the photon energy $\hbar \omega$ and the occupation of states. The dielectric tensor is therefore a function of $\omega$. In a single particle formulation the elements $\varepsilon_{\alpha\beta}$ of the dielectric tensor are given by [9]

$$\varepsilon_{\alpha\beta} = \delta_{\alpha\beta} + \frac{4\pi e^2}{\omega m^2 \hbar V} \sum_{nn'} \frac{f(E_n) - f(E_{n'})}{\omega_{nn'}} \frac{\Pi^\alpha_{nn'} \Pi^\beta_{n'n}}{\omega - \omega_{nn'} + i/\tau}.$$

(2.9)

The electron charge and mass are represented by $e$ and $m$, $E_n$ is the energy of state $n$, $\hbar \omega_{nn'} = E_n - E_{n'}$, $f(E)$ is the Fermi-Dirac function, $\Pi^\alpha_{nn'} = <n|p_\alpha|n'>$ the matrix element of the momentum operator and $\tau$ the lifetime broadening of the transition. The matrix elements $\Pi^\alpha_{nn'}$ determine the transition strengths, while the Fermi-Dirac function accounts for the occupation of states. In a non-equilibrium situation, for example present shortly after optical excitation by an intense laser pulse, one may expect deviating magneto-optical signals due to changes in the occupation of states.

Figure 2.1 shows calculated spectra by Oppeneer et al. using Eq. 2.9 and ab initio bandstructure calculations. In the figure the solid and dashed-dotted lines represent calculations using different values for $\tau$, the other curves represent a collection of experimental data. There is a good qualitative correspondence, but the calculated position of the peaks is incorrect. This is related to the fact that the method used (local spin density approximation) has problems predicting the correct exchange splitting and width of the d-bands.
Fig. 2.1: (a) Real and (b) imaginary part of the off-diagonal optical conductivity $\sigma_{xy}(\omega)$. $\epsilon_{xy}$ is directly related to $\sigma_{xy}$ by $\epsilon_{xy} = \frac{\omega \sigma_{xy}(\omega)}{(4\pi i)}$, i.e. the real part of $\sigma_{xy}$ is proportional to the imaginary part of $\epsilon_{xy}$. The solid and dashed-dotted curve are calculated spectra using a different broadening $\tau$, the other curves represent a collection of experimental data. Reproduced from Ref. [9].

2.2.3 Second harmonic generation

The MO-Kerr effect described above is also known as linear MOKE. Alternatively, one can use non-linear MO techniques as magnetization-induced Second Harmonic Generation (SHG) to measure the magnetization of a material. In a SHG experiment a probe pulse with photon energy $h\nu$ is focused on the sample. Non-linear processes, described by a second-order susceptibility tensor, will generate a small amount of light at the double photon energy $2h\nu$. Using appropriate filters and a sensitive detector, the second-harmonic light can be detected. The much smaller intensity of the SHG light is compensated by very large rotation angles, making it an experimentally feasible method [61]. For cubic symmetric materials SHG only takes place at interfaces. The technique therefore is explicitly sensitive to the magnetization dynamics at or near interfaces, which may be different from the bulk behavior. The high electric fields needed to generate second-harmonic light are easily obtained with the ultra-short laser pulses that are used in time-resolved pump-probe experiments anyway.

2.3 Detection of the Kerr effect

In the previous section it was shown that by detecting the polarization $\psi$ of light reflected from a magnetic material one is sensitive to its magnetization. The magnetization-induced changes in polarization are however small for many magnetic materials, e.g. for Ni in the order of tens of millidegrees, and a very sensitive measurement technique is therefore needed. In this work a detection scheme employing a Photo-Elastic Modulator (PEM) is used, which is schematically depicted in Fig. 2.2. The combination of PEM and polarizers will be shown to result in a detector signal that contains information on $\psi'$ and $\psi''$ at harmonics of the PEM modulation frequency. In the next
section the function of the PEM is described. Then the detection scheme is analyzed within the Jones formalism [58], deriving a relation between the detector signal and the sample-induced polarization change.

### 2.3.1 Photo-elastic modulator

A PEM consists of a transparant material that is periodically compressed in one direction by a piezo-electric crystal. The uniaxial compression changes the optical path for only one polarization component and therefore induces a periodically changing phase difference or retardation. In the Jones-formalism a PEM can be represented by a matrix,

\[
M_{\text{PEM}} = \begin{bmatrix}
1 & 0 \\
0 & e^{iA \cos(\Omega t)} 
\end{bmatrix},
\]  

(2.10)

with \( \Omega \) the modulation frequency and \( A \) the maximum retardation. With \( A \) set to \( \frac{1}{2} \pi \) incident light that is linearly polarized under 45\(^\circ\), i.e. represented by a Jones vector

\[
\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix},
\]

will be modulated between a left- and right-handed circular polarization,

\[
\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \end{pmatrix}.
\]

### 2.3.2 PEM in the 0\(^\circ\) configuration

Using the setup depicted in Fig. 2.2 the ellipticity and rotation induced by a sample can sensitively be measured by detecting the harmonics of the PEM modulation in the detector signal. The Jones-matrix of a general sample is given by

\[
M_{\text{sample}} = \begin{bmatrix}
 r_s & r_{ps} \\
r_{sp} & r_p 
\end{bmatrix},
\]  

(2.11)

with \( r_s \) and \( r_p \) the complex reflection coefficients for s- and p-polarized light. The off-diagonal elements, mixing the s- and p-polarization components, are a result of the magnetic character of the sample and have a value proportional to \( \varepsilon_{xy} \) (assumed \( \ll 1 \)). An incident, s-polarized beam will undergo a complex rotation \( \psi_s = r_{sp}/r_s \) after reflection of the sample, with the real part \( \psi'_s \) the rotation and the imaginary
part ψ′′ the ellipticity of the reflected beam. A similar expression can be written down for a p-polarized beam.

Applying the Jones formalism to the configuration in Fig. 2.2, the detector signal \( V \) is found to be

\[
V = V_{\text{static}} + V_{1f} + V_{2f} \tag{2.12}
\]

\[
V_{\text{static}} = V_0 \left[ 1 + 2J_0(\psi'' + \psi''') \right] \approx V_0 \tag{2.13}
\]

\[
V_{1f} = V_0 4 J_1(\psi'/\Omega) \cos(\Omega t) \tag{2.14}
\]

\[
V_{2f} = V_0 4 J_2(\psi'/\Omega) \cos(2\Omega t) \tag{2.15}
\]

with \( J_n \) the n-th order Bessel function and \( V_0 \) a constant depending on the detector sensitivity, laser power and sample reflectivity (\(|s|^2 \) or \(|p|^2\)). The cosine terms result from an expansion of \( \sin[A \cos(\Omega t)] \), neglecting terms higher than second order in \( \Omega \).

\( V_{\text{static}} \) is nearly independent of \( \psi \) since \( \psi' \) and \( \psi'' \) are much smaller than one. The DC detector signal is therefore a good measure of the laser power. The modulated part of the intensity consists of a term at the modulation frequency of the PEM, \( V_{1f} \), representing the induced ellipticity, and a term at the double frequency, \( V_{2f} \), which is proportional to the induced rotation. Using a lock-in scheme to measure the detector-signal at the PEM modulation frequency (\( f \)) will give a value proportional to the ellipticity \( \psi' \) of the reflected beam, while a measurement at the double modulation frequency (\( 2f \)) yields the rotation \( \psi'' \).

A great advantage of this method is the absence of a polarization-independent background on the signals at \( 1f \) and \( 2f \), i.e. they are purely proportional to the ellipticity and rotation. In practical situations small misalignments generally still cause a background on the \( 1f \) or \( 2f \) signal. It is however possible to tune the rotation- or ellipticity-signal to zero by slightly changing the orientation of P2. It must be noted that in the case of ellipticity the ‘zero-tuning’ relies on the presence of a phase difference between \( r_s \) and \( r_p \), and thus might fail. This is especially true for perpendicular incidence, where \( s \) and \( p \) no longer have a meaning.

### 2.3.3 PEM in the 45° configuration

In the configuration discussed above the analyzer was oriented either parallel to the \( s \)- or p-direction to obtain a background-free measurement. A different configuration of interest is one in which the PEM and the polarizer are rotated over 45°. In a similar way it can be shown that in this configuration the signal at \( 1f \) is proportional to the ellipticity for analyzer orientations of 0° and 90°.

However, in absence of off-diagonal contributions the \( 2f \) signal is only zero at an analyzer orientation of \( \alpha_{\text{anal}} = \pm \arccos \left( \frac{(\rho^2 - 1)}{\rho^2 + 1} \right) \), with \( \rho = |r_s/r_p| \). In this particular case the ‘zero-background’ orientation therefore strongly depends on the values of the (diagonal) \( s \)- and \( p \)-reflection coefficients. This can be made more clear by explicitly considering the effect of changes in \( r_s \) and \( r_p \), i.e. \( \Delta r_s \) and \( \Delta r_p \), on the \( 2f \) signal:

\[
I_{2f} = \left. \frac{1}{\rho^2 + 1} \right| \Re \left[ \rho^2 r_p \frac{\Delta r_p}{r_p} - r_s \frac{\Delta r_s}{r_s} + \rho(r_s + r_p)(r_s + r_p) \frac{r_{sp}}{r_s + r_p} \right] \tag{2.17}
\]

The dependence of \( \alpha_{\text{anal}} \) on \( r_s \) and \( r_p \) is expressed by the first two terms, the magnetic contribution to \( I_{2f} \) is represented by the last term. We will use the 45° configuration.
for time-resolved reflectivity measurements. In these measurements the changes in $r_s$ and $r_p$ are induced by excitation with a pump pulse and are measured by monitoring the $2f$ signal.

### 2.4 Time-resolved MOKE

In this work the magnetic response of a ferromagnetic material upon heating by a sub-picosecond laser pulse is studied. To gain access to the magnetization dynamics on these extremely short time scales an all-optical pump-probe scheme is used, employing ultrashort laser pulses to excite the sample and to probe the magnetization by using the magneto-optic Kerr effect. This section describes the experimental setup, tagged time-resolved MOKE or TRMOKE. Also various modulation schemes that are used to sensitively detect magnetization changes are discussed.

#### 2.4.1 TRMOKE setup

The Time Resolved MOKE (TRMOKE) setup used to study the magnetization dynamics is schematically depicted in Fig. 2.3. A $\sim 60$ fs long laser pulse from a pulsed laser source is split in an intense pump pulse and a weak probe pulse by a beam-splitter. The pump pulse, used to excite the magnetic material, is directly focused on the sample. The probe pulse is first send through a delay-line that creates a controllable delay $\Delta t$ between the pump and probe. The delay line consists of a retroreflector mounted on a translation stage, allowing for a precise variation of the optical path.

The magnetization is measured by analyzing the polarization state of the reflected probe using the configuration of Fig. 2.2. In the TRMOKE experiments the magne-
Fig. 2.4: The double-modulation technique. Lock-in 1 (see Fig. 2.3) selects the high-frequency PEM-modulation of the probe-beam, lock-in 2 is placed in series and specifically detects the pump-induced effects by locking to a chopper placed in the pump-beam (at 60 Hz).

The quantity of interest in a pump-probe demagnetization experiment is the pump-induced reduction of the magnetization, reflected by $\Delta \psi$. Using the PEM-modulation we obtain $\psi'(\Delta t)$ and $\psi''(\Delta t)$. In principle one could directly measure these quantities as a function of delay time. However, for increased sensitivity a double modulation scheme is used.

Apart from the modulation of the probe beam by the PEM, also the pump beam is modulated by a chopper. As depicted in Fig. 2.4, the detector signal at a fixed time delay consists of a fast oscillation due to the PEM, which is operated at $\Omega = 50$ KHz. The amplitude of this oscillation shows a slow modulation at the frequency of the chopper ($\sim 60$ Hz). The latter modulation is caused by the pump-induced change of the Kerr-effect and its amplitude directly yields $\Delta \psi$.

Analyzing the detector signal with a lock-in amplifier that is referenced by the PEM, the amplitude of the fast oscillation is filtered out (labeled 'lock-in 1' in Fig. 2.4), obtaining either $\psi'(\Delta t)$ or $\psi''(\Delta t)$. Using a second lock-in, referenced by the chopper and connected to the output of the first lock-in, the amplitude of the pump-induced modulation $\Delta \psi(\Delta t)$ is filtered out (lock-in 2). The output of the second lock-in is thus a direct measure of the effect of the pump pulse on the Kerr-effect at a certain time delay.

The advantage of this method is the greatly increased sensitivity, primarily due to the cancellation of drift. A direct measurement of the Kerr-effect always suffers from a certain amount of drift caused by instabilities in the optical components that affect the small angular differences (several tens of millidegrees) measured. Also systematic, delay time dependent offsets on the Kerr-signal that are introduced by
Fig. 2.5: (a) Time-resolved MOKE measurement using the pump-modulation scheme. The pump-induced change of the Kerr-ellipticity is shown for opposite magnetization directions. (b) TRMOKE using the magnetization-modulation scheme. $\psi_{\text{mag}}''$ represents the magnetic contrast in the Kerr-ellipticity.

small misalignments of the delay line are completely cancelled.

Figure 2.5(a) shows results of a typical TRMOKE measurement on a polycrystalline Ni film using the above modulation scheme. $\Delta\psi(\Delta t)$ is plotted for two opposite magnetization orientations, i.e. $M^+ = -M^-$. Since $\varepsilon_{xy}$ is odd in the magnetization this will result in a sign change of $\Delta\psi$, i.e. $\Delta\psi|_{M^+} = -\Delta\psi|_{M^-}$. In some experiments also non-magnetic contributions to $\Delta\psi$ are observed, for example resulting from a pump-induced change in reflectivity. The magnetic contribution to $\Delta\psi$ can however be filtered out by using the difference of two measurements taken with opposite magnetization $\Delta\psi|_{M^+} - \Delta\psi|_{M^-}$. In a similar fashion the non-magnetic contribution follows from $\Delta\psi|_{M^+} + \Delta\psi|_{M^-}$.

An alternative double modulation scheme uses a modulation of the magnetic field instead of the pump intensity. In this scheme an alternating field is applied to the sample, continuously switching the direction of the magnetization. With the second lock-in referenced by the field modulation it is easily shown that its output is proportional to the magnetic contrast in the Kerr-signal $\Delta\psi(\Delta t)|_{M^+} - \psi(\Delta t)|_{M^-}$. Since the magnetic contrast is the difference between the Kerr signals at opposite magnetization drift effects on the absolute Kerr-signal are efficiently canceled. Figure 2.5(b) shows a typical measurement using the magnetization-modulation technique, plotting the magnetic contrast in $\psi''$ as a function of $\Delta t$.

With the magnetization modulation technique the magnetic contrast in the Kerr signal is directly measured as a function of delay time. If the magnetization-independent component is not of interest, magnetization-modulation has an advantage in speed (only one measurement is required) and in the high accuracy in quantitatively determining the relative magnetic contrast. However, in the current set-up this tech-
nique can only be used on soft-magnetic materials due to limitations to the amplitude of the field modulation. Also, the switching time of the magnetization should be sufficiently short compared to the period of the field modulation.

2.4.3 Signal analysis

During a measurement the DC-signal from the detector \( (V_{\text{static}}) \), the output of lock-in 1 \( (V_{nf}) \) and the output of lock-in 2 \( (\Delta V_{nf}) \) are recorded as a function of delay-line position (see Fig. 2.3). Using Eqs. 2.13, 2.14 and 2.15 the Kerr rotation and its pump-induced change can be calculated for the pump-modulation setup,

\[
\psi'' = \frac{1}{\sqrt{2}} J_1(A) V_{lf}/V_{\text{static}},
\]

\[
\Delta \psi'' = \frac{\sqrt{2} C}{J_1(A)} \Delta V_{lf}/V_{\text{static}}.
\]

The Kerr rotation \( \psi' \) is obtained in a similar way, only using the 2f signal and \( J_2(A) \). Since the lock-in outputs RMS values the sinusoidal \( V_{nf} \) signals have to be corrected by a factor \( \sqrt{2} \) to obtain the amplitude. The chopper introduces a square-wave modulation, so the \( \Delta V_{nf} \) signal is corrected by an additional factor of 2. To output the amplitude of a periodic signal, a lock-in averages over a certain time. Due to the averaging by the first lock-in, the square wave signal becomes somewhat rounded. To correct for this, an extra factor \( C \geq 1 \) is introduced that is experimentally determined. The averaging effect is minimized by fixing the pump chopping frequency at 60 Hz and using an (averaging) time-constant of 1 ms on the first lock-in.

Using the magnetization modulation technique, the signal of the second lock-in is simply proportional to the magnetic contrast in either the rotation or ellipticity signal, i.e.

\[
(\psi_{M^+} - \psi_{M^-}) \propto \Delta V_{lf}/V_{\text{static}}.
\]

In this work mostly the magnetic part of the pump-induced effect is plotted. To shorten the notation we use \( \Delta \psi \) to represent the magnetic contrast in the pump-induced effect, i.e. \( \Delta \psi = \Delta \psi_{M^+} - \Delta \psi_{M^-} \). Similarly, \( \psi \) represents the change in the total Kerr signal upon magnetization reversal as measured at a negative pump-probe delay, \( \psi = \psi_{M^+}(\Delta t) - \psi_{M^-}(\Delta t) \) for \( \Delta t < 0 \). In this notation \( \Delta \psi/\psi \) represents the relative pump-induced change in magneto-optic contrast.

2.5 Ultrashort pulse experiments

For the pump-probe experiments described in this thesis we have used \( \sim 60 \) fs laser pulses generated by a pulsed, titanium-sapphire laser. The duration of the pulses at the sample position determines the temporal resolution of the pump-probe technique. For the interpretation of the experimental transients an accurate measure of the pump-probe coincidence, i.e. \( \Delta t = 0 \), is needed.

In this section issues concerning the use of laser pulses in pump-probe experiments will be addressed. First a short background on ultrashort laser pulses is given, in particular addressing the effect of chirp on the duration of the pulses. Then the technique used to determine \( \Delta t = 0 \) is discussed, followed by an analysis of the effect of the pump and probe spotsize on the observed Kerr effect.
2.5.1 Ultrashort laser pulses

Ultrashort laser pulses show some special characteristics that are quite different from continuous wave lasers. Here the duration-bandwidth product, chirp, and group velocity dispersion compensation are discussed.

Duration-bandwidth product

Continuous laser beams generally have a very well defined frequency. The frequency of ultrashort pulses, however, is less well defined due to their extreme short duration. This effect follows directly from the properties of the Fourier transformation.

The relation between pulse duration and spectral width can be described by the duration-bandwidth product,

\[ \Delta \omega_p \tau_p \geq 2\pi C_B, \]  

(2.21)

with \( \Delta \omega_p \) the full width-half maximum (FWHM) bandwidth of the pulse, \( \tau_p \) its (FWHM) duration in time and \( C_B \) a pulse-shape dependent constant that is 0.44 for Gaussian shaped pulses. Eq. 2.21 puts a limit to the spectroscopy that can be done using time-resolved pump-probe techniques. Inversely, using a spectrometer to decrease the spectral width will increase the pulse duration.

Chirp

The greater-than-or-equal sign in Eq. 2.21 is related to another property of ultrashort pulses: chirp. The electric field of a linearly chirped pulse can be written as \[ E(t) = E_0 e^{-t^2/(\tau^2[1+b^2])} \cos(\omega - bt/\tau^2)t, \]

(2.22)

with \( b \) the chirp parameter, \( \omega \) the center frequency and \( \tau \) the unchirped Gaussian width. The chirp on the pulse causes a changing instantaneous frequency with time, i.e. \( \omega_{\text{inst.}} = \omega - bt/\tau^2 \). This effect is shown in Fig. 2.6 where the electric field of an unchirped pulse, panel (a), and a pulse with negative chirp, panel (b), are plotted.

Equation 2.22 also gives a relation between the length of the pulse, \( \tau_p = \tau \sqrt{1+b^2} \), and the chirp parameter \( b \). This relation is not general, but describes to good approximation the effect on a pulse when traveling through a medium which shows a linear Group Velocity Dispersion (GVD). In that case \( b = L/L_d \), with \( L \) the length of travel and \( L_d \) a material dependent characteristic length. Travelling through a medium showing GVD therefore increases the length of the laser pulses, something that is experimentally undesirable.

Upon Fourier transforming Eq. 2.22 it is found that the bandwidth-duration product is independent of \( b \). With increasing \( b \) the duration of the pulse does however increases, hence the greater-than-or-equal sign in Eq. 2.21. Only for so-called bandwidth limited pulses the equal sign is valid.

GVD compensation

As mentioned earlier, chirp is added to ultrashort laser pulses by the GVD of the materials with which the laser pulses interact. A finite GVD creates a difference in group velocity between different wavelengths. Since an ultrashort pulse consists of a broad spectrum of wavelengths, this will cause a broadening of the pulse, i.e. for a positive GVD the ‘red’ light will be faster than the ‘blue’ light. Since lenses, polarizers
and other materials in the setup contribute a positive chirp, the pulse at the sample position will be much longer than right after leaving the laser.

One can compensate for this effect by adding negative chirp to the laser pulse with a GVD compensation line. The amount of negative chirp should be tuned such as to minimize the chirp, and thus the pulse length, at the sample position. To this effect a prism GVD compensation line was built, as depicted in Fig. 2.7. Details of compensating GVD with prisms are described in Ref. [14]. The distance between the two prisms determines the maximum negative GVD added. Fine-tuning of the chirp is possible using the micrometer screw on one of the prisms. By moving a bigger portion of the prism into the beam more positive chirp is added, allowing for a precise control of chirp. Since the prisms are used close to the Brewster angle, the energy losses are minimized.

2.5.2 Determination of pump-probe coincidence

For the interpretation of transient MO and reflectivity data it is important to know the exact point of pump-probe coincidence, i.e. zero time delay, and their crosscorrelation profile. To this effect we employ an interferometric technique. If a fraction of the pump beam is scattered into the detector, the pump and probe electric fields will interfere and cause a delay time dependent intensity oscillation,

\[
I_{\text{det}}(\Delta t) = \int_{-\infty}^{\infty} \left[ E_{\text{probe}}(t) \cos(\omega t) + E_{\text{pump}}(t + \Delta t) \cos(\omega (t + \Delta t)) \right]^2 dt \quad (2.23)
\]

\[
\approx I_{\text{probe}} + I_{\text{pump}} + \frac{1}{2} \cos(\omega \Delta t) \int_{-\infty}^{\infty} E_{\text{probe}}(t) E_{\text{pump}}(t + \Delta t) dt.
\]

From Eq. 2.23 it follows that the amplitude of the fluctuating intensity component represents the electric field crosscorrelation, which is a factor $\sqrt{2}$ wider than the intensity crosscorrelation.

**Fig. 2.6:** Effect of chirp on pulses. (a) unchirped pulse, (b) pulse with positive linear chirp.
Fig. 2.7: Group Velocity Dispersion (GVD) compensation line. The incoming beam (from the left) passes two prisms and is then reflected back by the end-mirror on the right. The amount of GVD is controlled by the distance between the two prisms and the position of the first prism.

Although the current pump-probe setup is not interferometrically stable, the oscillation due to the scattered pump light can be observed. Figure 2.8(a) shows a 5 fs trace of the observed interference pattern, nicely showing the 2.7 fs period of the laser light. The amplitude of the oscillating component is plotted in Fig. 2.8(b). Fitting the curve with a Gaussian the position of the pump-probe coincidence can be determined with an accuracy of ±10 fs. The width of the Gaussian, however, is not necessarily representative for the pulse length. When the laser pulses arrive at the sample with a finite chirp, their length is increased as for example can be seen in an intensity crosscorrelation. On the other hand, the interference between two pulses is reduced as their instantaneous frequency now changes within the pulse duration. These effects turn out to cancel each other, and therefore the electric field crosscorrelation of two identical pulses yields the length of the unchirped pulse.

2.5.3 Spotsize considerations

To obtain a sufficient temperature rise of the magnetic materials, the pump beam is focused to a ~10 µm (FWHM) spot. Upon absorption of a pump pulse the excitation density is therefore given by the spatial intensity profile. In this work also the probe beam is focused to 10 µm and therefore the effect of a spatially varying excitation profile should be considered. Here we will consider the effect of this profile on the interpretation of TRMOKE measurements.

The spatial intensity profile of a Gaussian beam can be written as

$$ I(r) = \frac{I_0}{\pi r_0^2} \exp\left(-r^2/r_0^2\right), $$

with $r_0$ the Gaussian radius and $I_0$ the total beam intensity. When the pump beam is used to heat an optically thin layer, the resulting excitation/temperature profile is initially also Gaussian,

$$ \Delta T(r) = T_0 \exp\left(-r^2/r_0^2\right) $$

$$ T_0 = \frac{U_{\text{pump}}}{\pi r_0^2 \delta c}, $
with $U_{\text{pump}}$ the energy in a single pump pulse and $c$ the heat capacity of the layer with thickness $d$. Consider a non-linear temperature dependence of the magnetization $M$:

$$M(T_a + \Delta T) = M_0 + a\Delta T + b\Delta T^2,$$  \hspace{1cm} (2.26)

with $T_a$ the ambient temperature and $a$ and $b$ constants. A measurement with a pump and probe beam of equal diameter would thus yield

$$M_{\text{probe}} = \int_0^\infty 2\pi r \left[ M_0 + a\Delta T(r) + b\Delta T(r)^2 \right] I(r)/I_0dr = M_0 + \frac{a}{2} T_0 + \frac{b}{3} T_0^2. \hspace{1cm} (2.27)$$

Neglecting the non-linear term a change in magnetization corresponding to half the peak temperature $T_0$ is observed. Only for strongly non-linear $M(T_s)$ profiles or for a comparison with calculated temperature profiles the effects of Eq. 2.27 should explicitly be considered. At moderate pump excitations $M(T_s)$ is approximately linear and then the non-uniform temperature profile does generally not affect the interpretation.
3. SAMPLES

3.1 Introduction

This chapter gives a description of the different structures that were used in both the demagnetization and precession experiments, and is primarily intended for reference. For each sample a short description of its structure and a magnetic characterization is given. Also, calculated optical and thermal properties are presented. Understanding of the thermal properties is of great importance for a proper interpretation of the spin dynamics described in Chap. 4. Throughout this chapter results of transient MO experiments are included, used as a ‘thermometer’ for comparison with calculated temperature transients.

The optical characteristics of the layered structures are calculated using an optical matrix formalism that is described in Ref. [58]. The resulting absorption profiles serve as input to the thermal diffusion equation,

\[ c(z) \frac{dT}{dt} = \lambda(z) \frac{d^2T}{dz^2} + p(z, t), \]  

with the laser power density \( p(z, t) \) the absorption source term derived from the optical model. For the volumetric heat capacity \( c \) and thermal conductivity \( \lambda \) equilibrium values are chosen, as found in Refs. [30, 54]. \( z \) is the spatial coordinate on the axis perpendicular to the film surface. The one dimensional approximation used in Eq. 3.1 is easily justified. The optical heating has a lateral extent that is defined by the spot diameter of \( \sim 10 \mu m \). Due to the limited penetration depth of the light in the metallic magnetic layer the material is only heated to a depth of \( \sim 0.01 \mu m \). The largest temperature gradient, and thus the main route for heat diffusion, is therefore in the depth of the structure.

Equation 3.1 is only valid in thermal equilibrium. Directly after excitation by a laser pulse the system is however far from equilibrium as only the electronic system gains energy by absorption of the incident photons. As will be shown in Chap. 4 it takes about \( \sim 2 \) ps before electron and lattice system are in equilibrium, leading to deviations from Eq. 3.1 during the first picoseconds.

In the first two sections epitaxial Cu/Ni/Cu wedge structures and polycrystalline Ni samples will be discussed. The magnetic material in these structures is nickel, which shows the lowest Curie temperature (627 K) of the 3d-ferromagnets. This is advantageous in magnetic pump-probe experiments as for a given temperature rise nickel will show the largest relative change in magnetization. To check if the observed magnetization dynamics is more general also a Co-Pt alloy, described in the last section of this chapter, is looked at.
3.2 Epitaxial Cu/Ni/Cu wedge structures

Using molecular beam epitaxy two Ni wedges were grown, a 0-30 nm (001)-oriented Ni wedge on a Cu(001) substrate and a 0-8 nm (111)-oriented wedge on a Cu(111) substrate. A region with a uniformly increased thickness serves as a marker for an accurate position calibration. Both wedges were capped with 3 nm of Cu to prevent oxidation of the Ni layer. Epitaxial growth was checked in situ by LEED, showing perfectly coherent growth for thin layers and an increasing number of dislocations for thicker films.

3.2.1 Magnetic characterization

Both epitaxial structures show two magnetization reorientation transitions with Ni layer thickness. As depicted in Fig. 3.1, for very thin films the preferential orientation of the magnetization lies in-plane (IP), followed by a region with an out-of-plane (OOP) orientation. Upon further increase of the film thickness the easy axis orientation gradually changes to IP again. The origin of these reorientations is believed to lie in a combination of strain-induced anisotropy and a Néel interface anisotropy [29, 45]. Figures 3.2(a) and (b) show the remanence and coercive field as a function of Ni thickness, as measured with polar MOKE. The (001) sample shows a distinct region with 100% out-of-plane remanence followed by a steep drop at $d_{\text{Ni}} \approx 9$ nm, indicating a transition to an in-plane orientation. For very small Ni thickness an IP orientation of the magnetization is found. The (111) structure shows the same transitions, but 100% remanence is not achieved and the transition to IP is more gradual.

The (001) wedge was also characterized using a vectorial MOKE technique [15], allowing for the separate measurement of the in- and out-of-plane magnetization components. In Fig. 3.3 magnetization loops for two Ni thicknesses are plotted, showing both the OOP component as a function of OOP field and the IP [100] component of the magnetization as a function of IP field (applied along the [100] direction). At $d_{\text{Ni}} = 9$ nm the out-of-plane measurement shows a typical easy-axis loop, indicative of an OOP easy-axis. This is confirmed by the IP loop that shows almost zero remanence, characteristic of a hard-axis loop. This situation is reversed for $d_{\text{Ni}} = 16$ nm. At this Ni thickness no OOP remanence is found while the in-plane measurement is reminiscent of a loop taken at 45° with respect to the easy-axis. The latter is caused by the crystalline anisotropy of the layer, which in combination with shape anisotropy results in [110] easy axes. Since the field is applied along the [100] direction the maximum remanence is 71%.
Fig. 3.2: Coercive field and remanence (relative to the saturation magnetization) as measured with MOKE in the polar configuration. (a) Cu(001)/Ni/Cu wedge, (b) Cu(111)/Ni/Cu wedge. The lines drawn serve as a guide to the eye.

Fig. 3.3: In-plane ($\vec{M}, \vec{H} \parallel [100]$) and out-of-plane ($\vec{M}, \vec{H} \parallel [001]$) magnetization loops on the Cu(001)/Ni/Cu wedge for two Ni thicknesses, as obtained by vectorial MOKE. At $d_{\text{Ni}} \approx 9$ nm the easy-axis orientation is out-of-plane. For the 16 nm layer the magnetization is largely in-plane. The crystalline anisotropy easy-axis is directed along the [110] axis.
Fig. 3.4: Absorption profile in a Cu/Ni(5)/Cu(1.5) and a Cu/Ni(10)/Cu(1.5) stack. Plotted is the absorption versus depth in the sample $z$, with $z = 0$ corresponding to the surface of the Cu substrate. The light, $p$-polarized and incident under $15^\circ$, has an intensity of 1 W/m$^2$ and a wavelength $\lambda = 780$ nm.

Altogether, the magnetic characterization of both wedge systems confirms a good epitaxial growth of the Ni layers, showing two spin reorientation transitions and effects of the crystalline anisotropy.

3.2.2 Thermal and optical properties

For the time-resolved pump-probe measurements on the epitaxial systems a polar configuration was used, with the pump and probe beam incident under an angle of $15^\circ$ with the film normal. Figure 3.4 shows calculated absorption profiles for the structures. For the optical constants values from Ref. [54] were used at a wavelength of 780 nm, c.f. Tab. 3.1. The profiles show that the major part of the absorption takes

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon$ (1.6 eV)</th>
<th>$\lambda$ [W/m/K]</th>
<th>$\rho$ [$10^3$ kg/m$^3$]</th>
<th>$c$ [$10^3$ J/m$^3$/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>-17.8 + i20.1</td>
<td>70</td>
<td>8.8</td>
<td>0.46</td>
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<tr>
<td>Cu</td>
<td>-21.7 + i2.2</td>
<td>390</td>
<td>8.9</td>
<td>0.39</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>4</td>
<td>10</td>
<td>3.3</td>
<td>0.71</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.3</td>
<td>1</td>
<td>2.6</td>
<td>0.84</td>
</tr>
<tr>
<td>Si</td>
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<td>2.3</td>
<td>0.76</td>
</tr>
<tr>
<td>Pt</td>
<td>-15.8 + i26.7</td>
<td>71</td>
<td>21.4</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Tab. 3.1: Dielectric constant, heat conductivity, density and specific heat as used in the calculations. Derived from Refs. [42, 54].
place within the Ni layer, i.e. the pump pulse will mainly heat the Ni layer.

Using the optical absorption profiles the diffusive heat transport is calculated. Figure 3.5(a) shows the average temperature of the Ni layer during the first 20 ps after excitation. For the specific heat $c$, density $\rho$ and thermal conductivity $\lambda$ of Cu and Ni equilibrium values from Refs. [30, 54] were taken, reproduced in Tab. 3.1. The time dependence of $p(z,t)$ in Eq. 3.1 was described by a Gaussian with a width of 100 fs, i.e. the duration of the laser pulse. It must be noted that during the first two picoseconds the equilibrium model is a poor approximation, as on this time scale the electron and lattice system are not yet in equilibrium with each other. The simulations show that for thicker Ni layers the heat diffusion proceeds less rapid, evidenced by the slower decrease of temperature in time. This effect is mainly caused by the much lower thermal conductivity of Ni compared to Cu, slowing down the thermal diffusion for thicker Ni layers.

In Fig. 3.5(b) the relative change in the measured MO ellipticity, $\Delta \psi''/\psi''$, is plotted versus delay time $\Delta t$ between pump and probe pulse. For small excitations the change in MO signal $\Delta \psi$ can be used as a ‘thermometer’, i.e. $\Delta \psi \propto \Delta M \propto \Delta T$, an approach that is discussed in detail in Chap. 4. This allows for a comparison between the calculated temperature transients in Fig. 3.5(a) and the measured MO effect. The measured transients indeed show a slower decrease of $\Delta \epsilon/\epsilon$ with increasing Ni layer thickness, in correspondence with the calculated decrease in heat diffusion. The size of the effect is however not in quantitative agreement with the calculated results, possibly due to the neglect of interface thermal resistances, initial non-equilibrium diffusion effects and ballistic electron transport. Also the very sharp peak for $\Delta t < 2$ ps is not expected from the simple diffusive calculations.

For the long-term behavior the all-metallic structure can be considered uniform,
and in this approximation Eq. 3.1 can be solved analytically. For a delta peak excitation, \( T(z, 0) = T_0 \delta(z) \), one finds

\[
T(z, \Delta t) = \frac{1}{2} \frac{T_0}{\sqrt{\pi \alpha \Delta t}} \exp \left( -\frac{z^2}{4\alpha \Delta t} \right) \tag{3.2}
\]

The diffusivity \( \alpha = \frac{\lambda}{\rho c} \) determines the rate of temperature equilibration within the material. The resulting temperature profile is a Gaussian, with an increasing width and decreasing peak value in time. In the Cu/Ni/Cu systems we can thus eventually expect a

\[
T_{Ni}(\Delta t) = \frac{T_0}{\sqrt{\Delta t - t_0}} \tag{3.3}
\]

behavior, with a finite \( t_0 \) to account for the initial width of the absorption profile. The inset in Fig. 3.5(b) shows the long term behavior of the MO signal, together with a fit to Eq. 3.3. The good correspondence confirms that on a longer time scale the MO signal follows the lattice temperature.

Summarizing, for \( \Delta t \gg 2 \) ps the MO signal is well-described by diffusive heat transport. However, for the first picoseconds, i.e. during electron-phonon relaxation, a much faster dynamics is found. In this regime the diffusive approximation is no longer valid and electron and lattice dynamics should be treated separately. The unexpectedly large peak during the first picoseconds does however indicate that either the initial heat diffusion out of the Ni layer is much faster, or that the initial MO effect does not follow the lattice temperature.

### 3.3 Polycrystalline Ni structures

Apart from epitaxial systems also different polycrystalline Ni structures are investigated. This allows for the separation of structural effects by comparing their mutual dynamics. Also, for polycrystalline samples the thermal conductivity is more easy controlled. To reduce the heat transport effects, the Ni was grown on Si/Si\(_3\)N\(_4\)(60) and Si/SiO\(_2\)(5) substrates. The insulating layers strongly decrease the diffusive transport and also block possible ballistic electron transport directly after excitation, simplifying the interpretation of the data. For both substrates most of the heat has diffused out of the Ni layer after 12 ns, the time between two pump pulses. This prevents excessive cumulative heating and experimentally only a modest \( \sim 10 \) K ‘DC’ temperature rise is observed on the Si/Si\(_3\)N\(_4\)(60)/Ni structure.

A number of different polycrystalline samples was grown by evaporation in a MBE system. In the demagnetization experiments mainly results on homogeneous Si(001)/Si\(_3\)N\(_4\)(60)/Ni(10)/Cu(3) and Si(001)/SiO\(_2\)(5)/Ni(10)/Cu(3) are presented. In the precessional experiments also wedge structures, Si(001)/SiO\(_2\)(5)/Ni(30-50)/Cu(3) are used.

#### 3.3.1 Magnetic characterization

All polycrystalline Ni films show an in-plane magnetization and a low coercivity. Thin Ni layers on Si\(_3\)N\(_4\) probably grow cluster-like, as evidenced by the magnetic characterization of a Si(001)/Si\(_3\)N\(_4\)(0-15)/Ni(10)/Cu(3) wedge shown in Fig. 3.6. The first 3 nm of Ni are not magnetic, but upon further increase of the nominal Ni thickness a strong increase of the Kerr signal is observed. Such behavior can be caused by the
3.3.2 Thermal and optical properties

Figure 3.7 shows the results of optical absorption calculations for different polycrystalline structures used in the experiments. From the absorption in the Si$_3$N$_4$/Ni structure shown in panel (a), a strong dependence of the pump induced effects on Ni thickness is expected since the average absorption changes with almost a factor of two going from 5 to 10 nm of Ni. The heating is relatively uniform since the films are thin compared to the optical penetration depth. Also, the absorption for an identical 10 nm Ni layer on SiO$_2$(5), panel (c), is a factor of two lower compared to the same layer on Si$_3$N$_4$(60). This effect is mostly related to different thickness of the insulating layer, i.e. the refractive properties of SiO$_2$ and Si$_3$N$_4$ do not greatly differ.

In these structures with transparent layers the plots of the perpendicular component of the Poynting vector, shown in panels (b) and (d), give important additional information. The $z-$component of the Poynting vector represents the rate of flow of energy per unit area in the $z$ direction. Therefore the derivative $d/dz$ of Fig. 3.7(b) simply yields Fig. 3.7(a), the absorption per unit volume. In panels (b) and (d) also the transport in transparent layers is visible. The plots indicate that even after the Ni layer a considerable amount of energy is flowing deeper into the sample, showing that not all the laser light is absorbed by the Ni. Since the SiO$_2$ and Si$_3$N$_4$ layers are transparent, this does not show up in the absorption profiles. The transmitted energy is absorbed by the Si substrate, although this is not visible in, e.g., panel (c) due to formation of small, non-magnetic clusters for small nominal thicknesses that at certain coverage coalesce to form a closed, magnetic layer. The step observed in intensity and Kerr signal at 15 nm is due to a 20 nm marker that is used for position calibration.

Fig. 3.6: Saturation Kerr ellipticity (longitudinal) and reflectivity versus Ni-thickness. The end of the wedge is marked by a 20 nm step, that is clearly visible in the intensity signal. The dotted curve represents the calculated reflectivity (p-polarized, 35° incidence), the solid line is a guide to the eye.
Fig. 3.7: (a) Optical absorption in the Si/Si$_3$N$_4$(60)/Ni/Cu structure for two Ni thicknesses. The light, p-polarized and incident under 35°, has an intensity of 1 W/m$^2$ and a wavelength $\lambda = 780$ nm. (b) Perpendicular component of the Poynting vector, indicating the rate of flow of energy per unit area in the $-z$ direction, for the two structures. (c),(d) Similar to (a) and (b), but for a Si/SiO$_2$(5)/Ni/Cu structure.

The large (8 $\mu$m) optical penetration depth of Si at 1.6 eV. For the interpretation of the magnetic experiments of Chap. 4 the heating of the Si substrate has no consequences since only contributions odd in magnetization are considered and the total transient reflectivity change effect is small. However, in Sect. 4.6 it is found that the heating of the Si substrate does have severe effects on the interpretation of transient reflectivity experiments.

The transient MO experiments on these structures, again used as ‘thermometer’, support the predictions from the calculations. Figure 3.8(a) shows a series of MO ellipticity transients for various Ni thicknesses on a Si$_3$N$_4$/Ni wedge structure. The predicted larger heating for thin films, c.f. Fig. 3.7, clearly shows as an increased MO effect for the thinner layers. The induced effects can be very large, up to 40% for the 4.8 nm film. Since the $M(T)$ behavior is non-linear $\Delta M$ increases more than proportional with $\Delta T$. The shift in peak position, indicated by the dotted line, is also related to the larger energy absorption as will be discussed in Sect. 4.9. Also the factor of two higher absorption for the Si$_3$N$_4$/Ni film is reproduced, as can be seen
Fig. 3.8: (a) Relative change in the MO ellipticity as a function of Ni thickness on a Si$_3$N$_4$/Ni wedge for the first 1.3 ps. The dashed line represents a convolution of the pulse shape with a step function. (b) Calculated long-term temperature transients for SiO$_2$/Ni(10) and Si$_3$N$_4$/Ni(10) for indicated values of $\lambda$. (c),(d) Long-term ellipticity transients on Si$_3$N$_4$/Ni(10) and SiO$_2$/Ni(10). Dotted lines are scaled versions of the thermal simulation.

Comparing Fig. 3.8(c) and (d).

Results of thermal diffusion calculations for the two structures are plotted in Fig. 3.8(b). Reported values for the thermal conductivity of Si$_3$N$_4$ vary between 5 – 30 W/m/K, therefore results for two values of $\lambda$ are shown. The measured dynamics compare well with the calculated transients using $\lambda_{Si3N4} = 10$ W/m/K, as shown in Figs. 3.8(c) and (d). The dotted lines in the two figures are scaled versions of the calculated transients. As in the epitaxial Ni structures, the sharp peak in $\Delta\psi''/\psi''$ is very much unexpected from diffusive transport. In this case enhanced (electronic) heat transport during the first picoseconds can be excluded because of the insulating underlayer.

Concluding, the optical and long-term thermal properties of the polycrystalline Ni layers are well-described by optical matrix calculations and diffusive transport. However, the MO response is again sharply peaked for $\Delta t < 2$ ps. Since the Ni is grown on insulating underlayers this effect can not be explained by transport effects.
Fig. 3.9: (a) Magnetization loops measured using the polar MOKE for two different N$^+$ dosages. (b) Magnetization loops measured at a dosage of $0.5 \cdot 10^{15}$ cm$^{-2}$. The temperature was varied from 35 to 95°C in steps of 20°C.

The sharp peak in the transient MO response thus indicates that the MO effect does not follow the lattice temperature.

3.4 Co-Pt alloy

Besides structures containing nickel also cobalt-platinum alloys are studied, allowing for a check of the general character of the observed magnetization dynamics. Thin films of CoPt show an out-of-plane magnetization and large MO effects. Recently it was found that irradiating CoPt multilayers with energetic ions can drastically change their magnetic properties [20, 77]. The irradiation affects the anisotropy and magnetization of the material, even allowing for a reorientation of the easy-axis from out-of-plane to in-plane. Irradiation may also alter the magnetization dynamics, which is of interest for the current investigation.

In this work a Pt(20 nm)/Co(0.5 nm)/Pt(1 nm) trilayer was used, sputter-grown on a Si/SiN(40 nm) substrate at IBM Almaden. The layers were damaged by irradiation with 700 keV N$^+$ ions, varying the dose from $10^{14}$ cm$^{-2}$ to $10^{16}$ cm$^{-2}$ over the structure. The ion bombardment causes an intermixing of the Co and Pt, resulting in an alloy with a decreased coercivity and a lower Curie temperature as compared with the original sample. Co$_{1-x}$Pt$_x$ alloys remain magnetic at room temperature up to a platinum content of $x = 0.75$. The net magnetic moment per atom decreases from 1.7 $\mu_B$ for $x = 0$ to 0.75 $\mu_B$ for $x = 0.75$, while the Curie temperature decreases from 1400 K to 300 K [76].

3.4.1 Magnetic characterization

Using the MOKE in the polar configuration the dependence of coercive field $H_c$ on radiation dosage is evident. In Fig. 3.9(a) measured magnetization loops are plotted
for two different $N^+$ dosages, showing a clear decrease of $H_c$ with increased radiation. At the maximum dosage the easy-axis orientation is still out-of-plane, i.e. no spin reorientation transition is observed.

Also, the coercive field is strongly dependent on temperature. Figure 3.9(b) shows a series of magnetization loops taken at different substrate temperatures. Increasing the temperature from 35°C to 100°C the coercive field decreases with almost a factor of two. A similar effect is observed when the pump beam is turned on. Optical heating by the pump pulses results in a decrease of the coercivity with $\sim 20\%$ for an external fluence of 1.5 mJ/cm$^2$. This effect is not caused by 'DC' heating of the sample, but is related to the longer-lasting transient temperature rise.

### 3.4.2 Thermal and optical properties

Using the optical matrix method the absorption in the structure is calculated. From Figs. 3.10(a) and (b) it follows that most of the energy is deposited in the Pt layer and that only a small amount leaks through the Si substrate. The heating is not uniform, although initial ballistic electron transport will flatten the profile. From the average absorption a maximum temperature rise of 92°C is expected for a external fluence of 1.9 mJ/cm$^2$. Like the polycrystalline Ni structures the trilayer is deposited on top of an insulating substrate. The thermal diffusion is therefore similar to that of the Si$_3$N$_4$/Ni sample plotted in Fig. 3.8(b), i.e. showing a slowly decreasing temperature transient. As for the previous samples, the time-resolved MO measurements (not shown) show a strongly peaked response near $\Delta t = 0$ that does not follow from diffusive transport simulations.
3.5 Conclusion

In this chapter a structural description and magnetic characterization was given for the samples investigated in this work. Also a detailed analysis of the optical and thermal properties was presented. The optical simulations are used to identify to what extent the laser light is absorbed in the different layers, and show a very good agreement with experimental observations. The absorption profiles are subsequently used to calculate the diffusive transport in the layered structures after heating by a pump pulse. For delay times $\gtrsim 2$ ps a good correspondence between the simulated temperature transients and the magneto-optical measurements is found, showing that on this time scale the MO signal is proportional to the lattice temperature.

During the first picoseconds after excitation much larger MO effects are observed than predicted by the simple diffusive model. In this regime the model is no longer valid as the lattice and electron system are not in equilibrium. However, even for magnetic layers on insulating substrates sharply peaked MO effects are observed. Since the insulating substrates effectively block all energy transport this is a strong indication that the MO effect does not follow the lattice temperature.
4. DEMAGNETIZATION DYNAMICS

4.1 Introduction

In future spintronic devices the control and life time of the electron spin orientation is of utmost importance. However, a detailed understanding of the interactions that change the spin direction on a femtosecond time scale is still lacking, especially for the ferromagnetic metals. In this chapter we will investigate the processes leading to the loss of magnetization, i.e. net spin moment, upon femtosecond laser heating.

It is well known that the magnetization of a ferromagnetic material decreases when it is heated. Upon reaching the Curie temperature the long-range order is lost and no net magnetization is left. In the time-resolved experiments presented in this chapter the relaxation of the spin system towards its new equilibrium is followed in time after sudden laser heating. Optical excitation leads to an instantaneous increase of the energy of the electron system. Subsequently, the lattice is heated by electron-phonon scattering and the magnetization is reduced by spin scattering processes.

The aim of demagnetization studies is to determine the timescale and mechanisms involved in the demagnetization process. To this effect, nearly all ultrafast demagnetization studies employ magneto-optic pump-probe techniques. We will show here, however, that under certain circumstances MO measurements do not yield the magnetization dynamics, complicating the interpretation of the data. To identify the spin scattering processes, it is common to compare the time scales for loss of magnetization and loss of energy in the electron system. In this work, we also systematically study the temperature and fluence dependence of the dynamics. Comparing not only the time scales, but also the magnitude of the observed effects, the processes leading to the demagnetization can be identified.

In the first sections a basic background on laser-induced demagnetization is given. In Sect. 4.2, an overview is given of recent experimental work on magnetization dynamics. The dynamics of the electron and lattice system upon optical excitation is discussed from a theoretical perspective in Sect. 4.3. Next, in Sect. 4.3.2, the spin dynamics is looked at using both microscopic and phenomenological models. Finally, in Sect. 4.5 different experimental techniques are presented to probe the electron and spin dynamics.

To measure the dynamics of the electron system we performed transient reflectivity measurements. The results of these experiments and a comparison with values measured by other groups are presented in Sect. 4.6. The relaxation times found here can be used for comparison with magnetic time scales addressed in subsequent sections.

In this work time-resolved MOKE measurements are used to measure the magnetization dynamics. The use of magneto-optical techniques is well-established in equilibrium conditions, but an extrapolation to the highly excited state shortly after
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: electron energy relaxation time.
\( \tau \)

: characteristic electron thermalization time,
\( t \)

: delay with respect to the pump-probe crosscorrelation,
\( \tau \)

: time at which the maximum demagnetization is reached,
\( t \)

: intensity ratio.

R(T): reflection/transmission,
l(p)-MOKE: longitudinal/polar linear MOKE,
(\( -SHG \)): (transverse)

Results of selected spin-dynamics experiments from 1996.

Table 4.1: Results of selected spin-dynamics experiments from 1996.

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Guidoni results: polarized and spin-dependent.

Gudde results: polarization dependent.

Regensburger results: polarization dependent.

Hohlfeld results: polarization dependent.

Conrad results: polarization dependent.

Hohlfeld results: polarization dependent.

Beaurepaire results: spin-dependent.

Debnath results: spin-dependent.

Scholl results: spin-dependent.

Kampfrath results: spin-dependent.

Hohlfeld results: spin-dependent.
laser excitation is not trivial. In Sect. 4.7 it is shown that in some cases the time-resolved MO signal does not represent the magnetization dynamics, and different causes for this effect are discussed.

To obtain information on the demagnetization process temperature and pump fluence dependent measurements were performed, presented in Sects. 4.8 and 4.9, respectively. By comparing transient MOKE measurements taken at different ambient temperatures and fluences, it is shown that the spin dynamics are closely coupled to the electron dynamics.

All pump-probe demagnetization experiments point at an extremely rapid decrease of the magnetization after laser heating, i.e. within hundreds of femtoseconds. In Sect. 4.10 it is investigated whether or not the magnetization dynamics is delayed with respect to the electronic response. Finally, Sect. 4.11 summarizes the results of this chapter and in Sect. 4.12 an outlook is given.

4.2 Earlier work

Agranat et al. [2] were among the first to study the dynamics of light-induced demagnetization in the mid-1980’s. They heated a Ni film by an intense laser pulse of variable duration, and afterwards measured the remanent MO-contrast. It was found that using pulses of 5-20 ps duration the Ni layer could not be demagnetized, although the film temperature was raised to double the Curie temperature. However, a 40 ns pulse could demagnetize the heated section. It was thus concluded that the spin relaxation time lies between 1-40 ns.

The first true time-resolved experiments were done at the ETH Zürich by Vaterlaus et al. in the beginning of the 1990’s [74, 75]. They employed a time-resolved spin-polarized photo-emission technique, using a pump pulse of $\sim 10$ ns duration to heat the material. A probe pulse of 30 ps at a high photon energy subsequently excited electrons from the Fermi level to the vacuum level where they could be spin-selectively detected. Experiments on Gd yielded a spin relaxation time of $100 \pm 80$ ps. Similar experiments on iron put the relaxation time between 30 ps and 20 ns. Although the reported figures were at the edge of the experimental resolution, which was limited by the length and rise time of the laser pulses, they agreed well with a theoretical estimate by Hübner et al. [40] based on spin-lattice relaxation.

In 1996 surprising results were published by Beaurepaire et al. [5]. Using a magneto-optical pump-probe technique with pulses of only 60 fs duration they found that the magnetization of a 22 nm nickel film reached its minimum value already $\sim 2$ ps after laser heating, i.e. orders of magnitude faster than previously published values. The key figure of this work is reproduced in Fig. 1.3. Using a three-temperature model to describe the dynamics in the electron, phonon and spin system they concluded that the spin relaxation was not driven by spin-lattice interactions, but that an efficient electron-spin scattering was the main mechanism responsible for the observed fast demagnetization.

Beaurepaire’s paper triggered a new interest in the demagnetization phenomena and different groups soon confirmed the ultrafast demagnetization. Hohlfeld et al. [36] from the Freie Universität Berlin measured the magnetization dynamics of Ni and Co using pump-probe Second Harmonic Generation (SHG). In their experiments on a bulk Ni crystal the observed response of the magnetization was instantaneous within the experimental resolution. Moreover, after 300 fs the magnetization of a
bulk Ni crystal could simply be described by the electron temperature using the equilibrium magnetization dependence, \( M(t) = M[T_e(t)] \). For even smaller delay times (\( \Delta t < 300 \text{ fs} \)), i.e. before complete electron thermalization, deviations from \( M[T_e(t)] \) were observed.

Table 4.1 gives a chronological overview of selected spin dynamics experiments. The spin-resolved photoemission experiments by Scholl et al. [63] on thin Ni layers seemed to bridge the gap between the ultrafast demagnetization reported by Beaurepaire and Hohlfeld and the much slower relaxation observed earlier. Scholl found that after laser-heating the spin polarization of photo-emitted electrons dropped within the pump-probe crosscorrelation (300 fs). However, also a gradual decay over hundreds of picoseconds was observed. This result has, however, never been reproduced.

In 1998, Beaurepaire was the first to drive a ferromagnetic material, CoPt\(_3\), from the ferromagnetic to the paramagnetic state using intense pump pulses. The decrease in magnetization followed the absorbed pump-power on a characteristic time scale \( \tau = 100 \text{ fs} \), similar to the electron thermalization. Conrad et al. from the Berlin group reproduced such an ultrafast, complete demagnetization for 7 to 8 monolayer thick films of Ni [11, 26], which have a reduced Curie temperature. The same group also repeated the experiments on bulk poly-crystalline Ni, but now using 40 fs pulses [26, 35]. The magnetic and non-magnetic part of the SHG signal dropped within the crosscorrelation of the pump and probe pulse, which would be indicative for an instantaneous response.

At this time doubts started to rise on the interpretation of MO-effects in the highly excited state present right after excitation. Regensburger et al. [60] and Koopmans et al. [51] (Sect. 4.7 of this thesis) showed a strong dependence of the observed dynamics on the measured polarization components, pointing at a non-trivial relation between magnetism and magneto-optics. Later, polarization dependent effects were also observed by Guidoni [27] and Melnikov [57]. Kampfrath et al. [46] observed a dependence of the dynamics on both polarization and probe wavelength.

### 4.3 Electron and lattice dynamics

In the optical demagnetization experiments the ferromagnetic material is heated by an intense laser pulse. When photons are absorbed in a metal their energy is transferred to the electron system, creating highly energetic electrons (\( \gtrsim 1 \text{ eV} \)). The subsequent electron thermalization due to e-e interactions and energy relaxation by electron-phonon scattering have been extensively studied in non-magnetic metals. In this section the fundamental interactions between electrons and phonons, as well as the two-temperature model will be introduced.

Upon absorption of a short laser pulse electrons are excited from the occupied states below the Fermi level to the empty states above. This creates a non-equilibrium distribution of highly energetic electrons, depicted in Fig. 4.1(a), I. In the subsequent relaxation processes, three different regimes can be recognized.

First, the non-equilibrium electrons will rapidly thermalize to a Fermi-Dirac distribution by e-e scattering. This greatly increases the number of excited electrons but reduces their average energy, c.f. Fig. 4.1(a), II. After thermalization, an equilibrium description in terms of an electron temperature \( T_e \) becomes valid. The lattice system, characterized by a lattice temperature \( T_l \), is initially unaffected by the optical excitation. Electron-phonon (e-p) interactions will however equilibrate the electron and
Fig. 4.1: (a) Schematic representation of the changes in the electron occupancy after pulsed laser excitation. (I) non-equilibrium distribution right after optical excitation with a photon energy $h\nu$. (II) Thermalized electron distribution, but with an elevated temperature $T_e$. (III) Electron-phonon interactions equilibrate the electron and lattice system, reducing the electron temperature. During the different stages also ballistic and diffusive transport out of the illuminated region will reduce the energy density in the electron system. (b) The two-temperature model. Optical excitation by a laser pulse increases the energy in the electron system, raising its temperature $T_e$. Electron-phonon relaxation, characterized by a coupling parameter $g_{el}$, subsequently equalizes the temperature of the electron and lattice ($T_l$) system.

lattice temperature, increasing the energy in the lattice system. When finally the e-p relaxation is completed, the system is in internal equilibrium and can be characterized by a single temperature. The subsequent processes are described in more detail below.

4.3.1 Thermalization

The internal equilibration of the electron system after optical excitation is governed by electron-electron interactions. The evolution of the electron distribution in time can be described by a Boltzmann equation, [24, 33]

$$\frac{dn_i}{dt} = K_{ee} \int \int \int [(1 - n_1)(1 - n_2) \cdot n_3 \cdot n_4 - n_1 \cdot n_2 \cdot (1 - n_3)(1 - n_4)] \delta(E_1 + E_2 - E_3 - E_4) dE_2 dE_3 dE_4,$$  \hspace{1cm} (4.1)

with $n_i = n(E_i)$ the value of the electron distribution $n$ at energy $E_i$, and $K_{ee}$ the electron-electron scattering constant. In deriving Eq. 4.2 a constant density of states was assumed. Also, $K_{ee}$ is considered constant, i.e. independent of electron energy and momentum. Using Eq. 4.2, the lifetime of a single, highly excited electron can be derived. Consider $n(E)$ given by the Fermi-Dirac distribution, but with a small occupation at $E - E_F \gg k_B T_e$. It is readily shown that the occupation decreases
Fig. 4.2: Lifetime of excited electrons in Ag and Ni as a function of energy above the Fermi level. The solid lines represent calculations using Eq. 4.2. For the top curve describing Ag, $K_{ee}$ was derived from Fermi liquid theory. The bottom curve represents an approximation for Ni, using $1/K_{ee} = 3$ fs eV$^2$. The data in the figure is reproduced from Ref. [3].

exponentially on a characteristic time scale

$$\tau_{ee}(E) = \frac{1}{K_{ee}(E - E_F)^2},$$  \hspace{1cm} (4.2)

i.e. the lifetime is proportional to $(E - E_F)^2$.

Results of time-resolved 2PPE experiments on the free-electron metal Ag [50] show a good agreement with Eq. 4.2. In Fig. 4.2 the measured energy dependence of the lifetime of optically excited electrons in Ag is indicated by triangles. The solid line represents Eq. 4.2 with a value for $K_{ee}$ that was calculated from Fermi liquid theory [3]. Although for Ag the measured lifetimes show a good agreement with the $(E - E_F)^{-2}$ relation, deviations occur for materials with d-bands close to, or intersecting with, the Fermi level. This is apparent for the measured values on Ni, depicted by squares in Fig. 4.2. In the transition metal the availability of d-bands greatly increases the phase-space for scattering, and a ten-fold reduction in life time is observed compared to Ag [50]. The excitation of the strongly bonded d-electrons near $E_F$ does however result in deviations from Eq. 4.2 [3]. Note that for the ferromagnetic Ni the spin-up and spin-down electrons have different lifetimes [50]. The values reported in Fig. 4.2 are spin-integrated.

After optical excitation, the combined effect of many e-e scattering events leads to the thermalization of the electron gas. This process has been well studied in literature, both experimentally and theoretically [6, 16, 17, 19, 24, 68, 70]. Here we present an alternative estimate of the thermalization time that uses a rather crude
approximation, but allows for a simple analytical result. For simplicity we replace the distribution of excited electrons by a single excitation at an energy $E_0$ above the Fermi level. For a Fermi sea at 0 K, its lifetime is given by Eq. 4.2. After the first scattering event, three new particles are created: two electrons and one hole. The total number of excited particles $N_e$ thus triples after this scattering event. The average energy per particle is, at any time, given by $\langle E \rangle = E_F + \langle E \rangle$. We make the severe approximation that the lifetime of the excited particles is given by $\tau_{ee}(E_F + \langle E \rangle)$.

This yields a differential equation for $N_e$,

$$\frac{dN_e(t)}{dt} = 3 \frac{N_e(t)}{\tau_{ee}(E_F + \langle E \rangle)} = 3 \frac{K_{ee}E_0^2}{N_e(t)}, \quad (4.3)$$

with the solution

$$N_e(t) = \sqrt{6E_0^2K_{ee}t + 1} \approx \sqrt{6}E_0\sqrt{K_{ee}t}, \quad (4.4)$$

$$\langle E \rangle(t) \approx \frac{1}{\sqrt{6}}(K_{ee}t)^{-1/2}. \quad (4.5)$$

The approximate expressions are valid for $t \gg (6E_0^2K_{ee})^{-1}$. The number of excited particles is thus found to increases with time as $\sqrt{t}$. The divergent behavior of $n_E(t)$, i.e. $N_e(t) \to \infty$ for $t \to \infty$, is related to the fact that the Fermi distribution of the undisturbed electrons is assumed to remain at 0 K. However, in a practical situation the electron gas will have a finite temperature $T$. Therefore, the thermalization can be considered completed when $\langle E \rangle(t) \approx k_B T$, yielding a thermalization time $t_{th}$ of

$$t_{th} = \frac{1}{6K_{ee}(k_B T)^2} = \frac{2.2 \cdot 10^7 \text{ K}^2/\text{eV}^2}{K_{ee}T_e^2}. \quad (4.6)$$

In the approach taken above $n_E(t)$ was calculated starting from a single excitation at energy $E_0$. In Ref. [70], an approximate expression is derived for $\langle E \rangle(t)$ after optical excitation. Assuming a rectangular excitation profile, c.f. Fig. 4.1(a), the authors derive

$$N_e = 2.7E_a\sqrt{K_{ee}t} \quad (4.7)$$

$$\langle E \rangle(t) = 0.38(K_{ee}t)^{-1/2}, \quad (4.8)$$

with $E_a$ the (total) absorbed laser energy. These expression are closely identical to Eq. 4.5 when substituting $E_0$ for $E_a$, showing only a $\sim 10\%$ deviation due to the different numerical factor. From this analogy, Eq. 4.6 is also expected to be a reasonable estimate for a more realistic calculation based on a rectangular excitation profile. Note that this implies that the thermalization time is independent of the photon energy $h\nu$. In this model, only the amount of absorbed energy affects the thermalization time, Eq. 4.6, by raising $T_e$.

To verify Eq. 4.6 we also studied the thermalization process by solving Eq. 4.2 numerically. Figure 4.3 shows results of the numerical evaluation of Eq. 4.2 using a rectangular excitation profile. When a system is not in internal equilibrium, the concept of ‘temperature’ is not well-defined. In the figure the results for three different definitions are displayed:

1. $T_{e,\text{distr}} \;$, derived by a least-squares fit of $n(e)$ to the Fermi-Dirac distribution.
Fig. 4.3: Electron thermalization after sudden excitation at $\Delta t = 0$ using a rectangular excitation profile. Eq. 4.2 was numerically evaluated for three different initial temperatures $T_0$. Plotted are $T_e$ derived from a least-squares approximation to the Fermi-Dirac distribution ($T_{e,\text{distr}}$), from the slope of $n(E)$ at $E = E_F$ ($T_{e,\text{slope}}$) and from the excess energy in the system ($T_{e,E}$). The dash-dotted line represents an exponential fit to $T_{e,\text{distr}}$. The absorbed energy was chosen such as to increase the electron temperature $T_e$ by 1 K. Due to scaling of the horizontal axis the curves nearly overlap.

2. $T_{e,\text{slope}}$, derived from the slope of $n(E)$ at the Fermi level.

3. $T_{e,E}$, derived from the excess energy $E_E$ in the electron system using
   \[ T_{e,E} = \sqrt{2E_E/\gamma}. \] (4.9)

$T_{e,E}(t)$ increases instantly at $t = 0$ because it is a measure of the energy in the electron system. In contrast, $T_{e,\text{slope}}$ and $T_{e,\text{distr}}$ display a continuous increase at $t = 0$. $T_{e,\text{slope}}$ is determined by the slope of $n(E)$ at $E = E_F$, whereas $T_{e,\text{distr}}$ is also affected by excitations at higher energies. Therefore, $T_{e,\text{slope}}$ lags behind $T_{e,\text{distr}}$ as it takes time for the optically excited electrons to reach the Fermi level. Strikingly, the temperature transients calculated for different initial temperatures $T_0$ nearly overlap after scaling the time axis by $K_{ee}T_0^2$, confirming the validity of Eq. 4.6.

The dash-dotted line in Fig. 4.3 represents an exponential fit to $T_{e,\text{distr}}$, yielding a characteristic thermalization time
   \[ \tau_{th} = \frac{0.7 \cdot 10^7 \text{K}^2/\text{eV}^2}{K_{ee}T_e^2} \] (4.10)

with $T_e$ the temperature of the electron gas after thermalization. Alternatively, adopting the definition $T_{e,\text{distr}}(t_{th}) = 0.9 \cdot T_e(\infty)$ for the full thermalization time one finds
   \[ t_{th} = \frac{1.6 \cdot 10^7 \text{K}^2/\text{eV}^2}{K_{ee}T_e^2} \approx 2.3\tau_{th}, \] (4.11)
The $T^{-2}$ dependence of $\tau_{ee}$ is also found in Refs. [24, 33], but with numerical factors of $6.7 \cdot 10^7$ and $1.9 \cdot 10^7$, respectively.

Using $1/K_{ee} = 3$ fs eV$^2$ for Ni, estimated from Fig. 4.2, one finds a thermalization time of $\sim 300$ fs at 400 K. However, it can be seen in Fig. 4.2 that the experimentally determined lifetimes for Ni do not adhere to the $(E - E_F)^{-2}$ relation, showing a much slower increase of $\tau_{ee}$ with decreasing energy. The thermalization time is mostly determined by the electrons with the longest lifetime. The smaller lifetimes at low energies therefore suggest that the thermalization of Ni will actually proceed faster than calculated above. Based on the low-energy values $1/K_{ee} = 1.5$ fs eV$^2$ seems more appropriate, resulting in a thermalization time of 150 fs.

### 4.3.2 Electron-phonon scattering

The lifetime of highly excited electrons is mainly determined by e-e interactions. However, when the electrons get closer to the Fermi level $\tau_{ee}$ becomes much longer and electron-phonon scattering processes start to dominate. Collisions between electrons and phonons transfer energy between the electron and lattice system, equilibrating the temperature of both systems.

For a free-electron like metal and using the Debye approximation, the rate of change of $n(E)$ due to e-p scattering can be calculated by [24]

$$\frac{dn(E)}{dt} = \frac{2^2 \pi^2 \hbar^3 g_\infty}{m^2 K_D^2 \Theta_D q_D^4} \int_{q_D}^{q} \frac{d^3q}{4 \pi^2} E^{-\frac{3}{2}} \cdot (\cdots) + (\cdots).$$

(4.12)

with $m$ the electron mass, $g_\infty$ the electron-phonon coupling constant, $\Theta_D$ the Debye temperature, $q_D$ the Debye wavenumber, $\omega_q$ the frequency of a phonon with wavenumber $q$, and $n_q$ the occupancy of the phonon states at energy $\hbar \omega_q$. The integral runs over all phonon wavevectors, summing the contributions to $dn(E)/dt$ due to phonon absorption ($n_q$ terms) and phonon emission ($n_q + 1$ terms). Eq. 4.12 only considers interactions with longitudinal phonons, e.g. umklapp scattering is neglected.

To gain more insight we consider a simplified model, only taking into account coupling with a single phonon state $q$ at an energy $\hbar \omega_q \sim k_B \Theta_D$, and assuming a constant electron density of states. This transforms Eq. 4.12 to

$$\frac{dn(E)}{dt} = K_{ep} \cdot (\cdots) + (\cdots),$$

(4.13)

with $K_{ep}$ an appropriate constant that depends on the scattering probability and density of states. We also assume that the phonon system remains in thermal equilibrium. In thermal equilibrium, $n_q$ is given by the Planck distribution

$$n_q = \frac{1}{\exp(\hbar \omega_q/k_B T_l) - 1}.$$

(4.14)

After optical excitation, the lattice temperature $T_l$ rises by electron-phonon scattering. When an amount of energy $\Delta E$ is transferred from the electron to the phonon system, the lattice temperature increases by $\Delta T_l = \Delta E/c_l$, with $c_l$ the lattice heat capacity.
Fig. 4.4: (a) Electron thermalization and electron-phonon relaxation after sudden excitation at $\Delta t = 0$ using a rectangular excitation profile. The electron and lattice temperature transients were obtained from numerical simulation using Eqs. 4.2 and 4.13. We used parameters representative for our experiments on Ni, $c_l = 2.4c_e(300\, \text{K})$, $1/K_{ee} = 3\, \text{fs}^2\, \text{eV}^2$, and $K_{ep}$ was chosen such as to have an exponential relaxation time of 0.6 ps. The short-dashed lines represent exponential fits to the transients after electron thermalization. (b) $T_e,\text{distr.}$ transient from panel (a) with a corresponding exponential fit (short-dashed line, $\tau_E = 0.6\, \text{ps}$) and a fit to Eq. 4.15 (white dashed line, $\tau_{th} = 83\, \text{fs}$ and $\tau_E = 0.6\, \text{ps}$, nearly completely overlapping with $T_e,\text{distr.}$).

Figure 4.4 shows results from simulations using Eqs. 4.2, 4.13 and 4.14. After excitation at $\Delta t = 0$, e-e scattering thermalizes the electron distribution, increasing the number of excited electrons and raising the electron temperature. In absence of e-p scattering an equilibrium temperature $T_e = 516\, \text{K}$ is reached, as can be seen from the value of $T_{e,E}$ at $\Delta t = 0$ in Fig. 4.4(a). However, e-p scattering transfers energy from the phonon to the electron system. With the current choice of $K_{ee}$ (from Fig. 4.2), and $c_l$ and $K_{ep}$ (to mimic experimental results described later in this chapter), the e-p scattering is sufficiently rapid to prevent $T_e$ from reaching 516 K. As noted previously, the measured electron lifetimes in Ni are poorly described by Eq. 4.2 and a more rapid thermalization is expected.

In the next section we will show that after electron thermalization the energy transfer rate between electron and lattice system is proportional to $T_e - T_l$. It can be shown that in this regime the temperature transients are to good approximation described by exponential functions. The short-dashed lines in Figs. 4.4(a) and (b) represent exponential fits to the temperature transients. They yield a characteristic relaxation time $\tau_E$, c.f. Fig. 4.4(b), describing the e-p energy-relaxation after electron thermalization.

To extract the electron thermalization time from a profile such as shown in Fig. 4.4, one can use the time at which the electron temperature reaches its maximum value, $t_{ex} = 220\, \text{fs}$. Although this procedure has been used frequently in literature [5, 36, 57], $t_{ex}$ does depend on both the electron thermalization ($K_{ee}$) as well as on
the e-p scattering ($K_{ep}$). Alternatively, the data can be described by [19, 27]

$$\Delta T_{e,\text{dist}}(\Delta t) = \Delta T_1 \left[ 1 - \exp\left(-\Delta t/\tau_{th} \right) \right] \exp\left(-\Delta t/\tau_E \right) + \Delta T_2 \left[ 1 - \exp\left(-\Delta t/\tau_E \right) \right]$$

(4.15)

with $\tau_{th}$ the (characteristic) thermalization time, $\Delta T_2$ the temperature rise after e-p relaxation and $\Delta T_1$ describing the peak temperature rise. The electron temperature reaches its maximum value at

$$t_{ex} = \tau_{th} \ln \left[ \frac{\Delta T_1 (\tau_E + \tau_{th})}{(\Delta T_1 - \Delta T_2) \tau_{th}} \right]$$

(4.16)

showing the dependence of $t_{ex}$ on $\tau_E$ and $\tau_{th}$. The dashed line in Fig. 4.4(b) is a fit of Eq. 4.15 to $T_{e,\text{dist}}$, almost completely overlapping with the results from the full simulation. The fit yields a thermalization time $\tau_{th} = 85 \text{ fs}$, a value that compares well with the $\tau_{th} = 95 \text{ fs}$ derived from Eq. 4.10 using $T_e = 470 \text{ K}$ and $1/K_{ee} = 3 \text{ fs eV}^2$. The value $\tau_{th}$ thus obtained is independent of the e-p scattering rate. Therefore, we will employ this procedure for the analysis of our experiments.

In Fig. 4.4 the system was excited by a laser pulse of infinitesimal duration. However, experimentally the laser pulses have a finite width. We verified that Boltzmann calculations using Gaussian pulses give results that are nearly identical to calculations employing a delta excitation, when afterwards the transients are broadened with a Gaussian. Therefore, Eq. 4.15 can be used to describe experimental data after broadening it with the pump-probe crosscorrelation.

### 4.3.3 Two-temperature model

When the electron and lattice systems are both in internal equilibrium, a two-temperature model (2TM) can be used to describe their transient behavior. In the 2TM, depicted in Fig. 4.1(b), the electron-phonon interactions are lumped in one linear coupling term $g_{el}(T_e - T_l)$. This yields a set of coupled equations for the time-evolution of $T_e$ and $T_l$:

$$c_e(T_e) \frac{\partial T_e}{\partial t} = -g_{el}(T_e - T_l) + P(t),$$

$$c_l(T_l) \frac{\partial T_l}{\partial t} = g_{el}(T_e - T_l).$$

(4.17)

$P(t)$ is the source term describing the laser heating of the electron system, $c_e$ and $c_l$ are the electron and lattice heat capacity, respectively, and $g_{el}$ is the electron-phonon coupling constant. In introducing Eqs. 4.17 it is assumed that electron and lattice system remain in internal thermal equilibrium. This, in itself, is not trivial. For example, electrons mainly scatter with high-$q$ phonons. Without sufficiently rapid p-p scattering, a non-thermal phonon distribution is created [72]. Equation 4.17 does not account for heat diffusion or a laser absorption profile, and is thus only valid for optically thin films on insulators. Descriptions including transport do however exist [38, 67]. In the 2TM, the coupling between electron and lattice system is assumed linear. In the next part this assumption is checked, and models for the electron and lattice heat capacity are presented.

To derive the e-p coupling constant from Eq. 4.12 or Eq. 4.13 we need to calculate the rate of change of the energy in either the electron or lattice system as a function
of their temperature difference. In the simplified model, Eq. 4.13, this rate can be written as

\[
\frac{c_l(T_l)}{dT_l} = K_{ep} h \omega_q \int_{-\infty}^{\infty} (n_q + 1)n(E)[1 - n(E - h \omega_q)] - n_q n(E)[1 - n(E + h \omega_q)]dE,
\]

with the \( n_q \) term signifying phonon absorption and the \( n_q + 1 \) term phonon emission.

When electron and lattice system are both in internal thermal equilibrium, \( n(E) \) and \( n_q \) are given by the Fermi-Dirac and Planck distribution. Substitution in Eq. 4.18 gives

\[
\frac{c_l(T_l)}{dT_l} \approx K_{ep} h \omega_q k_B (T_e - T_l).
\]

The last expression yields the linear relationship used in the 2TM, resulting in a coupling constant

\[
g_{ep} = K_{ep} h \omega_q k_B.
\]

The approximations made in deriving Eq. 4.19 are valid for \( k_B T_e \gg h \omega_q \) and \( k_B T_l \gg h \omega_q \). Since \( h \omega_q \leq k_B \Theta_D \), these constraints can also be written as \( T_e \gg \Theta_D \) and \( T_l \gg \Theta_D \). Also, the full model, Eq. 4.12, yields a linear relationship in this limit, with \( g_{ep} \) equal to \( g_\infty \). For Ni, the Debye temperature is 450 K [49], i.e. of the same order as the electron and lattice temperatures probed in the experiments (300 – 500 K). It can be shown that even in this regime \( g_{ep} \), as calculated with Eq. 4.12, is constant within 6%, but about 10% lower than \( g_\infty \) [33].

The observed dynamics also depend on the electron and lattice heat capacities, which are generally a function of temperature. For a free electron metal, \( c_e \) is given by

\[
c_e(T_e) = \gamma T_e
\]

with \( \gamma \) a constant that depends on the electron density and Fermi temperature [49]. The specific lattice heat capacity (per mole) can be described using the Debye model,

\[
c_l(T_l) = 9 N_A k_B \left( \frac{T}{\theta_D} \right)^3 \int_{0}^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx,
\]

with \( N_A \) the Avogadro constant and \( \theta_D \) the material-dependent Debye temperature [49]. At low temperature Eq. 4.22 predicts a strong, \( T^3 \), temperature dependence. For \( T \gg \theta_D \) the lattice heat capacity approaches the classical value of \( 3 N_A k_B \).

When \( c_e \) and \( c_l \) are reasonably temperature independent in the temperature range probed, Eqs. 4.17 can be solved exactly. It follows that \( T_e(\Delta t) \) and \( T_l(\Delta t) \) can be described by simple exponential functions with a characteristic time

\[
\tau_E = \frac{c_e c_l}{c_e + c_l} g_{ep}^{-1},
\]

see e.g. the dotted curves in Fig. 4.4.

Knowing the coupling constant \( g_{el} \) and the heat capacities \( c_e \) and \( c_l \), one can simulate the relaxation process. For Ni, low temperature heat capacity measurements yield a \( \gamma \) of \( 1.1 \cdot 10^3 \) J/m\(^3\)/K\(^2\) [30]. Given the total heat capacity \( c_{tot} \) at room
temperature of $4.0 \cdot 10^6$ J/m$^3$/K one can derive $c_l(300 \text{ K}) = 3.7 \cdot 10^6$ J/m$^3$/K and $c_e(300 \text{ K}) = 0.3 \cdot 10^6$ J/m$^3$/K, i.e. for Ni at room temperature $c_l$ is a factor of ten larger than $c_e$. Note that this approach neglects possible magnetic contributions to the heat capacity.

Figure 4.5(a) shows temperature transients as calculated with the 2TM using the above values and $g_{el} = 180 \cdot 10^{16}$ W/m$^3$/K. The electron temperature shows a sharp peak upon heating while the lattice remains unaffected. The coupling between electron and lattice system then decreases this difference until the equilibrium value is reached. The sharp peak in $T_e$ is caused by the low electronic heat capacity compared to the lattice heat capacity. For small changes in $T_e$, i.e. neglecting the temperature dependence of $c_e$, the ratio of the peak value of $\Delta T_e$ and its equilibrated value is given by $\Delta T_{e,\text{peak}}/\Delta T_{e,\text{eq}} = (c_e + c_l)/c_e = 13$. The simulation shown in Fig. 4.5(a) yield a smaller ratio $\Delta T_{e,\text{peak}}/\Delta T_{e,\text{eq}} = 7$. This is related to the large rise in $T_e$. The increase of $c_e(T_e)$ with temperature reduces $\Delta T_{e,\text{peak}}$ compared to the value expected on the basis of a constant electronic heat capacity.

In pump-probe experiments on Ni much lower ratios $\Delta T_{e,\text{peak}}/\Delta T_{e,\text{eq}}$ are found than expected on the basis of the literature values used in the simulation in Fig. 4.5(a). This issue will be discussed in Sect. 4.4.4. Figure 4.5(b) shows results of 2TM calculations using a set of parameters that better describe the experimental results. Also added are transients calculated within the Boltzmann model. Comparing the
2TM and $T_{e,\text{dist}}$, the effects of a finite thermalization time are evident. However, using the excess energy in the electron system as a measure for the temperature, represented by $T_{e,E}$, a very good correspondence is found. Actually, this means that for the parameters used the 2TM reproduces the heat-exchange between electron and phonon system surprisingly well, even for times $t < t_{th}$.

### 4.3.4 Transport effects

For an accurate interpretation of the electron and magnetization dynamics one should also consider the effect of energy transport out of the illuminated region. The highly energetic electrons excited by an optical pump pulse ($\sim 1.6$ eV) will initially travel ballistically with speeds in the order of the Fermi velocity. In pump-probe experiments on Au this ballistic transport is found to redistribute the energy over a distance of around 100 nm at room temperature [37]. For Ni no experimental pump-probe data is available. In Ref. [38] the electron mean free path is estimated by

$$\Lambda = 3 \cdot \frac{K}{(cLv_l)}. \quad (4.24)$$

with $K$ the heat conductivity, $c_l$ the lattice heat capacity and $v_l$ the speed of longitudinal phonons. For Ni, this yields $\Lambda = 11$ nm. Electrical conductivity measurements on in GMR structures [28] yield mean free paths $< 10$ nm for most 3d-ferromagnets.

After electron thermalization the electron system is still not in equilibrium with the lattice. In this regime the energy transport is governed by the thermalized – though still hot – electrons in a cold lattice, resulting in a diffusion that is generally faster than that of a fully equilibrated system. This type of transport can be accounted for by combining the 2TM with a diffusion model, see e.g. Eq. 3.1, adding a diffusion term to both the electron and the lattice system [38]. For metallic systems the thermal conductivity of the electron system is generally dominant, showing a larger value of $\Lambda$ at increased electron temperature. Only after electron-phonon relaxation the equilibrium thermal diffusion is recovered.

To eliminate transport effects on the dynamics one can use optically thin films on insulating substrates. In this case the pump-induced heating will be uniform throughout the depth of the film and the electron-mediated heat transport will be efficiently blocked by the insulator. The Si/SiO$_2$/Ni and Si/Si$_3$N$_4$/Ni structures described in Chap. 3 are examples of such structures.

### 4.3.5 Summary

In this section the electron and lattice dynamics after optical excitation have been theoretically investigated. Taking a least-squares approximation to the electron distribution to define the electron temperature $T_e$, a characteristic thermalization time $\tau_{th}$ could be defined. $\tau_{th}$ is proportional to $T_e^{-2}$, and, using a value of $1/K_{ee} = 1.5$ fs eV$^2$ for Ni, a (90%) thermalization time $t_{th} \approx 2.3\tau_{th}$ of 150 fs is expected ($T_e = 400$ K). Despite the complex dynamics, after thermalization the electron and lattice temperature transients are well-described within a simple two-temperature model. To determine the thermalization time from experimentally measured electron temperature transients, we use Eq. 4.15.
4.4 Spin dynamics

In pump-probe experiments on magnetic materials not only the electron and lattice system are affected by the optical excitation, but also the magnetization is influenced. In this section we discuss microscopic and more phenomenological approaches to understand the magnetization dynamics. Also, the model we used to analyze our experimental data will be presented.

4.4.1 Paths leading to the reduction of the magnetization

As was discussed in Sect. 4.3, the absorption of a laser pulse creates highly excited electrons. The lattice (or phonon) system, however, is initially unaffected. Subsequently, electron-electron scattering restores the Fermi-Dirac distribution and electron-phonon scattering balances the electron and lattice temperature. In magnetic materials, the laser heating also results in a reduction of the magnetic (spin-)moment. Using the separation in an electron and a lattice system, this reduction can be achieved in two ways. First, the net spin moment can be reduced by interactions with the electron system, i.e. by spin flip scattering via electron-electron interactions. Second, interactions between the lattice, i.e. phonons, and the electron spin can change the magnetization.

The first path describes purely electronic processes. Microscopically, the interactions are caused by the spin-orbit (SO) coupling:

\[ H_{SO} = \lambda \vec{L} \cdot \vec{S} = \lambda \left[ L_z S_z + \frac{1}{2} (L^+ \cdot S^- + L^- \cdot S^+) \right], \tag{4.25} \]

with \( \vec{L} \) and \( \vec{S} \) orbital and spin momentum operators and \( \lambda \) a constant describing the strength of the interaction. Due to the spin-orbit interactions, the spin-up and spin-down states are mixed, introducing a finite spin flip probability. The righthand part of Eq. 4.25 explicitly shows the momentum conservation by using the ladder operators \( S^\pm \) and \( L^\pm \). Through SO interaction the spin expectation value can be raised \((S^+)\) if simultaneously the orbital momentum is lowered \((L^-)\) and vice versa. Interestingly, the conservation of angular momentum allows a maximum reduction of the magnetization with only \( \sim 50\% \), as will be shown by the following analysis. The local magnetic moment of a material is given by

\[ \vec{\mu} = \vec{L} + g \vec{S}, \tag{4.26} \]

with an electron \( g \) factor of approximately 2, while the total angular momentum \( \vec{J} \) can be written as

\[ \vec{J} = \vec{L} + \vec{S} \tag{4.27} \]

Without coupling to the lattice and neglecting the small photon contribution to the angular momentum \( \vec{J} \) is conserved. Therefore a transfer of \( \vec{S} \) (responsible for 90% of the magnetic moment in Ni) to \( \vec{L} \) can maximally reduce \( \vec{M} \) with \( \sim 50\% \). Interactions with the lattice thus are required to absorb the angular momentum and further reduce \( M \).

It must be noted that following the same momentum conservation argument electron-magnon scattering can not reduce the magnetization when \( \vec{L} \) remains constant. In an electron-magnon scattering event the spin of an electron is changed by
creation or absorption of a magnon, i.e. a collective spin excitation. This collective excitation does however carry the change in spin moment of the electron, and therefore the total spin moment remains unchanged.

As was argued above, interactions within the electron system can not fully reduce the magnetization. Therefore, also interactions with the lattice are needed. This is nicely demonstrated by the Einstein-de Haas experiment. In the experiment, a bar magnet, which is suspended from a thin wire, starts to rotate when its magnetization is reversed. Altering the magnetization implies a change of spin momentum. Since the total angular momentum is conserved, this requires a transfer of spin to orbital momentum, inducing a rotation of the magnet.

### 4.4.2 Microscopic models

So far, a thorough theoretical understanding of the interactions involved in the laser-induced demagnetization is missing. Here we will discuss two microscopic models to describe the laser-induced demagnetization time. One is based on spin-lattice interactions, the other describes a purely electronic mechanism.

To explain the $\sim 80$ ps demagnetization time on Gd, reported in Refs. [74, 75], Hübner et al. investigated spin-lattice relaxation as the main route for spin scattering [40]. In their work, a relation is derived between the spin-orbit induced magnetocrystalline anisotropy energy (hundreds of $\mu$eV) and the spin-relaxation time. The calculated value of 48 ps was in good agreement with the experimental results available halfway the 1990’s.

As is known now, however, the magnetic response occurs at least two orders of magnitude faster. Later, the same group investigated purely electronic, SO induced mechanisms in an attempt to derive the sub-picosecond response [41, 84, 85]. Numerically solving an approximate Hamiltonian that describes ferromagnetic Ni, the temporal response of the system on excitation is investigated. Interactions with the lattice are not considered. In Ref. [85] the coupling with the electric field of the pump pulse is explicitly taken into account by adding it to the model Hamiltonian. Together with the effect of SO coupling this is shown to result in an ultrafast demagnetization upon laser excitation. The effect is explained by the SO coupling that mixes singlet and triplet states, allowing the laser field to induce transitions that change the spin moment. Ferromagnets have most of their high-spin states close to the ground state while the low-spin states mainly appear at high energies. In this picture absorption of a laser pulse will therefore directly reduce the net spin moment. With increasing pump intensity a maximum reduction of the magnetization of 50% could be achieved within 20 fs, using 10 fs laser pulses. The maximum reduction of 50% looks remarkably similar to the number reported in Sect. 4.4.1, which was based on angular momentum conservation arguments. The authors, however, attribute this limit to a bleaching effect, i.e. the material became transparent for larger intensities. Altogether, it can be concluded that a satisfactory interpretation of the sub-picosecond demagnetization is still lacking.

### 4.4.3 Three-temperature model

Rather than aiming at a microscopic interpretation, one might try to come to a phenomenological description of the interaction of the spins, electrons and lattice at a short time scale. Figure 4.6 presents a conceptual picture of the processes upon
laser excitation of a ferromagnetic material. After laser excitation, a non-equilibrium electron distribution is excited in the spin-up and spin-down band (I). Neglecting the small angular momentum carried by the phonons, the number of spin-up and spin-down electrons remains the same. Subsequently, the electron gas thermalizes (II), and electron-phonon scattering will balance the electron and lattice temperature (III). In this example, spin scattering is assumed to proceed slow compared to \( \tau_{th} \) and \( \tau_E \). In the final stage (IV) the magnetization is reduced, decreasing the difference between the number of spin-up and spin-down electrons.

Beaurepaire et al. [5] introduced a phenomenological 3TM to describe the dynamics after electron thermalization. This model, schematically depicted in Fig. 4.7, is based on the separation in three subsystems: the electron, lattice and spin system. It is thus closely related to the 2TM described in Sect. 4.3. The interaction with the electric field of the pump pulse proceeds through the electrons and since the optical transitions will (mostly) preserve the spin only the electron system is heated. After thermalization of the electron system a thermodynamic temperature can be defined for each of the subsystems. The spin temperature \( T_s \) is related to the magnetization through the (equilibrium) \( M(T) \) relation, i.e. \( M(T_s(\Delta t)) = M_{\text{transient}}(\Delta t) \). The temperature difference between the electron, lattice and spin systems will act as a driving force for energy transfer. Assuming a linear response, a set of coupled differential equations can be derived to describe the temperature evolution of the three systems upon laser heating:

\[
\begin{align*}
c_e(T_e) \frac{\partial T_e}{\partial t} &= -g_{el}(T_e - T_l) - g_{es}(T_e - T_s) + P(t), \quad (4.28) \\
c_l(T_l) \frac{\partial T_l}{\partial t} &= -g_{el}(T_l - T_e) - g_{sl}(T_l - T_s), \quad (4.29) \\
c_s(T_s) \frac{\partial T_s}{\partial t} &= -g_{es}(T_s - T_e) - g_{sl}(T_s - T_l). \quad (4.30)
\end{align*}
\]

\( c_i(T_i) \) represents the (temperature dependent) heat capacity of system \( i \), \( P(t) \) is the
laser source term and $g_{ij}$ represents the coupling constant between two baths $i$ and $j$. In introducing Eqs. 4.28-4.30, it is assumed that all systems remain in internal thermal equilibrium.

Models for the temperature dependence of the electron and lattice system were already presented in Sect. 4.3. The spin contribution to the heat capacity appears at low temperatures as a small, $T_s^3/2$ dependent term that follows from spinwave excitations [30, 49]. At higher temperatures, $c_s$ shows up as a rapid increase of the total heat capacity up to the Curie temperature, followed by a steep drop.

Beaurepaire et al. derived $c_s(T)$ from the experimental total heat capacity $c_{\text{tot}}$. In their approach they choose $\gamma = 6 \times 10^3 \text{ J/m}^3\text{K}^2$ as it most correctly described the experimental data. Next, the lattice heat capacity was calculated by $c_l = c_{\text{tot}}(300 \text{ K}) - c_e(300 \text{ K}) = 2.2 \times 10^6 \text{ J/m}^3\text{K}$. $c_l$ was assumed temperature independent, which is a fair approximation for temperatures close to and above the Debye temperature. Finally, the spin contribution $c_s(T_s)$ was determined from the experimental heat capacity by subtracting the contributions from the lattice and electrons. Below, this choice of parameters is discussed in more detail.

### 4.4.4 This work

In the first ultrafast demagnetization experiments by Beaurepaire et al., a sizeable delay between the electron and spin response was observed. To describe the dynamics, the authors introduced a 3TM, allowing for a delayed response of the spin system. However, later experiments published by this and other groups generally showed a very similar behavior of the electron and spin temperature transients. In Ref. [36], Hohlfeld et al. even suggested a direct connection between the magnetization and electron temperature, i.e. $g_{es}/c_s = \infty$ and therefore $M(t) = M[T_e(t)]$.

In this work we will use a three-temperature model. However, it is experimentally found that the spin temperature transients are only slightly delayed with respect to the electron temperature. It therefore appears that electron-spin scattering is the dominant route for the loss of magnetization. Since the electron-spin scattering is
extremely rapid, we use a simplified three-temperature model (S3TM),
\[
c_e(T_e) \frac{\partial T_e}{\partial t} = -g_{el}(T_e - T_l) + P(t) \tag{4.31}
\]
\[
c_l(T_l) \frac{\partial T_l}{\partial t} = g_{el}(T_e - T_l)
\]
\[
\frac{\partial T_s(t)}{\partial t} = \tau_M^{-1} [T_e(t) - T_s(t)].
\]
The electron and lattice temperature transients are described within a 2TM. The 2TM is extended with a spin bath, characterized by a spin temperature that follows the electron temperature with a characteristic delay \(\tau_M\). For \(\tau_M \to 0\) the relation \(T_s = T_e\) is recovered. In the coupling with the spin system the spin contribution to the heat capacity is neglected. In passing, we want to note that before electron thermalization \(T_e\) strictly has no meaning. During thermalization, \(T_e\) should be considered as a measure of the excess energy in the electron system, i.e. \(T_{e,E}\), as shown in Fig. 4.5. Therefore, \(\tau_M\) also includes a possible delay in the magnetic response due to thermalization of the electrons system. The above model will be used to compare experimental temperature and fluence dependencies with calculated results.

An important point in using either the 2TM or the 3TM is the choice of parameters \(c_{ij}\), \(g_{ij}\) and their temperature dependence. We discuss here the case of ferromagnetic Ni. In Fig. 4.5(a) a two temperature simulation was plotted using the (low-temperature) literature value for \(\gamma\) of \(1.1 \cdot 10^3\) J/m\(^3\)/K, showing a large peak in \(T_e\). However, experimentally a much more modest peak is observed, see e.g. [36]. Beaurepaire et al. accounted for that in their 3TM by using \(\gamma = 6 \cdot 10^3\) J/m\(^3\)/K. The same approach was followed by Regensburger et al. in Ref. [60] to describe magneto-optic transients in a 2TM, also using \(\gamma = 6 \cdot 10^3\) J/m\(^3\)/K. The discrepancy with the low-temperature value was attributed to strong singularities in the density of states of Ni near the Fermi level that become predominant at elevated temperatures. It must be noted that the assumed linear temperature dependence of \(c_e\) may not be valid if such effects exist.

In Fig. 4.8 the experimental total heat capacity \(c_{tot}\) of Ni is plotted. The drop in \(c_{tot}\) at the Curie temperature (627 K) is evident and shows the effect of magnetic contributions to the heat capacity. In the figure also a calculation of the sum of the electronic and lattice heat capacity is shown by the curve labeled \(c_{el+l}\), using Eqs. 4.21 and 4.22, and literature values \(\gamma = 1.1 \cdot 10^3\) J/m\(^3\)/K and \(\theta_D = 450\) K. For \(T > T_C\) the correspondence is good, but in the ferromagnetic regime the calculated values are too low. When using \(\gamma = 6.0 \cdot 10^3\) J/m\(^3\)/K and a constant \(c_l\), as in Refs. [5, 60], the short-dashed line is found. This value for \(\gamma\) largely overestimates the experimental temperature dependence of \(c_{tot}\), especially when the spin heat capacity is considered separately as in Ref. [5].

In this work \(\gamma\) is taken \(3.8 \cdot 10^3\) J/m\(^3\)/K\(^2\) and \(c_l = 2.8\) MJ/m\(^3\)/K, correctly reproducing our experimental results and the experimental total heat capacity (long-dashed line in Fig. 4.8). The value for \(\gamma\) should be seen as an ‘effective’ value, since it also includes magnetic contributions to the heat capacity. The lattice heat capacity is considered constant, a reasonable approximation since Eq. 4.21 predicts a maximum variation of 7% in the experimental temperature range of 300 to 500 K. In passing, we want to note that \(c_l\) represents the full lattice heat capacity, although electrons couple most efficiently to longitudinal phonons [33, 72]. It is therefore implicitly assumed that the energy is rapidly redistributed over all phonon modes.
Fig. 4.8: Experimental total heat capacity $c_{\text{tot}}$ of Ni [30] and the sum of the electronic and lattice heat capacity, Eqs. 4.21 and 4.22, using the (low temperature) literature values of $\Theta_D = 450$ K and $\gamma = 1.1 \cdot 10^3$ J/m$^3$K ($c_{\text{EL}}$). Also plotted is $\gamma T + c_l$ for two values of $\gamma$ and with $c_l$ a constant chosen to reproduce $c_{\text{tot}}$ at 300 K. Short dash: $\gamma = 6.0 \cdot 10^3$ J/m$^3$K. Long dash: $\gamma = 3.8 \cdot 10^3$ J/m$^3$K.

Finally, we want to note that the theoretical models for the heat capacity, Eqs. 4.21 and 4.22, were derived for a material at a constant volume. On the other hand, in equilibrium experiments generally the heat capacity at constant pressure $c_p$ is measured\(^1\). For Ni at temperatures below 500 K $c_p$ and $c_V$ are identical within 4\% (with $c_p > c_V$), a difference that is expected to play a minor role in the interpretation of the experimental data. Correcting the theoretical heat capacity curve $c_{\text{EL}}$ in Fig. 4.8 to $c_p$ values it is found that the theory actually overestimates the heat capacity for $T > 700$ K [79]. A much larger value for the purely electronic $\gamma$ therefore seems unjustified.

### 4.4.5 Summary

Up to now, a thorough theoretical understanding of the light-induced demagnetization process is still lacking. In this section microscopic and phenomenological models were presented to describe the demagnetization process. Also the model used in this work to analyze experimental results was introduced. It allows us to link the electron

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\(^1\) In ultrafast pump-probe experiments $c_V$ is the proper quantity before significant lattice expansion has occurred.
Fig. 4.9: Schematic representation of the density of states (DOS) of an sp-like metal. The d-band (dark grey) is completely filled and lies below the Fermi level. The states near the Fermi level ($E_F$) have an sp-character. In optical experiments the photon energy at which transitions from d-states to unoccupied sp-states become possible is known as the interband transitions threshold (ITT).

dynamics with the spin dynamics, and to quantify the delay of the spin system with respect to the excess energy in the electron system.

4.5 Experimental techniques

In this work optical pump-probe techniques are used to determine the spin and electron dynamics. The spin dynamics is measured using the magneto-optical Kerr effect and the electron dynamics by measuring transient reflectivity changes. This section discusses various experimental techniques to measure electron and spin dynamics, including the transient reflectivity and MO Kerr measurements we have employed.

4.5.1 Measuring electron dynamics

Transient electron dynamics is mostly studied by time-resolved reflectivity or transmission experiments [8, 19, 24, 38, 68]. The interpretation of these transients is however only well-established on sp-like metals that have their d-bands well below the Fermi level, as depicted in Fig. 4.9. Since the part of the dielectric constant that is determined by sp-intraband excitations usually has a weak electron temperature dependence, d-sp interband transitions are used to probe the electron dynamics. Heating of the electron population causes a modification in the electron distribution function close to the Fermi level, thereby changing the interband absorption spectrum. The photon energy at which transitions from low lying d-bands to sp-like states near the Fermi level start to play a role is given by the interband transition threshold (ITT). Two approaches are used to measure the electron dynamics:

1. Off-resonance probing. When the probe photon energy is well below the ITT, it can be shown that at any time after application of the pump pulse the induced change in the real part of the dielectric constant $\Delta \epsilon' (\Delta t)$ scales with the change in excess energy $\Delta E_E$ in the electron system [24]. For $\Delta E_E/E_E \ll 1$, $\Delta E_E \propto \Delta T_{e,E}$, c.f. Eq. 4.9, and thus $\Delta \epsilon' \propto \Delta T_{e,E}$. 
2. Resonant probing. When the probe photon energy is tuned close to the ITT, the change in the real and imaginary part of the dielectric constant is proportional to $\Delta T_{e,\text{dist}}$ [62]. At higher excitation densities and less favorable probe energies deviations from this linear behavior can occur [38]. Using the resonant technique, thermalization of the highly excited electron distribution can be observed as a delayed response of the transmission/reflectivity transients [19, 68].

Thus, during electron thermalization contrasting reflectivity transients can be measured, depending on the resonance condition. In thermal equilibrium ($t \gg \tau_{th}$), and for a moderate excitation density, both methods yield a value proportional to $\Delta T_e$. The difference between (1) and (2) is therefore mainly the absence of a thermalization effect in the off-resonance approach. When studying the (ambient) temperature dependence the difference is however important, since the increase in electron temperature is affected by the electronic heat capacity while the excess energy is not.

To determine the electron dynamics in (magnetic) 3d-transition metals, the same techniques are generally used as for the sp-like metals. However, the interpretation of these data may be much more complicated. For example, the ferromagnetic 3d-metal Ni has spin-split d-bands. The top of the majority d-band lies about 0.3 eV below the minority band intersects with the Fermi level. The simple analysis in the form of d-sp interband transitions described before is thus not valid for this system. Also, electron thermalization may proceed differently in the two spin bands since the electron life time is spin-dependent [50]. The different character of the thermalized electrons in the spin-up and spin-down band may also cause a spin-dependence in the electron-phonon scattering rate.

Despite the potential difficulties in the analysis of the transient reflection, transmission or SHG yield data it is generally assumed that the observed effect is proportional to the temperature of the thermalized electron distribution. This seems to be confirmed by the observation of a delayed response of about 260 fs for Ni [5, 36] and 120 fs for CoPt$_3$ [27] reflecting the electron-electron thermalization time. However, Melnikov et al. [57] showed that SHG on Ni is actually much more complicated, with a significant dependence of the observed time-dependence of the response on the polarization of both the pump and probe polarization. The latter effect was explained by a different sensitivity to surface and bulk contributions when using a different probe polarization.

Of particular interest are data presented in Ref. [7] and reproduced in Fig. 4.10. By analyzing both transient reflectivity and transient transmission data on Ni, changes in the real and imaginary part of $\epsilon$ could be separated. A similar recovery was found for $\epsilon'$ and $\epsilon''$, but only in $\epsilon''$ the nonthermal electron population was visible as a sharp peak near $\Delta t = 0$. This difference was attributed to a different contribution of intraband and interband transitions to $\Delta \epsilon'$ and $\Delta \epsilon''$. Thus, even at a single photon energy $\epsilon'$ and $\epsilon''$ give a different view on the electron dynamics.

An alternative to optical reflection/transmission techniques to determine the electron dynamics is time-resolved photoemission spectroscopy. This pump-probe technique employs a pump pulse of moderate photon energy to heat the electron system, and a UV probe pulse to excite carriers from near the Fermi level to the vacuum level. Using an energy sensitive detection scheme of the photoemitted carriers the electron distribution $f(E)$ around the Fermi level can directly be followed in time. This way the electron thermalization and the e-p scattering processes can be determined from the transient changes in $f(E)$. The method has been applied, e.g., to gold [16, 17],
silicon [23] and carbon nanotubes [31]. We are, however, not aware of similar measurements on 3d-transition metals. It may be that their complicated bandstructure around the Fermi level makes them unsuitable for the photoemission technique.

4.5.2 Measuring spin dynamics

To probe the sub-picosecond magnetization dynamics upon laser heating, a limited number of techniques exists. In linear magneto-optical Kerr studies, and using a pump-probe configuration, the polarization $\psi$ of the reflected probe pulses is measured at a certain time-delay after pump excitation. $\psi$ is related to the magnetization of the material by the MO Kerr effect. Also most other studies on the demagnetization dynamics have employed MO effects, using either the linear or second harmonic Kerr effect. The only study employing a non-optical technique to measure the magnetization is the pump-probe photoemission experiment by Scholl [63], described in Sect. 4.2. In this work we will fully concentrate on the linear MOKE.

In Sect. 2.2 it was argued that $\psi$ shows a linear relation with a projection of $\vec{M}$, e.g. in polar MOKE $\psi \propto M_z$. In time-resolved experiments, whether using linear or second harmonic MO techniques, this is used to derive the magnetization dynamics. However, one must be very cautious extrapolating equilibrium MO-concepts to the highly excited situation that exists shortly after pumping the material. Magneto-optics is rather an indirect way of probing the magnetization, using the relatively small spin-orbit induced orbital momentum to obtain information on the electron spin system. In Sect. 4.7 data are presented that show that transient MO measurements do not necessarily reflect the magnetization dynamics.

In this section a generally neglected aspect of magneto-optics is considered: the use of MO techniques to measure the temperature dependence of the magnetization. The equilibrium MO effect at a fixed temperature is linear in $M$ and thus reproduces the hysteresis loop $M(H)$, e.g. in polar MOKE $\psi(H) \propto M_z(H)$. It is, however, not necessarily true that the MOKE is a suitable technique to measure the temperature dependence of the magnetization $M(T)$. In the low-temperature regime the reduction of magnetization with temperature can be described by the excitation of long-wavelength magnons. Within this approach, the temperature dependence of the
magnetization is given by the Bloch $T^{3/2}$ law

$$\frac{\Delta M(T)}{M(0)} = cT^{3/2},$$  

(4.32)

in agreement with experimental low temperature data [49]. However, at higher temperatures also the reduction of the exchange splitting $\Delta E_{ex}$ between the spin-up and spin-down bands should be taken into account when considering the MO response. Although it is still a matter of debate whether for transition metals, such as Ni, $\Delta E_{ex}$ is zero at the Curie temperature [55] or that at $T_C$ only the long-range order is lost [52], the exchange splitting is certainly reduced with increasing temperature.

This poses an interesting problem for time-resolved MO measurements. In the magnon-model the band structure of the ferromagnet remains unchanged, but the direction of the magnetization (and thus the quantization axis) varies on a microscopic scale due to the magnetic excitations. In this situation the temperature dependence of the macroscopic MO signal simply reflects the average magnetization.

However, when the exchange splitting changes with temperature the complete bandstructure of the material becomes temperature dependent, directly altering the optical transitions and thus the observed Kerr effect as well. In this case a simple linear relation between $M(T)$ and $\psi(T)$ may no longer be valid. Di and Uchiyama [9, 13] found a 35% increase in the polar MO rotation of Ni at a photon energy $h\nu = 3.2$ eV when cooling from 300 to 84 K, a value clearly not corresponding to the increase of just 4% in magnetization. Theoretical spectra calculated by Oppeneer [9] reproduce this non-linear behavior in magnetization when the exchange splitting is considered temperature dependent. The effect does, however, strongly depend on wavelength.

We explicitly checked that the MO Kerr effect at 780 nm (1.6 eV) measured on Ni films does correctly reproduce the magnetization as a function of temperature. Figure 4.11 shows a comparison between the temperature dependence of the Kerr ellipticity and SQUID measurements. Using the SQUID, a quantitative measure of the net sample magnetization can be obtained as a function of applied field and temperature. The Kerr measurement is scaled to overlap the SQUID data since the MO effect does not yield an absolute value of the magnetization. In the shared temperature range, limited by the maximum temperature of 90° C for the SQUID and the room temperature minimum for the Kerr measurement, slopes $M^{-1}dM/dT$ of 0.0014/K and 0.0016/K are found for the SQUID and MOKE measurements, respectively. The reasonably good correspondence validates the used of the MO technique for this specific system to monitor the temperature dependence of the magnetization.

The measured relation between MO effect and temperature can also be used to 'calibrate' the time-resolved MO experiments and express the results as a spin temperature $T_s$. This approach will be used in the analysis of the TRMOKE experiments, and is also valid when $\psi(T)$ is not proportional to $M(T)$.

4.5.3 Summary

In this section experimental techniques were presented to measure the transient electron and spin dynamics following optical excitation. We will use time-resolved reflectivity measurements to probe the electron dynamics, interpreting (with care) the change in reflectivity as a measure of the electron temperature. The magnetization dynamics is studied by the time-resolved MO-Kerr effect.
Fig. 4.11: Comparison of the temperature dependent magnetization of nickel obtained with SQUID and using the MO Kerr effect [Si/Si$_3$N$_4$(60)/Ni(10)/Cu(3)].

4.6 Transient reflectivity measurements

In this section transient reflectivity data are used to determine the electron-phonon relaxation rate in Ni films. It is found that lattice expansion greatly influences the reflectivity, and in some structures also contributions from the substrate play an important role.

4.6.1 Experimental

All experiments were performed on Ni thin film samples, described and analyzed in Sect. 3. In order to avoid ballistic and diffusive transport effects as much as possible, we focus on samples with an insulating substrate. All results are obtained at room temperature, unless specified otherwise. We used laser pulses of 1.6 eV with a FWHM of 85 fs. In the analysis of the data, broadening due to the finite length of the laser pulses is explicitly taken into account.

Two different configurations were used to measure the generally small transient reflection changes. In Sect. 2.3.1 it was found that for a 45° orientation of the PEM the ‘2f’ signal is strongly dependent on the reflective properties of the sample, see e.g. Eq. 2.17. The modulation of both pump and probe beam makes this method very insensitive to scattering of pump light into the detector. It is therefore well-suited when it is difficult to suppress scattered pump light. The method yields a value proportional to a linear combination of changes in $r_s$ and $r_p$.

In a more straightforward approach, applicable when there is no significant pump scattering towards the detector, the pump beam is modulated with a chopper and the induced intensity changes in the reflected probe are detected using a lock-in scheme.
This scheme simply yields a value proportional to the change in reflectivity, $\Delta R$.

4.6.2 Thermalization

Figure 4.12(a) shows results of transient reflectivity measurements using both techniques on a 10 nm Ni film on a Si/Si$_3$N$_4$(60) substrate. In the figure the relative
change in reflectivity, $\Delta R/R$, is plotted versus pump-probe delay $\Delta t$ for the first 0.6 ps. During pump-probe overlap the PEM technique and the direct measurement yield different results. This is related to a coherent process, i.e. a non-linear optical process in which both pump- and probe-photons are involved and that is described by the third-order optical susceptibility. The coherent process is found to affect the polarization of the probe. Magnitude and shape of the coherent effect depend on the chirp of the laser pulses. Such chirp dependencies will be analyzed in more detail in Sect. 4.7.3.

After the coherent process the two techniques yield the same results, showing that both give the same view on the electron dynamics. The $2f$ signal and the directly measured reflectivity reach a minimum after 190 fs. The delayed minimum in reflectivity suggests that the method is mainly sensitive to thermalized electrons, i.e. resonant probing of $T_{e,distr}$. In case of a high sensitivity to non-thermal electrons, or when measuring the excess energy, an instantaneous response would have been expected.

Combining different reflectivity measurements, the extremum is found at $t_{ex} = 200 \pm 20$ fs, using pulses of 85 fs. This is somewhat faster than other values reported on Ni, e.g. of 260 fs (Ref. [5] using 60 fs pulses) and 280 fs (Ref. [36] using 150 fs pulses and SHG). Although the position of the extremum depends both on the thermalization of the electron gas and the electron-phonon scattering rate, it is often used as a measure of the thermalization time $t_{th}$ [5, 36].

Alternatively, we used Eq. 4.15, broadened by the pump-probe crosscorrelation of 120 fs (FWHM), to describe the reflectivity transients, Fig. 4.12(b). The solid line in the figure represents a fit excluding the region showing coherent contributions ($-0.1 < \Delta t < 0.1$ ps). Using a value $\tau_E = 0.32$ ps, which will be discussed later in this section, a thermalization time $\tau_{th} = 0.08$ ps is found, i.e. ‘complete’ (90%) thermalization in $t_{th} = 0.18$ ps. The correspondence during pump-probe overlap (in time) is not very good, and the onset of the reflectivity response seems to be shifted to positive delay times. It was carefully checked that $\Delta t = 0$ was correctly determined. Most likely, a coherent contribution is responsible for the observed discrepancy. Fitting with an additional Gaussian contribution with the width of the pump-probe crosscorrelation, the dashed curve is found that much better describes the transient data.

### 4.6.3 Acoustic strain wave effects

An important issue after, and even during, e-p relaxation is the effect of the distorted lattice on the reflectivity. Figure 4.12(c) shows a reflectivity trace for the Si$_3$N$_4$/Ni structure up to $\Delta t = 25$ ps. After a rapid e-p relaxation, showing up as a steep drop of $\Delta R/R$ during the first 2 ps, a complex series of oscillations is visible with amplitudes of up to 10% of the initial step around $\Delta t = 0$. It was found that the details of the response depend on the position on the sample, see e.g. Fig. 4.12(d), most likely due to inhomogeneities.

The wavelike phenomena are related to strain waves in the sample that are caused by the rapid heating. They can be described by the equation of thermoelasticity, which in one dimension reads [56]

$$\frac{\partial^2 u}{\partial t^2} = v_l^2 \frac{\partial^2 u}{\partial z^2} - \frac{3\beta B}{\rho} \frac{\partial T_i}{\partial z}. \quad (4.33)$$

Equation 4.33 gives the spatial and temporal variations in the $z$-component of the
Fig. 4.13: (a) Acoustic strain waves in a uniformly heated free-standing film, showing a triangular oscillation of the surface displacement $u$ with a period $2d/v_l$, $d$ is the thickness of the film and $v_l$ the sound velocity. (b) After sudden laser heating of an opaque (i.e. absorbing) film a strain wave is launched in the structure, traveling with $v_l$ and (partially) reflecting from interfaces.

lattice displacement $u(z,t)$, with $v_l$ the longitudinal phonon velocity, $\rho$ the specific mass, $B$ the bulk modulus and $\beta$ the linear thermal expansion coefficient. The driving force for the dynamics is a change in the equilibrium position of the atoms by a rise in lattice temperature $T_l$.

In Fig. 4.13 different scenarios for strain wave formation are depicted. Figure 4.13(a) shows the solution of Eq. 4.33 for a suddenly heated free-standing film of thickness $d$. Upon heating, the equilibrium distance between neighboring atoms is increased and the film will start to expand. The surface displacement of the film shows a triangular oscillation with period $2d/v_l$, with $v_l$ the sound velocity in the material. Another scenario is depicted in Fig. 4.13(b). Here an opaque film on top of a transparent layer is suddenly heated by a laser pulse. The strain wave that is generated by the expansion of the opaque layer travels into the structure with the speed of sound, reflecting at the different interfaces [69, 81].

In the Si$_3$N$_4$/Ni case, a thin Ni film situated on top of a transparent layer is uniformly heated. Si$_3$N$_4$ has a lower acoustic impedance than Ni and it can be shown that in this case the surface displacement of the Ni layer is similar to that of the free-standing film. From Fig. 4.13(a) one may thus expect a thickness oscillation with period $2d_{Ni}/v_{l,Ni}$. The actual sample is capped by an originally 3 nm Cu layer to prevent oxidation of the Ni. Cupper capping will increase the oscillation period and thus leads to an underestimation of $v_{l,Ni}$ when using $d_{Ni}$. The sudden heating of the Ni film may also launch a strain wave in the Si$_3$N$_4$. Strain waves in transparent films can be observed in optical experiments since they provide an extra interface for reflection.

In Fig. 4.12(c) the extrema of the fast oscillation in $\Delta R/R$ are indicated by vertical lines. The inset shows the position of the extrema versus their order number. The linear slope extracted from the first four points results in $v_l = 4.5$ km/s ($2d = 20$ nm), close to but somewhat lower than the literature value for the velocity in sound of Ni (5 km/s). Also, the intercept with the y-axis lies at a positive $\Delta t$. This is expected since the lattice is heated during e-p relaxation and not directly at $\Delta t = 0$.

The thickness oscillation of the Ni film is however not the only contribution to
The solid lines in Figs. 4.12(c) and (d) represent fits assuming a linear background due to diffusive cooling and two damped sines to account for strain wave phenomena. Although this is expected to be a coarse approximation to the lattice dynamics and its effect on the reflectivity, it allows us to determine the main frequency components. The fits show a good correspondence with the observed transients. Moreover, consistently two contributions are found with a $\sim 5.2$ and $\sim 7.8$ ps period, respectively. The 5.2 ps period corresponds to the Ni contribution ($v_l = 3.8$ km/s), while the slower component is attributed to acoustic strain waves generated in the 60 nm Si$_3$N$_4$ layer. This results in a sound velocity of 15 km/s, in reasonable agreement with the literature value of 11 km/s.

Altogether, it has to be concluded that lattice effects are of importance in the interpretation of transient reflectivity experiments on Ni thin films. Even when analyzing $\Delta R$ during the first picoseconds, their contribution can not be fully neglected. Based on the good correspondence of the two component fit for $\Delta t > 2$ ps, we believe it a good approximation to extrapolate the fitted curve to the first picoseconds after excitation. This procedure will be adopted in Sect. 4.6.5.

### 4.6.4 Substrate heating

In reflectivity measurements on multilayer structures all excited layers contribute to $\Delta R$. It is therefore very important to check whether the reflectivity changes are solely caused by heating of the Ni layer, or that other layers also contribute. Here we will discuss results for Ni thin films on different substrates, i.e. Si/Si$_3$N$_4$(60)/Ni(10) and Si/SiO$_2$(5)/Ni(10). It is shown that reflectivity measurements on the Si/SiO$_2$/Ni sample contain a large contribution from the silicon substrate, making the structure unsuitable for the derivation of thermalization and e-p relaxation times. In contrast, the Si/Si$_3$N$_4$/Ni structure yields relatively reliable information on the electron dynamics.

Figure 4.14(a) shows transient reflectivity measurements for the first 3 ps after excitation at two different temperatures. Strikingly, the transients show a large positive offset at negative delays that constitutes $\sim 50\%$ of the peak amplitude. This background is caused by long-lasting pump-induced effects that do not decay within the 12 ns pulse repetition time. In contrast, magneto-optic measurements that specifically probe the Ni layer only show a $\sim 5\%$ effect at negative delay times, i.e. do not indicate long-lived effects in the Ni layer.

In Figs. 4.14(b) and (c) $\Delta R$ is plotted for a Si$_3$N$_4$(60)/Ni(10) and a SiO$_2$(5)/Ni(10) structure while moving the two samples perpendicular to the focus plane of the objective ($z$-axis). As indicated in the inset in Fig. 4.14, changing the $z$-position will not only alter the size of the pump and probe spots, but it also changes the distance $d$ between the center of the spots. Therefore, the width of the peaks in Figs. 4.14(b)

<table>
<thead>
<tr>
<th>structure</th>
<th>$R_p$</th>
<th>$\frac{dR_p}{d\epsilon_s'}$</th>
<th>$\frac{dR_p}{d\epsilon_s''}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Si$_3$N$_4$(60)/Ni(10)</td>
<td>0.42</td>
<td>$3.7 \cdot 10^{-3}$</td>
<td>$-5.0 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>Si/SiO$_2$(5)/Ni(10)</td>
<td>0.47</td>
<td>$7.8 \cdot 10^{-3}$</td>
<td>$3.4 \cdot 10^{-3}$</td>
</tr>
</tbody>
</table>

Tab. 4.2: Effect of a change in Si substrate dielectric constant ($\epsilon_{Si} = 13.79 + 0.059$) on the p-reflectivity for two different structures.
Fig. 4.14: (a) As measured reflectivity changes for SiO$_2$/Ni at two temperatures, (b) $\Delta R$ as a function of focus position $z$ on Si$_3$N$_4$/Ni. As indicated in the inset, changing the sample position with respect to the focus changes the distance $d$ between the centers of the pump and probe spot. (c) Same, but on SiO$_2$/Ni structure. The curves show a sharp negative and a large, spatially extended positive contribution to the signal.

and (c) is a measure of the spatial extend of the induced effects. For the Si$_3$N$_4$/Ni structure a single, narrow peak is found independent of $\Delta t$. On the other hand, the SiO$_2$/Ni sample shows a superposition of a narrow, negative peak on a broad positive background. This shows that on the SiO$_2$/Ni structure $\Delta R$ is made up of two contributions, one that is spatially narrow and another that is spatially wide.

The observations all point at a positive contribution of the Si substrate to $\Delta R$ in the Si/SiO$_2$ structure. This is supported by optical matrix calculations presented in Sect. 3.3.2. The calculated reflectivity of both samples is nearly equal and close to 50%. Though, in the Si$_3$N$_4$/Ni sample twice as much light is absorbed in the Ni layer. Also experimentally a 50% reflection is found and the difference in absorption is confirmed by the factor of two higher effects observed in $\Delta R/R$ on the Si$_3$N$_4$/Ni structure. The remaining energy heats the Si substrate, which is only slightly absorbing at the wavelength used and thus has a large penetration depth of about 8 $\mu$m. Combined with lateral heat diffusion this results in a wide spatial extend of the heated region in the Si substrate.

The large difference between the $\Delta R/R$ measurements on the Si/Si$_3$N$_4$ and Si/SiO$_2$ substrates follows from a combination of factors. In the SiO$_2$/Ni sample the Si substrate is estimated to be heated 1.5 times more (s-polarized pump beam) while the heating of the Ni layer itself is two times less than on the Si/Si$_3$N$_4$ substrate. Moreover, changes in $\epsilon'_S$ also affect $\Delta R$ of the Si/SiO$_2$/Ni more efficiently by a factor of 2 (Tab. 4.2). Altogether, this results in a 6 times larger sensitivity of $\Delta R$ to heating of the Si substrate.
In conclusion, the prominent contribution of Si makes the transient reflection experiments on Si/SiO$_2$/Ni(10) unsuitable to derive the electron-phonon relaxation time of the Ni layer. The Si/Si$_3$N$_4$/Ni structure shows no sign of substrate contributions to $\Delta R$, making it suitable to determine the electron dynamics.

### 4.6.5 Electron-phonon relaxation

In Sect. 4.3 it was shown that, for moderate excitation densities and in absence of transport effects, the electron-phonon scattering results in an exponential decay of the electron temperature for $t \gg \tau_{th}$,

$$\Delta T_e(t) = \Delta T_\infty + (\Delta T_0 - \Delta T_\infty) e^{-\frac{t}{\tau_E}},$$  \hspace{1cm} (4.34)

with $\Delta T_\infty$ the temperature rise after electron-phonon relaxation, $\Delta T_0$ the temperature extrapolated to $t = 0$ and $\tau_E$ the e-p (energy) relaxation time, c.f. Eq. 4.23. The change in electron temperature results in a different reflectivity of the structure. We will assume here a linear relation between $\Delta R$ and $\Delta T_e$, i.e. $\Delta R_e(t) \propto \Delta T_e(t)$.

From the analysis presented in Sect. 4.6.3, it is clear that also the expansion of the lattice contributes significantly to $\Delta R(\Delta t)$. The lattice expansion is driven by the lattice temperature, which for the uniformly excited film can be approximated by

$$\Delta T_l(t) = \Delta T_\infty \left(1 - e^{-\frac{t}{\tau_E}}\right).$$  \hspace{1cm} (4.35)

The expansion of the lattice upon transient heating can in principle be calculated using Eqs. 4.33 and 4.35. Next, the lattice-induced change in reflectivity should be
calculated for the (non-uniform) displacement of the atomic layers. Here we will employ a simple model, approximately valid as long as the lattice expansion is still much smaller than its final equilibrium. It is assumed that the rate of change of the thickness $d$ of the Ni layer is proportional to $\Delta T_l$, $d\Delta d(t)/dt \propto \Delta T_l(t)$, and that the lattice-induced change in reflectivity, $\Delta R_l$, is proportional to $\Delta d$. Using Eq. 4.35, it then follows that

$$\Delta R_l(t) \propto \Delta d(t) \propto t + \tau_E \left( e^{-\frac{t}{\tau_E}} - 1 \right).$$

(4.36)

Note that for $t \gg \tau_E$, this expression reduces to $\Delta R_l(t) \propto t - \tau_E$, i.e. a linear expansion delayed by the e-p relaxation.

Combining the electron and lattice contributions to $\Delta R$, the transient change in reflectivity can be described by

$$\frac{\Delta R(t)}{R} = A + B e^{-\frac{t}{\tau_E}} + C \left( t + \left[ e^{-\frac{t}{\tau_E}} - 1 \right] \right),$$

(4.37)

with $A$, $B$ and $C$ appropriate constants. The first two terms describe the contribution of the electron system to $\Delta R$, the last term that of the lattice system. Equation 4.37 is similar to the function used in Ref. [24] to describe reflectivity measurements on gold films.

Fig. 4.15 shows fits of Eq. 4.37 to reflectivity data taken on a polycrystalline Si$_3$N$_4$/Ni and an epitaxial Cu(001)/Ni sample. It was already shown in Fig. 4.12 that strain waves play an important role in the polycrystalline sample. From the analysis of the strain wave phenomena it follows that the lattice contribution $\Delta R_l$ reaches its first, positive extremum at $\Delta t \sim 3$ ps. To derive the electron-phonon relaxation time, the reflectivity data were fitted up to 2 ps with a positive $C$ to correct for lattice effects. In Fig. 4.15(a) the lattice contribution is plotted separately, together with an extrapolation to $\Delta t = 0$ of a fit to the strain wave phenomena on the interval 2-25 ps. The electron-phonon relaxation time is found to be very sensitive to the exact slope of the lattice contribution. The good correspondence with the slope of the extrapolated curve gives confidence that lattice effects are correctly accounted for. However, still a considerable uncertainty remains and values for $\tau_E$ vary between 0.25 and 0.45 ps, depending on the fit interval and measurement used.

Reflectivity transients measured on the epitaxial sample, plotted in Fig. 4.15(b), show a faster decay time $\tau_E = 0.28$ ps. It can be expected that in this all-metallic structure transport effects do have a significant influence, resulting in a more rapid decay of $T_e$ by (electronic) heat diffusion into the Cu substrate. The all-metallic structures are therefore less suited to determine the electron-phonon relaxation time, unless one can reliably measure or model the heat transport. It is however surprising that the largest values for $\tau_E$ in Ni (3 ps) are reported on a six monolayer Ni film on Cu(001) [11].

### 4.6.6 Discussion

After sudden laser heating a range of processes take place that change the reflectivity of a material. Our transient reflectivity data on Ni show a delayed extremum at $t_{ex} = 200 \pm 20$ fs that is attributed to the thermalization of the electron gas. This number can be compared with literature values of 260 and 280±30 fs, reported in Refs. [5, 36], respectively. As discussed in Sect. 4.3.2, however, $t_{ex}$ is not a fundamental parameter in the sense that it depends on $K_{ee}$, $\tau_E$ (i.e. $K_{ep}$) and the length of the
Fig. 4.16: Transient reflectivity data on Ni from literature, analyzed using Eq. 4.37. (a) Linear reflectivity data from Beaurepaire et al. on a 22 nm polycrystalline Ni film on glass [5], yielding $\tau_E = 1.0$ ps. (b) Linear reflectivity data from Hohlfeld on bulk polycrystalline Ni [33], yielding $\tau_E = 0.6$ ps. (c) Even SHG yield measured by Regensburger et al. on a single crystalline Ni sample [60], yielding $\tau_E = 1.3$ ps. (d) Even SHG yield measured by Melnikov et al. on a 100 nm polycrystalline Ni film on quartz. $\tau_E$ is found to depend on the pump and probe polarization, yielding values ranging from 0.4 to 1.0 ps. In the figure data for both an s- and p-polarized incoming probe are shown. The pump was s-polarized, the intensity of the p-polarized part of the reflected probe was measured.

laser pulses used. For example, in Refs. [5, 36] relaxation times $\tau_E$ of, respectively, 1.0 and 0.7 ps are found. Here a shorter $\tau_E$ is observed, which is indeed expected to lead to a smaller value for $t_{ex}$.

The analysis of the reflectivity data is complicated by strong lattice contributions. Separating electron and lattice dynamics, an electron-phonon relaxation time of 0.25-0.45 ps is found for Ni. Literature values on the electron-phonon relaxation time show a much wider spread. Using Eq. 4.37 we reanalyzed different data sets published. The resulting values for $\tau_E$ are listed in Tab. 4.1. Transient transmission experiments of Beaurepaire et al. [5], reproduced in Fig. 4.16(a), yield $\tau_E = 1.0$ ps. The SHG data
of Ref. [36] result in a $\tau_E$ of 0.7-0.8 ps, very much independent of the fluence used. From transient reflectivity data on the same structure, published in Ref. [33] and reproduced in Fig. 4.16(b), follows a $\tau_E$ of 0.6 ps. SHG experiments by Regensburger et al. [60], Fig. 4.16(c), yield $\tau_E = 1.3$ ps. The SHG results of Melnikov et al. [57], Fig. 4.16(d), on thick polycrystalline Ni films show a strong dependence on the polarization of both pump and probe beam. The spread in relaxation times of 0.4 to 1 ps is attributed to different sensitivities to surface and bulk dynamics, with the faster relaxation attributed to surface dynamics. In Ref. [11] the thickness dependence of $\tau_E$ is investigated for epitaxial Ni films on Cu(001). The authors report an increasing relaxation time from 0.6 ps for a one monolayer film to 3 ps for six monolayers of Ni, the maximum thickness investigated.

In comparing these values it must be noted that $\tau_E$ is not a fundamental quantity. From Eq. 4.23 it follows that $\tau_E$ depends on the electron and lattice heat capacity. Therefore $\tau_E$ will also be affected by the excitation density as $c_e$ and $c_l$ are a function of temperature, see e.g. Fig. 4.5. The large spread in $\tau_E$ can however not solely be explained by this effect as the fluences used in the different reports are very similar, c.f. Tab. 4.1.

When performing experiments on bulk crystals, thick films or all-metallic structures, electron diffusion can influence the decay time of $T_e$. However, comparing the $\tau_E$ derived for the different structures, no obvious relation is found. For example, the samples used in Fig. 4.16(b) and (c) are bulk, while also the 100 nm Ni layer from Fig. 4.16(d) can be considered bulk. The range of $\tau_E$ observed there (0.4-1.3 ps) includes the 1.0 ps measured on a 22 nm Ni film on glass, i.e. a thin film on an insulating substrate, Fig. 4.16(a).

Also extrinsic effects such as morphology could influence the dynamics, complicating a proper comparison. In Refs. [36, 60] bulk Ni was used, which in the latter case was single crystalline. The 60 and 100 nm polycrystalline films from Ref. [57] can also be considered bulk. The different values of $\tau_E$ found in the first two experiments (0.75 versus 1.3 ps) should then be ascribed to structural effects. As mentioned before, the experiments of Ref. [57] did not yield a unique value of $\tau_E$. The long relaxation times found in epitaxial monolayer films on Cu are puzzling, and seems to suggest that the dynamics of thin Ni films on Cu is, unexpectedly, not dominated by ballistic or diffusive energy transport into the copper substrate.

Concluding, transient reflectivity, transmission and SHG experiments on Ni films and bulk crystals yield a wide range of electron-phonon relaxation times, from 0.4 to 1.3 ps. The origin of this spread is unknown, and may be related to variation in diffusion effects or structural properties of the samples used as well as to the dependency of the effective value of $\tau_E$ on the measurement method. The value of 0.25-0.45 ps reported in this thesis lies on the lower boundary.

### 4.7 Magnetism or magneto-optics?

In pump-probe demagnetization experiments the magnetization dynamics is monitored by the transient Kerr effect. The use of magneto-optical methods to probe the magnetization has however only been validated in equilibrium conditions. This section presents experimental results that show that the MO Kerr effect is not always a good measure of the magnetization, and that one should thus be careful when interpreting transient MO data.
In the first part of this section it is shown that a difference between rotation and ellipticity transients shows that at least one of the MO signals does not represent the magnetization dynamics. In Sect. 4.7.2 results of rotation and ellipticity measurements on Cu/Ni wedge structures are presented, and the cause of the observed differences is discussed. Section 4.7.3 investigates the dependence of the MO transients on chirp on the laser pulses, showing coherent contributions to the MO effects during pump-probe overlap. The experiments were performed on a variety of Ni thin film samples, at room temperature and using a wavelength \( \lambda = 780 \text{ nm} \).

### 4.7.1 The relation between \( M \) and \( \psi \)

In static MOKE experiments the Kerr rotation and Kerr ellipticity are used to probe the field dependence of the magnetization. This requires an unambiguous relation between the complex Kerr rotation \( \psi \) and the magnetization \( M(H) \). The Kerr rotation is generally considered proportional to \( M(H) \), see e.g. Eq. 2.8, an assumption that is experimentally well tested and that is certainly valid for small applied fields. In Sect. 4.5.2 the non-trivial relation between \( M(T) \) and \( \psi(T) \) was investigated under equilibrium conditions. It was found that for a 10 nm polycrystalline Ni layer the Kerr ellipticity was simply proportional to \( M(T) \). Considering the direction of the magnetization fixed, Eq. 2.8 can therefore be written as

\[
\psi = F \cdot M(H, T),
\]

with \( F \) a complex constant that depends on material parameters, layer structure, angle of incidence, etc.

However, in time-resolved MO experiments the material is not in equilibrium. Upon pulsed laser excitation a non-thermal electron distribution is created. This distribution subsequently thermalizes and interactions between the lattice, electron and spin system return the material to internal equilibrium. During these relaxation processes Eq. 4.38 may not be valid. A simply way to test its validity is by measuring both the transient rotation \( \psi' \) and ellipticity \( \psi'' \). If Eq. 4.38 is correct then the relative change in ellipticity and rotation should be equal and identical to the relative change in magnetization, i.e.

\[
\Delta \psi'(\Delta t)/\psi' = \Delta \psi''(\Delta t)/\psi'' = \Delta M(\Delta t)/M
\]

with \( \Delta \psi \) the pump-induced change of \( \psi \). If in an experiment Eq. 4.39 is shown not to hold, one knows that Eq. 4.38 is violated. In order to describe the experimental results, a general version of Eq. 4.38 can be used that adds an explicit time-dependence to \( F \),

\[
\psi(\Delta t) = F(\Delta t) \cdot M(\Delta t).
\]

Such an explicit time-dependence of \( F \) certainly complicates the use of MO techniques in the dynamic regime.

### 4.7.2 Comparison of rotation and ellipticity

Figures 4.17(a) and (b) show the measured time-dependence of \( \Delta \psi/\psi \) on the two epitaxial Ni-wedges described in Section 3.2. During the first picoseconds a clear difference is observed between the rotation and ellipticity transients. For the Cu(111)/Ni/Cu wedge, the rotation and ellipticity signal already converge after 2 ps. However, for the
Cu(001)/Ni/Cu structure the difference persists much longer and only after $\sim 50$ ps ellipticity and rotation become identical. The rotation transient of the Ni(001) film is also puzzling as it seems to indicate that already after 2 ps no pump-induced effects are left. Figures 4.17(c) and (d) show MO transients over a 500 ps range. On this time scale $\psi'$ and $\psi''$ are identical for both the (111) and (001) structure. As will be described in Chap. 5, the second minimum near $\Delta t = 150$ ps is caused by an optically excited precession of the magnetization, and is thus not related to a delayed demagnetization process.

To understand the anomalous transient MO response, it is of importance to notice that static MOKE measurements on the Ni(111) film show a ratio of ellipticity to rotation of $\sim 10$. Measurements on the Ni(001) structure show a change in ratio from 20 at 6.4 nm Ni to 3 at 12.4 nm. Ellipticity is thus clearly the dominant MO component at the wavelength of 780 nm used. In Fig. 4.18 rotation traces measured on the Ni(001) film are plotted for different Ni thickness. For the thinnest 6.4 nm film even an increase in MO contrast is observed. With increasing Ni thickness, i.e. decreasing ellipticity to rotation ratio, the rotation transients gradually start to look more like their ellipticity counterparts.

The differences observed between the relative changes of the ellipticity and of the rotation on a short timescale show that for these structures the Kerr effect is not a good measure for the magnetization dynamics, i.e. Eq. 4.38 is not valid. A possible explanation for this deviation is a transient, pump-induced change in reflectivity of the sample. The observed Kerr effect does not only depend on the off-diagonal component of the dielectric tensor, $\varepsilon_{xy}$, but also on its diagonal component $\varepsilon_{xx}$ that is responsible for the non-magnetic optical properties of the material. This diagonal component will also be affected by the optical excitation. In fact, in Sect. 4.6 we studied the electron dynamics by measuring the transient reflectivity, i.e. transient changes in $\varepsilon_{xx}$.

For polar MOKE on a bulk material the MO signal $\psi$ can be written as

$$\psi = r_{sp}/r_s \approx \frac{\varepsilon_{xy}}{\sqrt{\varepsilon_{xx}}(\varepsilon_{xx} - 1)} = Z \cdot \varepsilon_{xy},$$

(4.41)

see e.g. Sect. 2.2, directly showing the $\varepsilon_{xx}$ dependence. From measurements of $\Delta R/R$ (effects of $\sim 0.4\%$) we can get an impression of the pump-induced effects on $\varepsilon_{xx}$. The relation between $\Delta \varepsilon_{xx}$ and $\Delta R$ is however rather subtle, and this is even more true for its effects on $\Delta \psi$. Consider the present case with a structure that shows a much larger Kerr ellipticity than Kerr rotation, i.e. $\psi$ is mainly imaginary. In Eq. 4.41 this means that $Z \cdot \varepsilon_{xy}$ yields an imaginary value, with $Z = A \exp(i\phi)$ a complex number representing the non-magnetic properties of the sample. A small pump-induced change in $\varepsilon_{xx}$ can slightly change the phase $\phi$ of $Z$, introducing a real contribution to $\psi$. In the present situation the relative effect $\Delta \psi'/\psi'$ of this small perturbation will be 'infinite', i.e. the much smaller Kerr rotation is strongly affected by changes in reflective properties.

It must be noted that the same reasoning also applies to small variations in $\varepsilon_{xy}$. Since $\varepsilon_{xy}$ may not only change due to a different magnetization but for example also by a non-equilibrium electron occupation or strain, it may as well be responsible for the fact that $\Delta \psi'/\psi' \neq \Delta \psi''/\psi''$. Interestingly, the imaginary part of the experimentally determined $\varepsilon_{xy}$, plotted in Fig. 2.1, shows a zero crossing very close to the photon energy of 1.6 eV used in the current investigation, i.e. $\varepsilon_{xx}' \ll \varepsilon_{xy}'$. As it is experimentally found that the Kerr rotation is much smaller than the Kerr ellipticity...
one can conclude that $Z$ is mostly imaginary$^2$ and that $\psi' \propto \varepsilon''_{xy}$. It may therefore well be that the effects observed in $\Delta \psi'$ are directly caused by pump-induced, non-magnetic effects on the small $\varepsilon''_{xy}$ component, for example by a shift of the energy of its zero crossing. Since for long time scales ($> 1$ ps-30 ps) $\psi'$ and $\psi''$ do converge, deviations have to be ascribed to transient electron or lattice perturbations that are absent in the equilibrium temperature dependence.

Concluding, the difference between the ellipticity and rotation transients clearly shows that for the structures studied here on short time scales the MO Kerr effect is not a good measure of the magnetization. It was also shown that in the current situation, with a Kerr ellipticity much larger than the Kerr rotation, a small change in reflective properties or $\varepsilon_{xy}$ can induce large relative effects in the rotation part. Such a scenario seems to be confirmed by Fig. 4.18 where rotation transients are plotted for different Ni thicknesses. With increasing layer thickness the rotation transients more closely resemble their ellipticity counterparts, while at the same time the ratio ellipticity to rotation is observed to get closer to unity.

$^2$ A similar result also follows from optical matrix calculation on the multilayer structure.
The ellipticity and rotation transients converge on a longer time scale, showing that in equilibrium $\psi$ does reflect the magnetization. In the Ni(111) system the difference persists only during the first 2 ps, i.e. during e-p relaxation, while on the (001) system effects up to 50 ps are observed. On the latter time scale electron and lattice are in equilibrium. Therefore other effects, such as uniaxial strain in the heated layer, may also play a role.

Our original proof of the inequivalence of $\psi'$ and $\psi''$ [51] has later been confirmed by a number of groups. Similar polarization dependent effects are reported in SHG experiments, Refs. [57, 60], and in the linear pump-probe measurements of Guidoni et al. [27] on CoPt$_3$. In the latter experiment $\Delta \epsilon_{xy}(\Delta t)$ was explicitly recovered, showing a different behavior of the real and imaginary part of $\Delta \epsilon_{xy}$ during the first hundreds of femtoseconds, i.e. during electron thermalization.

### 4.7.3 Chirp dependence of the magneto-optic transients

A second indication of the indirect relation between $M(\Delta t)$ and $\psi(\Delta t)$ is obtained from experiments where the chirp of the laser pulses is varied. As explained in Sect. 2.5, adding linear chirp has two effects on short laser pulses.

First, the duration of the pulse increases. For this reason one generally tries to minimize the chirp at the sample position using a Group Velocity Dispersion (GVD) compensation line to obtain the highest temporal resolution.

Secondly, the instantaneous frequency of a chirped laser pulse varies within the pulse duration. The spectral width of the pulse does however remain the same. This effect is therefore not expected to directly influence the measurements by a change of spectral sensitivity, especially since the spectral features in metallic systems are relatively broad anyway.

Figs. 4.19(a) and (b) show rotation and ellipticity measurements on the Cu(001)/Ni structure for two different chirp settings. During the temporal overlap of the pump- and probe pulse a huge chirp dependence is observed in the rotation channel. The rotation signal shows a strong bipolar response, with an amplitude and sign that sensitively depends on the chirp. In contrast, the ellipticity data in Fig. 4.19(b) are only weakly affected by chirp. The fact that the ellipticity channel is not completely
Fig. 4.19: (a) Two rotation measurements for positively and negatively chirped pulses on the Cu(001)/Ni/Cu structure. (b) Idem, but for ellipticity. Lines are a guide to the eye.

Fig. 4.20: (a) Transient ellipticity measurement on Cu(001)/Ni without any GVD compensation, showing a shoulder during the temporal overlap of pump- and probe-pulse. The dotted line represents the pump-probe crosscorrelation. (b) Transient rotation measurements at two chirp settings on Cu(001)/Ni(15). The symbols represent different applied out-of-plane fields.

immune to chirp effects is demonstrated in Fig. 4.20(a), where a transient ellipticity measurement is shown that was taken without any GVD compensation. The falling edge at $\Delta t = 0$ shows an unexpected shoulder that is attributed to a coherent, chirp-dependent effect. The fact that the effect truly scales with the magnetization can be seen in Fig. 4.20(b). In the figure polar rotation transients are plotted as a function of applied out-of-plane field. At the Ni film thickness of 15 nm, the Cu(001)/Ni wedge structure used only shows a 10% out-of-plane remanence. Varying the applied field therefore greatly affects the out-of-plane component of the magnetization. However, after normalization on the static contrast an identical behavior is found, even for the
Fig. 4.21: (a) Pump and probe pulse with negative chirp at a small negative delay time. (b) Schematic density of states of a transition metal. The carriers excited by the pump pulse at $\hbar \omega_0$ bleach the transitions for the probe pulse. (c) Real and imaginary parts of $\Delta \epsilon_{xy}$ near a resonance.

coherent contribution. The small remaining differences can be ascribed to Faraday rotation in the focusing lens, slightly affecting the determination of the static contrast in rotation.

Two color experiment

The chirp dependence can be understood realizing that a pump-probe measurement using chirped pulses can be thought of as a two-color experiment. Fig. 4.21(a) shows a negatively chirped pump and a probe pulse at a small negative delay time. In this situation, the material is pumped with a higher frequency, labeled ‘blue’, and at the same instance probed by a lower frequency, labeled ‘red’. For a positive delay time, or $b > 0$, this situation is reversed. Control of the chirp thus allows one to pump and probe different electronic transitions, i.e. perform a two color experiment.

The chirp dependence can be qualitatively well described using a simple, incoherent oscillator model for $\epsilon_{xx}$ or $\epsilon_{xy}$. Here we will assume mainly $\epsilon_{xy}$ is affected. The pump-induced state filling causes a depletion of the oscillator strength at $\omega_0$, as schematically depicted in Fig. 4.21(b). This results in a dip in the real part of $\epsilon_{xy}(\omega)$, which is proportional to the absorption of circularly polarized light. In Fig. 4.21(c) the pump-induced change in $\epsilon_{xy}'$, $\Delta \epsilon_{xy}'$, is plotted, showing this dip centered at the pump-frequency $\omega_0$. $\Delta \epsilon_{xy}''(\omega)$ follows from the Kramers-Kronig transformation of $\Delta \epsilon_{xy}'(\omega)$ and shows a bipolar behavior as a function of $\omega$.

Since the rotational signal is mainly affected by $\epsilon_{xy}''$, measuring the induced rotation with a frequency just below that of the pump, as in Fig. 4.21(a) and labeled ‘1’ in Fig. 4.21(c), results in a bleaching contribution that has the opposite sign compared to probing with a higher frequency (‘2’). Measuring as a function of pump-probe delay time in a chirped experiment, one would expect a bipolar behavior of the MO signal. Changing the sign of the chirp should give the inverse picture, all exactly as observed.
Coherent representation in the density matrix formalism

In a more thorough description the simultaneous interaction of the pump and probe fields with the material should be described within a quantum mechanical formalism, also incorporating coherent effects. The latter means that a coherent electronic excitation, i.e. in phase with the pump laser-field, still exists in the medium upon arrival of the probe pulse. In particular in experiments with chirped laser pulses the situation is rather complicated; in that case the optical properties of the excited material as well as the probing wavelength change within the probe pulse duration. Although it will be shown to be necessary to calculate the full time-dependent (oscillating) polarization and electric fields, even a fast detector can only measure the time-averaged light intensity of the reflected probe pulse.

We will discuss the phenomenon based on the model electronic structure as depicted in Fig. 4.21(b). Only excitations from a localized d-level to a broad sp-band are being considered. Moreover, for simplicity, we will neglect relaxation processes within the sp-band, but do include relaxation from sp- to the d-states. In this specific case, the system can be described by a set of independent oscillators, and the optic response can be solved within the density matrix formalism [82].

In the density matrix formalism the system is described by a set of discrete states. The diagonal element $M_{nn}$ of the density matrix represents the occupation of state $n$, while the off-diagonal elements $M_{nm}$ represent the coherence between states $n$ and $m$. To describe the ensemble behavior a dephasing time $T_2$ is introduced that affects the coherence between states. The population or energy relaxation is described by a characteristic time $T_1$. Using the density matrix formalism the time-dependent polarization $P(t)$ of an oscillator upon interaction with an electric field $E(t)$ can be derived.

In the following we will consider the specific MO-experiment that is depicted in Fig. 4.22, with pump and probe beam incident near normal on a thin magnetic film (thickness $\ll 1/q$). Defining $\hat{z}$ the film normal and $\hat{x}$ and $\hat{y}$ two perpendicular in-plane axes, the incident pump and probe electric fields can be written as

\[
\vec{E}_{i,n}(t) = A_n(t)\hat{x} \cos(\omega_n(t) - \vec{q}_n \cdot \vec{r})
\]

\[
\vec{q}_{i,1} = q_z\hat{z} + k\hat{y}
\]

\[
\vec{q}_{i,2} = q_z\hat{z} - k\hat{y}
\]

with $k \ll q_z$, and $n = 1$ the pump and $n = 2$ the probe beam.
Consider first a continuous wave experiment using only the probe beam. In this ‘static’ case it is convenient to use complex amplitudes, allowing one to leave out the explicit oscillatory part of the electric fields. The polarization induced in the material then is given by

\[ P_x = \chi^{(1)}_{xx}A_2, \]

\[ P_y = \chi^{(1)}_{xy}A_2, \]

with \( \chi^{(1)} \) the first-order complex susceptibility. \( \chi^{(1)}_{xy} \) represents the off-diagonal element of the susceptibility tensor, which is present due to the MO Kerr effect. For a thin film the reflected electric field \( \vec{E}_r \) is directly proportional to \( \vec{P} \), i.e. \( \vec{E}_r \propto P_x \hat{x} + P_y \hat{y} \), and the complex Kerr rotation is thus simply

\[ \psi = \frac{P_y}{P_x} = \frac{\chi^{(1)}_{xy}}{\chi^{(1)}_{xx}}. \]

In a basic MO-experiment we can determine the real part of \( \psi \) by placing a polarizer in the reflected beam with its main axis oriented along \( \hat{x} + \hat{y} \). The transmitted intensity then is

\[ I \propto \frac{1}{2} |P_x + P_y|^2 \]

\[ = \frac{1}{2} |P_x|^2 + \frac{1}{2} |P_y|^2 + |P_x P_y| \]

\[ = |A_2|^2 \left( \frac{1}{2} |\chi_{xx}|^2 + \frac{1}{2} |\chi_{xy}|^2 + \text{Re} \left( \frac{\chi_{xy}}{\chi_{xx}} \right) \right) \]

where the last term in Eqs. 4.49 and 4.50 represents the MO rotation. This quantity is directly measured as the 2f signal in the PEM configuration, c.f. Eq. 2.15.

To describe the pulsed pump-probe experiments we need to use real amplitudes and explicitly include the full time-dependence of the fields. Using Eq. 2.22 for \( A_n(t) \) and \( \omega_n(t) \) in Eq. 4.42, the total incident electric field of pump and probe beam at the sample is given by

\[ E_i(t, y) = A_1 \exp \left[ -\frac{(t + \Delta t)^2}{\tau^2(1 + b^2)} \right] \cos \left[ \omega_l b(t + \Delta t)/\tau^2 + k y \right] + \]

\[ A_2 \exp \left[ -\frac{t^2}{\tau^2(1 + b^2)} \right] \cos \left[ \omega_l - bt/\tau^2 + k y \right], \]

with \( \omega_l \) the center laser frequency. Applying the density matrix formalism \( \vec{P}(t) \) can be calculated. The MO rotation, measured by the slow detector, then follows from the pulse-averaged value of \( P_x(t) P_y(t) \), c.f. Eq. 4.49. In actual samples, the MO-effects are solely caused by the magnetic layer. On the other hand, the substrate and overlayers also contribute to the normal reflectivity. For simplicity, we will therefore assume that only \( \chi_{xy} \) is affected by coherent effects and that \( \chi_{xx} \) is constant, i.e. \( P_x(t) \propto E_2(t) \) (apart from a phase shift). This allows us to define an effective, time-averaged (probe) susceptibility

\[ \chi_{xy}(\omega_l) = \int \int \tilde{E}_{i,2}(t, y) P_y(t, y) dtdy/ \int \int |\tilde{E}_{i,2}(t, y)|^2 dtdy, \]

\[ \tilde{E}_{i,2}(t, y) = \exp \left[ -\frac{t^2}{\tau^2(1 + b^2)} \right] \exp \left[ i(\omega_l - bt/\tau^2) t - ky \right] . \]
The integration over $y$ filters out the component of the polarization that radiates in the direction of the reflected probe beam. The integration over time yields the ‘pulse averaged’ susceptibility as measured by the detector. In the limit of a continuous beam ($\tau \to \infty$ and $b = 0$) Eq. 4.52 simply gives the Fourier transform of $P(t)$ at $\omega_l$, which is the usual definition of $\chi(\omega)$. Note that $P_y(t, y)$ represents the polarization induced by both the probe and the pump beam. $\chi_{xy}$ therefore includes higher-order (coherent) contributions.

We use the foregoing analysis to numerically investigate the MO response of the simple model system, Fig. 4.21(b), in the case of chirped laser pulses. As a first check, Fig. 4.23(a) shows $\chi_{xy}(\omega_l)$ for a single oscillator with resonance frequency $\omega_0$ at zero time-delay ($\Delta t = 0$) and without chirp ($b = 0$). Using a weak probe and without pump one finds a peaked response of $\chi'_{xy}$ at $\omega_l = \omega_0$ and a bipolar response of $\chi''_{xy}$. Note that for the off-diagonal element considered here the absorptive part is given by $\chi'_{xy}$. When the pump beam is turned on the optical transition is bleached and the amplitude of both the real and imaginary part of $\chi_{xy}$ decrease. The resulting difference, $\Delta \chi_{xy}$, is identical to the classical picture, Fig. 4.21(c).

Finally, we come to the full solution of the extended model. Denoting the susceptibility of a single two-level system with resonance frequency $\omega_0$ at a pump-probe delay of $\Delta t$ by $\chi_{xy}(\omega_l, \Delta t, \omega_0)$, the total response of the continuum of two-level oscillators is given by

$$\chi_{xy}(\omega_l, \Delta t) = \int \chi_{xy}(\omega_l, \Delta t, \omega_0) d\omega_0.$$ (4.53)

Fig. 4.23(b) shows the pump-induced change of this integrated $\chi_{xy}$ as a function of pump-probe delay for a phase relaxation time $T_2$ of 10 fs and population relaxation time $T_1$ of 20 fs. These relaxation times may be thought of typical for metallic systems. Though, the qualitative features of the model do not depend on the particular choice of the relaxation times. For an unchirped pulse ($b = 0$) the transition is bleached, i.e.

**Fig. 4.23:** (a) Frequency response $\chi_{xy}$ for a two-level system, with and without pump (maximum population of the upper level 40%). (b) Pump-induced change of $\chi$ as a function of pump-probe delay and chirp (maximum population of the upper level 4%). $T_1$ and $T_2$ were taken 20 and 10 fs, respectively. Pump and probe pulse have an intensity ratio of 100:1, photon energy of 1.6 eV, Gaussian width of 100 fs and a chirp $b$ as indicated in the figure.
the absorptive part $\Delta \chi'_{xy}$ shows a negative amplitude, but there is no contribution to $\Delta \chi''_{xy}$. However, when using pulses with a finite chirp $\Delta \chi''_{xy}$ shows a bipolar behavior with its sign depending on $b$, in agreement with the predictions based on the simple classical oscillator model.

4.7.4 Summary

From the observations described in this section it is clear that one should be careful in directly linking $\psi(\Delta t)$ with magnetization changes. The chirp dependence and the differences observed between transient rotation and ellipticity measurements show that magneto-optical techniques only give an indirect view of the magnetization dynamics.

In the Cu/Ni/Cu structures studied here the Kerr rotation was much smaller than the Kerr ellipticity. In Sect. 4.7.2 it was explained that the smallest Kerr component will be most susceptible to magneto-optic artifacts. Also the experiments point at stronger artifacts in the weak rotation transients, see e.g. the anomalous thickness dependence in Fig. 4.18. It may thus be hoped that the ellipticity transients do correctly reflect the magnetization dynamics.

Other samples studied in this work, e.g. polycrystalline Ni films on non-metallic substrates and a Co-Pt alloy, showed no difference between rotation and ellipticity, and both components were of similar magnitude. In the following sections we will assume that the dominant component of $\psi(\Delta t)$ (in most cases $\psi''(\Delta t)$) does reflect the magnetization dynamics, unless indicated otherwise. We do realize, however, that this assumption may not necessarily be valid and requires attention. In particular, in Sect. 4.8.5 magneto-optic artifacts will be considered as an explanation for observed temperature dependencies in MO transients.

4.8 Temperature dependence of the magnetization dynamics

In this section the temperature dependence of the ultrafast decrease of magnetization is investigated. At an elevated temperature the magnetization of a ferromagnetic material is smaller. However, the change in magnetization upon heating by a certain temperature $\Delta T$ will be larger because of the non-linear dependence of $M$ on $T$. This pronounced temperature dependence is specific for the demagnetization process. Thus, a study of the observed temperature dependence of the dynamics may yield valuable information on the processes involved in the ultrafast demagnetization.

In the first part of this section it is shown that, using a number of assumptions, the ratio of two magnetization transients measured at different temperatures should be time-independent. Then, experimental results are presented, demonstrating that during the first picoseconds the ratio based on MO experiments is in fact not constant. In the subsequent parts the different assumptions will be analyzed, allowing us to identify the electron temperature as the quantity that determines the reduction of the magnetization.

4.8.1 The relation between $M(T)$ and $\psi(T)$

The effect of the ambient temperature $T_0$ on the MO transients is best visualized by writing Eq. 4.38 in terms of a spin temperature $T_s$,

$$\Delta \psi(\Delta t) = F_0 M'(T_0) \Delta T_s(\Delta t),$$

(4.54)
with \( M' = dM/dT \) the slope of the magnetization versus temperature curve and \( \Delta T_s \) the transient increase in spin temperature. This is a linearization of \( M(T) \) around \( T_0 \) that is valid for sufficiently small \( \Delta T_s \). The magnetization decreases progressively when approaching \( T_C \), and its slope \( |M'(T)| \) therefore increases with temperature. The same temperature rise will thus result in a larger demagnetization at higher ambient temperatures.

In the analysis of the experimental data we will start with the naive assumption that the spin temperature transients \( \Delta T_s(\Delta t) \) are independent of ambient temperature. The assumption that the temperature transients \( \Delta T_e(t) \) are identical implies that the heat capacity of the different systems should be temperature independent. For the long-term behavior also the coupling constants and heat diffusion should be similar. Under these conditions a simple expression can be derived for the ratio \( r'' \) of two MO ellipticity transients measured at temperatures \( T_1 \) and \( T_2 \),

\[
 r''(\Delta t) = \frac{\Delta \psi''(\Delta t)}{\psi''} \bigg|_{T_2} / \frac{\Delta \psi''(\Delta t)}{\psi''} \bigg|_{T_1}. 
\]

Using Eq. 4.54, \( r''(\Delta t) \) can be written as

\[
 r''(\Delta t) = \frac{M'(T_2)}{M(T_2)} \frac{M'(T_1)}{M(T_1)},
\]

i.e. the ratio is time-independent. A similar expression follows for the rotation transients.

Note that we have assumed here that the MO transients reflect the true magnetization dynamics, i.e. \( F(t) \) is constant. In Sect. 4.7 it was shown that on Cu/Ni wedges transients of the small Kerr rotation were significantly affected by magneto-optic artifacts. Therefore, in this section we will use ellipticity transients to study the dynamics of the Cu/Ni wedges. In the other samples used here the Kerr ellipticity and Kerr rotation are of similar magnitude and show the same time dependence, giving confidence that they do represent the magnetization dynamics. In Sect. 4.8.5 it will be verified whether magneto-optic artifacts can explain the observed temperature dependence.

### 4.8.2 Experimental temperature dependence

To measure the temperature dependence of the magnetization dynamics the samples were placed on a copper sample holder that was supplied with a resistive heater. A thermocouple close to the sample was used for temperature control. The experiments were performed in air, introducing a risk of increased oxidation. In the temperature range used (308-393 K) no irreversible effects were observed, i.e. measurements could be reproduced irrespective of sample history. The experiments were performed using a longitudinal geometry, except for the Co-Pt alloy and the epitaxial Cu(001)/Ni structure where a polar configuration was used. A central wavelength \( \lambda = 780 \text{ nm} \) was used in all experiments.

Figures 4.24(a), (c), (e) and (g) show typical temperature dependent measurements on three different Ni structures and the Pt/Co/Pt sample. The closed squares represent the relative change in MO ellipticity at 308 K, the open circles depict the measurements at an elevated temperature (373 or 393 K). The pump-induced effects
at an elevated temperature are clearly higher, just as expected from the non-linear temperature dependence of the equilibrium magnetization and Eq. 4.54.

Eq. 4.56 predicts that the ratio of two transients measured at different temperatures is constant. The experimentally determined ratios $r''(\Delta t)$, plotted in Fig. 4.24, clearly show that this simple description fails. During the excitation the observed ratio is close to one, i.e. the pump-induced effect normalized on the equilibrium magnetization is temperature independent. This phenomenon is not only restricted to Ni. Also the Pt/Co/Pt sample shows the same effect, with again a ratio of approximately one during the first 100-200 fs after excitation. In the next picoseconds the value increases until it becomes, to good approximation, constant. Using the equilibrium magnetization curve [49] for Ni, a ratio of 1.6 is expected for two measurements at 373 and 308 K. This value is indeed in reasonable agreement with the observed ratios at 3 ps.

The fact that Eq. 4.56 is not valid, i.e. $\Delta r''$ is time-dependent, must be due to a failure of at least one of the assumptions made in its derivation:

1. $M(T_0 + \Delta T_s)$ can be considered linear in $\Delta T_s$ for the pump excitation used.

2. The spin temperature transients are identical at different ambient temperatures, i.e. the temperature dependence of the thermal properties $c$ and $\lambda$ as well as the coupling constants and $\tau_M$ can be neglected.

3. $\psi(\Delta t)$ represents the magnetization dynamics, i.e. $F$ in Eq. 4.54 is a constant independent of time.

In the next sections we will successively address these issues to check whether they can explain the experimental data.

### 4.8.3 Linearization of $M(T_s)$

In deriving Eq. 4.56 it was assumed that $M'(T_s)$ is constant in a single experiment. For a moderate pump-induced increase of the spin temperature this assumption is certainly valid. However, for larger excitations non-linear effects will become important and may influence the determined ratio.

When approaching the Curie temperature, $|M'(T)|$ will increase progressively. Therefore, any non-linear behavior will increase the magnitude of the pump-induced effect with rising ambient temperature, i.e. cause a larger ratio for small time delays when the pump-induced temperature rise is the highest. This is opposite to the behavior observed in Figs. 4.24(b),(d),(f) and (h).

Although non-linear effects are not responsible for the deviating ratio, it is interesting to get an impression of the magnitude of the spin temperature for the most intensely heated sample, Si$_3$N$_4$/Ni. In Fig. 4.25(a) the measured magnetic contrast in the MO-ellipticity $\epsilon$ is plotted as a function of delay time for different ambient temperatures. Using the Kerr values at negative time delay combined with separate temperature dependent SQUID and MO measurements on the same sample, c.f. Fig. 4.11, a quadratic approximation to $M(T)$ is derived. With the quadratic relation, plotted in Fig. 4.25(b) as a solid curve, the MO transients in Fig. 4.25(a) can be converted to spin temperatures. Since the Gaussian pump and probe spot have equal diameter, the temperature in the center of the spot is approximately twice the apparent temperature rise as determined from Figs. 4.25(a) and (b), see e.g. Eq. 2.27.
Fig. 4.24: TRMOKE measurements at two different ambient temperatures and their ratio. (a),(b) Cu(001)/Ni(6.4 nm) at 308 and 373 K. (c),(d) Si/SiO$_2$/Ni(10 nm) at 308 and 393 K. (e),(f) Si/Si$_3$N$_4$(60)/Ni(10 nm) at 308 and 373 K. (g),(h) Si/SiN(40)/Pt(20)/Co(0.5)/Pt(1) at 308 and 373 K. The dotted curves in the figures on the left represent the convolution of the pump-probe crosscorrelation with a step function. The dotted lines in the figures on the right represent the pump-probe crosscorrelation. The procedure is estimated to be accurate within 15 K. In Fig. 4.25(c) the thus derived spin temperature transients $\Delta T_s$ are plotted. Transients measured at different ambient temperatures are not identical. For short delay times, the observed rise in $T_s$ becomes smaller for elevated temperatures, i.e. as expected on the basis of the deviating rations.

In conclusion, the non-linear behavior of $M(T_s)$ is not responsible for the obser-
Fig. 4.25: (a) Ellipticity transients at three ambient temperatures as measured on the Si$_3$N$_4$/Ni(10) structure. (b) Quadratic fit to the temperature dependence of the magnetization. The black squares represent the points indicated in panel (a), the open stars and circles are respectively the SQUID and MO ellipticity data from Fig. 4.11. (c) Spin temperature transients derived from panel (a) using the quadratic approximation to $M(T)$ and Eq. 2.27.

The ratio of two MO transients is only constant if the temporal evolution of the spin temperature, $\Delta T_s(t)$, is identical at different ambient temperatures. However, the thermal properties of Ni are temperature dependent, see e.g. Fig. 4.8, and the deviating ratio may thus be related to a difference in spin temperature transients.

Figure 4.25 shows that the change in MO signal occurs extremely rapid, i.e. well within the electron-phonon relaxation time determined in Sect. 4.6. Assuming a direct relation between $\psi''(\Delta t)$ and $M(\Delta t)$, the observed effects would thus be driven by changes in electron temperature $T_e$. In the Si$_3$N$_4$/Ni and Si/SiO$_2$/Ni structures considered here the insulating Si$_3$N$_4$ and SiO$_2$ layers block all ballistic and hot electron transport. The films are also optically thin and will thus be uniformly heated. Therefore on short time scales, i.e. before significant electron-lattice relaxation, only the electronic heat capacity $c_e$ is of importance. In the present situation a possible spin contribution to the heat capacity will be considered part of $c_e$, as the demagnetization proceeds extremely fast.

For a free electron like metal $c_e$ increases linearly with temperature, see e.g. Eq. 4.21, resulting in a smaller electron peak temperature with increasing ambient temperature. When the demagnetization is driven by the electron temperature this causes a reduction of the induced effects at elevated temperatures, in particular as long as the added energy is confined to the electron system. This behavior is in accordance
Fig. 4.26: Spin temperature transients on Si$_3$N$_4$/Ni at three different ambient temperatures. The symbols represent the measured data, the solid lines are calculations using Eqs. 4.32 to describe a delayed spin response. The parameters used, $c_l = 2.8 \cdot 10^6$ J/m$^3$/K, $\gamma = 3.76 \cdot 10^3$ J/m$^3$/K, $g_{ep} = 150 \cdot 10^{16}$ W/m$^3$/K and $\tau_M = 100$ fs, are optimized to describe the 308 K measurement. The modeled temperature dependence of $c_e$ is not sufficient to describe the effects.

with the observed lower ratio near $\Delta t = 0$, and lower peak values of $\Delta T_s$ at elevated temperature in Fig. 4.25(c).

To get an impression of the appropriateness of this mechanism we can look at the magnitude of the effect. From Fig. 4.26 it is found that the peak spin temperature at 393 K is $\sim 30\%$ less than at room temperature. Assuming that in Fig. 4.24(d) the ratio of 1.6 at $\Delta t = 3$ ps represents $M'(T_2)/M'(T_1)$, the ratio of 1.1 directly after excitation also indicates a 30\% reduction of the peak temperature at 393 K. The theoretical temperature dependence of $c_e$ is given by Eq. 4.21, showing that $c_e$ is proportional to $T$. Therefore, $c_e(308)/c_e(393) = 0.78$, i.e. predicting a reduction of the peak temperature with 22\%. The actual effect will be somewhat less since $c_e$ also increases during heating by the pump pulse. Taking this into account, theoretically a net reduction of $T_{\text{peak}}$ with 18\% is expected, i.e. of the right order but somewhat less than experimentally is observed.

Calculations using Eqs. 4.32 to describe a delayed spin response confirm this estimate. Fig. 4.26 shows the measured spin temperature transients on the Si$_3$N$_4$/Ni structure together with simulated curves. The 308 K measurement is nicely described using $g_{ep} = 150 \cdot 10^{16}$ W/m$^3$/K, $\tau_M = 100$ fs, and the values for $c_l$ and $\gamma$ derived in Sect. 4.4.4. The reduction of $T_s$ with temperature is however underestimated, as expected from the rough estimated in the preceding paragraph. In passing, we note
small though significant discrepancies of the solid curve with the measurement at 308 K during temporal overlap of pump and probe ($|\Delta t| < 100 \text{ fs}$). Possibly, they are related to MO artifacts. If we nevertheless trust the outcome of the fit, a demagnetization time $\tau_M = 100 \text{ fs}$ is found. These issues, and the interpretation of $\tau_M$, will be discussed in more detail in Sect. 4.10.

It must be noted that the observed stronger temperature dependence of $\Delta T_s$ can not be explained by the different value of the electronic heat capacity in the constant pressure and constant volume situation. When changing the temperature of the complete sample, $c_{e,p}$ is the proper quantity. In the pump-probe experiment the electron system is heated before the lattice can expand, and $c_{e,V}$ is more appropriate. In Sect. 4.4.4 it was found that in the temperature range of interest $c_{e,V}$ and $c_{e,p}$ are identical within 4%, i.e. the effect is much less than the remaining difference observed here. One may also think that an increase in magnetic heat capacity is responsible for the decrease in peak temperature. However, the value for $\gamma$ used in Fig. 4.26 was derived from experimental heat capacity measurements on Ni, plotted in Fig. 4.8. Therefore, possible magnetic contributions are already included in $c_e$. Also, in the temperature range considered here no sharp rise in the experimental heat capacity is observed.

Experimentally, the electron dynamics can be probed by transient reflectivity measurements. Figures 4.27(a),(b) and (c),(d) show the relative reflection changes measured on the Si$_3$N$_4$/Ni and Si/SiO$_2$/Ni sample, respectively. Due to the insulating layers the deposited energy remains largely in the Ni layer and therefore the recovery of $T_e$ is directly related to e-p scattering. As described in Sect. 4.6, the recovery of $\Delta R/R$ contains both contributions from the electron as well as the lattice system, complicating the interpretation.

As displayed in Figs. 4.27(a) and (c), the peak change in reflectivity is independent of ambient temperature. This result is not anticipated. During the first tenths of picoseconds $\Delta R/R$ is not significantly affected by lattice effects and thus should represent changes in the electronic system. Within the usual ‘resonant’ interpretation $\Delta R/R$ is measure of $\Delta T_e$. This would imply that the electronic heat capacity is, unexpectedly, constant in the temperature range covered. In a strictly ‘off-resonant’ interpretation (see Sect. 4.5) $\Delta R/R$ would represent the excess energy in the electron system. Since at $\Delta t = 0$ this is just the absorbed pump energy the peak change is indeed expected to be temperature independent. In the off-resonant view one would, however, expect a change after e-p relaxation since at elevated temperatures a larger part of the absorbed energy will remain in the electron system. Only the transients measured on the SiO$_2$/Ni sample do show a temperature dependence for $\Delta t > 1 \text{ ps}$. In Sect. 4.6 it was however found that the Si substrate adds a large contribution to $\Delta R/R$ in this structure, possibly causing the temperature dependence. The transients on the Si$_3$N$_4$/Ni sample plotted in Fig. 4.27(b) are temperature-independent, apart from a small contribution related to acoustic strain waves. A final argument against an off-resonant interpretation is based on the observation of a finite thermalization time. A strictly off-resonant experiment should display an instantaneous response, being a measure of the excess energy in the electron system.

The temperature-dependent measurements show that the interpretation of reflectivity transients on the 3d-metal Ni is less straightforward than on noble metals. The data seemingly indicates that $c_e$ is independent of temperature. This is however in contradiction with theory, heat capacity measurements [79] and modeling of other
pump-probe experiments on Ni [4, 60, 78].

Concluding, the expected increase of $c_e$ with temperature can reasonably well explain the reduction of $\Delta T_s$ with temperature. Using the relation $c_e(T_e) = \gamma T_e$, a reduction of the peak value of $T_e$ with 18% is calculated when heating the sample from 308 to 393 K. Although this number is lower than the experimentally observed effect of $\sim 30\%$, the order of magnitude is correct. Furthermore, taking the electron temperature as the driving force for the demagnetization and assuming a rapid spin scattering nicely explains the rapid change in spin temperature upon laser heating, i.e. $T_s$ rises much faster than the lattice temperature. The sharp peak for small time delays, which was not expected from equilibrium diffusion calculations in Chap. 3, naturally follows from the decrease of electron temperature by the rapid electron-phonon scattering process.

Measurements of the transient reflectivity seemingly indicate that the thermal properties are completely temperature independent. This contradicts theory and other available data, and therefore indicates that the interpretation of reflectivity transients on 3d-metals is not yet fully understood.

### 4.8.5 MO artifacts

In the preceding section it was shown that a temperature dependence of $c_e$ can explain at least part of the temperature dependence of the observed MO transients. However, it was assumed that the MO Kerr effect is simply proportional to the magnetization.
This interpretation is supported by the fact that, except for the epitaxial structures, Kerr rotation and Kerr ellipticity transients show the same behavior and are of similar magnitude. However, in view of the results of Sect. 4.7 one may suspect that part of the time-dependence of the ratio \( r'' \) is caused by MO artifacts.

In this section we will explore whether MO artifacts can fully explain the deviations in \( r'' \), i.e. return to the assumption of similar spin temperature transients at different temperatures and using a linearization of \( M(T) \). Within these restrictions a method to separate the magnetization dynamics and magneto-optic artifacts is presented, and applied to transients measured on the Cu(001)/Ni and Si₃N₄/Ni structures. Despite plausible results it is concluded that the restrictions are violated in actual experiments, and that the method therefore is not complete – if valid at all.

**MO artifacts and \( \Delta \psi \)**

To include the effect of MO artifacts on the MO transients we follow the approach of Ref. [46] and modify Eq. 4.54 by introducing a time-dependence to the prefactor \( F \),

\[
\Delta \psi(\Delta t) = \Delta F(\Delta t) M(T_0) + F_0 M'(T_0) \Delta T_s(\Delta t). \quad (4.57)
\]

The linearization of \( F(t) \) is valid for small pump-induced changes \( \Delta F(t) \), and neglects the cross-term \( \Delta F(\Delta t) \Delta M(\Delta t) \). In this approach the MO effects discussed in Sect. 4.7 are described by the time-dependent \( \Delta F(\Delta t) M(T_0) \) term.

Shortly after excitation the system is in a highly non-equilibrium state. As shown in Sect. 4.7 this can directly change the MO signal by state-filling effects. The state-filling contribution to \( \Delta \psi(\Delta t) \) is expected to be relatively temperature-independent as it involves excitations at much higher energies than \( k_B T \). Pump-induced strain may add an additional (non-magnetic) contribution to the MO effect. Also the strain effect will to first order be independent of temperature: by increasing the ambient temperature the complete structure expands while the strain effect is specifically caused by local heating.

**Separation procedure**

The expected different temperature dependence of \( \Delta M(\Delta t) \) and \( \Delta F(\Delta t) \) can be used to separate the true magnetization dynamics \( \Delta T_s(\Delta t) \) from the non-magnetic contribution \( \Delta F(\Delta t) \). Under the assumption that \( \Delta F(\Delta T)_{T_1} - \Delta F(\Delta T)_{T_2} = 0 \), the difference of two ellipticity transients taken at different ambient temperatures yields a transient that is directly proportional to \( \Delta T_s \):

\[
\delta(\Delta t) = \left. \frac{\Delta \psi''}{\psi''} \right|_{T_1} - \left. \frac{\Delta \psi''}{\psi''} \right|_{T_2} = F_0 \left[ \frac{M'(T_1)}{M(T_1)} - \frac{M'(T_2)}{M(T_2)} \right] \Delta T_s(\Delta t). \quad (4.58)
\]

A similar equation follows for the Kerr rotation. Again, this procedure is only valid if \( M(T_s) \) can be considered linear within a single measurement and if the spin temperature transients \( \Delta T_s(\Delta t) \) at the two temperatures are identical or differ by a constant factor. The latter case only alters the proportionality factor and is to good approximation met when \( \Delta T_s \) follows \( \Delta T_l \).

By taking the appropriate linear combination of two MO transients also \( \Delta F(\Delta t) \) can be derived. After several picoseconds \( \Delta F \) is expected to vanish and the ratio
$r(\Delta t)$ of the transients will reach a constant value $r_c$ given by Eq. 4.56. Using this ratio the relative change in $F$ can be expressed as

$$\frac{\Delta F(\Delta t)}{F_0} = \frac{r_c}{r_c - 1} \left. \frac{\psi(t)}{\psi} \right|_{T_2} - \frac{1}{r_c - 1} \left. \frac{\psi(t)}{\psi} \right|_{T_1}.$$  \hspace{1cm} (4.59)

Note that $\Delta F(\Delta t)$ vanishes when $r(\Delta t) = r_c$ and, inversely, as long as the ratios plotted in Fig. 4.24 have not reached a constant value a finite $\Delta F$ contribution is present.

**Application to the Cu(001)/Ni structure**

In Sect. 4.7 it was found that ellipticity and rotation transients on the same structure resulted in a completely different view of the magnetization dynamics. The measurements on the 9 nm layer are reproduced in Figs. 4.28(a) and (b), depicting rotation and ellipticity transients at 308 K and 373 K, respectively. Both rotation measurements show a coherent effect within the pump-probe crosscorrelation, and the 308 K trace shows no net pump-induced effect after 3 ps. This is a notably different behavior from the ellipticity transients in panel (b).

In order to separate magnetic effects and optical artifacts, we take the difference of the rotation and ellipticity traces measured at two different temperature. Fig. 4.28(c) shows the ‘thermal difference’ $\delta(\Delta t)$ of the rotation and ellipticity transients from panels (a) and (b). Strikingly, ellipticity and rotation now yield exactly the same results, without any additional scaling. The coherent structure in the rotation channel is cancelled (apart from a spike related to the steep slope near $\Delta t = 0$) and also the long-term difference with the ellipticity signal is gone. The same result is obtained when applying the procedure at different thicknesses. Despite the anomalous rotation traces, see e.g. Fig. 4.18, the thermal difference scheme yields identical dynamics.

Using Eq. 4.59 the magneto-optic contribution can be calculated. Fig. 4.28(d) shows $\Delta F(\Delta t)/F$ for the ellipticity and rotation transients, using the ratio $r_c$ determined from the ellipticity transients. The magneto-optic contribution to the rotation signal shows an almost constant value for $\Delta t > 1$ ps, shifting the rotation measurement upwards.

**Application to the Si/Si$_3$N$_4$/Ni structure**

In the Cu/Ni/Cu structure heat diffusion into the Cu substrate plays an important role. Since the diffusion process may also be temperature dependent it is preferable to work with an optically thin layer on an insulating substrate. Here we will apply the separation procedure to the Si/Si$_3$N$_4$/Ni(10) structure. Moreover, we will use transients measured at three different temperatures for the separation. When the proposed procedure is valid it should yield $\delta(\Delta t)$ transients that have an identical shape independent of the choice of $T_1$ and $T_2$, at least as long as $|T_1 - T_2|$ is sufficiently large compared to $\Delta T_s$. The transients will differ by a constant factor due to the different $M$ and $M'$. Fig. 4.29(a) shows normalized $\delta(\Delta t)$ transients for different combinations of $T_1$ and $T_2$. The corresponding $\Delta F(\Delta t)/F_0$ transients are plotted in Fig. 4.29(b). The transients were derived from measurements taken at 308, 350 and 393 K, allowing for the use of three different pairs with Eqs. 4.58 and 4.59. The $\delta(\Delta t)$ transients are
Fig. 4.28: (a) Rotation and (b) ellipticity measurements on the Cu(001)/Ni(9) at 308 and 373 K. The rotation transients show a distinctly different dynamics than the ellipticity transients. The dotted lines represent the pump-probe crosscorrelation. (c) Difference $\delta(\Delta t)$ between the rotation (solid squares) and ellipticity (open circles) curves measured at two temperatures. Without any additional scaling $\delta(\Delta t)$ shows identical dynamics for rotation and ellipticity. (d) Bleaching contribution $\Delta F(\Delta t)/F$ to the rotation and ellipticity transients. Solid lines are filtered curves serving as a guide to the eye.

Fig. 4.29: Results on the Si/Si$_3$N$_4$(60)/Ni(10) structure. (a) $\delta''(\Delta T)$ for different combinations of $T_1$ and $T_2$. The transients are normalized to a value of 80 at $\Delta t = 3$ ps, corresponding to the spin temperature at 3 ps in Fig. 4.25(c). (b) The corresponding magneto-optic contributions.
normalized to a value of 80 at $\Delta t = 3$ ps. This corresponds to the spin temperature (in Kelvin) at 3 ps in Fig. 4.25(c), derived assuming $\Delta F(3\text{ ps})= 0$.

The transients in panel (a) and (b) indeed show the same dynamics, independent of the temperature interval chosen. In passing, we want to note that in this interpretation the non-linear behavior of $M(T)$ is much less important. The peak temperature rise now only is 90 K, c.f. Fig. 4.29(a), instead of the 180 K observed in Fig. 4.25(c).

Objections to the separation method

From the experimental results presented in the preceding sections it seemingly follows that the thermal separation procedure results in an unambiguous view of the magnetization dynamics. In the epitaxial system the initially very contrasting ellipticity and rotation transients could be brought in accordance with each other, and measurements on the Si$_3$N$_4$/Ni structure showed that the results of the separation method are independent of the chosen temperature interval. A temperature-independent $\Delta F(t)$ can also clarify the ratio $\Delta \psi''/\psi''|_{T_1}/\Delta \psi''/\psi''|_{T_2}$ of $\sim 1$ during the first hundred femtoseconds, see e.g. Fig. 4.24. In this period the MO response will be dominated by the $\Delta F(t)$ term, naturally explaining the ratio of one.

Despite the apparently convincing results there are strong objections to make against the method. From the transients plotted in Fig. 4.28(d) and Fig. 4.29(b) it follows that $\Delta F''(\Delta t)$ contributes for $\sim 2$ ps and decays with a characteristic time scale of 0.6 ps. This is much longer than the time $t_{th} \approx 0.2$ ps needed for electron thermalization. However, after thermalization state-filling effects are expected to play a minor role. Since the ultrafast decrease of MO-contrast has been observed in a range of different materials (Fe, Co, Ni, CoPt) an accidental ‘bottle neck’ in the thermalization seems unlikely.

Furthermore, the value of 0.6 ps corresponds well with the electron-phonon relaxation time $\tau_E$. One could explain this by a direct dependence of $\Delta F$ on the electron temperature. This mechanism should, however, also show up in the temperature dependence of $\psi$ measured in static experiments, resulting in a more rapid decrease of $\psi(T)$ with temperature. This has, however, not been observed, c.f. Fig. 4.11. Moreover, a direct scaling with $T_e$, independent of $M$, would mean that even at large delay times $\psi$ is no longer a good measure of $M$.

A more likely explanation is that the spin temperature transients are not temperature independent, a scenario already discussed in Sect. 4.8.4. It was shown there that the temperature dependence of $c_e$, together with the assumption of $T_e$ as the driving force for the demagnetization, leads to an ambient temperature dependence of $\Delta T_e(\Delta t)$. In this case the separation procedure is invalid. Thus, the $\delta(\Delta t)$ and $\Delta F(\Delta t)/F_0$ that are derived loose their simple interpretation. An improved separation procedure would have to account for the temperature dependence of $\Delta T_e(\Delta t)$, something that requires an intimate, a-priori knowledge of the processes involved in the demagnetization.

Assuming the S3TM is the correct description for the dynamics, it is easily possible to derive $\delta(\Delta t)$ from simulated transients. With the simulated transients plotted in Fig. 4.26, the experimental $\psi(T)$ relation and Eq. 2.27 it is found that the thus calculated $\delta(\Delta t)$ is also independent of the temperature interval chosen, explaining the experiments on Si$_3$N$_4$/Ni fully within the S3TM.
Conclusions

A procedure was proposed to separate magnetization dynamics and MO artifacts. Despite some stimulating results it is concluded that the assumptions on which the procedure is based are not met. The fact that the procedure lifts the difference between rotation and ellipticity transients on the Cu(001)/Ni structure does show, however, that the MO artifacts responsible for this difference are temperature independent. In that sense, the procedure is at least able to produce transient curves that are fully equivalent for rotation and ellipticity in all systems we addressed. In view of the previous discussion, however, the interpretation of the $\delta(\Delta t)$ transients is not trivial.

It must be noted that state-filling effects are expected to play an important role during excitation and thermalization, and as such will affect the interpretation of the MO data during the first hundreds of femtoseconds.

4.8.6 Summary

In this section the temperature dependence of the laser-induced demagnetization was investigated. Describing the experimental MO transients by a spin temperature $T_s$ it is found that the peak temperature rise decreases when increasing the ambient temperature.

Several explanations for this observation were considered, and it was found that the temperature dependence of the electronic heat capacity is the most plausible reason. At elevated temperatures $c_e$ is larger, resulting in a reduced peak electron temperature. When $T_s$ follows $T_e$ with a delay of $\approx 100$ fs, this explains both the decreased effects at higher temperatures and the almost instantaneous response and rapid recovery of $T_s$ after excitation. The latter effect is then simply related to the rapid electron-phonon relaxation. Although the temperature dependence of $c_e$ does correctly predict a reduction of $\Delta T_s$ with temperature, the magnitude of the effect seems slightly lower than observed experimentally.

4.9 Fluence dependence of the magnetization dynamics

From the measurements presented in the previous section it was concluded that the magnetization dynamics is driven by the electron temperature. The spin temperature transients therefore show a temperature dependence that is caused by $c_e(T_e)$. In this scenario also the pump fluence, i.e. the excitation density, should affect the MO transients. Here, fluence dependent measurements are introduced that support the interpretation that $T_s$ is driven by $T_e$.

In the following part experimental results on the Cu(001)/Ni, Si$_3$N$_4$/Ni and -Pt/Co/Pt structure are presented. In the Cu(001)/Ni structure the absorption is relatively low and non-linear effects in fluence are therefore small. However, the other two structures convincingly show that the rise in spin temperature is not linear in fluence. The Si$_3$N$_4$/Ni results are described within the S3TM, showing a good quantitative agreement.
To check the influence of the excitation density MO transients were measured at different fluences. It is important to maintain a good overlap of the pump and probe spots on the sample while changing the fluence. Also, the optical path should remain the same as to conserve the position of the pump-probe coincidence. We varied the fluence by a combination of a half/quarter wave plate and a polarizer.

Figure 4.30(a) shows a series of ellipticity transients, normalized on (external) fluences, as measured on the epitaxial Cu(001)/Ni structure. For $\Delta t < 0$ and $\Delta t > 3$ ps the normalized values are identical, but the recovery of the MO signal is found to proceed faster at lower fluences. This is also evident from the plots of $\Delta \psi$ versus fluence at a fixed delay times $\Delta t$, plotted in Figs. 4.30(b) and (c). The pump induced ellipticity at 0.2 ps scales linearly with applied fluence, but the 1 ps curve shows a more than linear increase. Similar effects are found in the pump induced rotation, shown in panel(c).

The non-linear effects in fluence observed on this structure are relatively small, making their interpretation difficult. The slower relaxation with increasing fluence found in Fig. 4.30(a) can for example be related to a slower electron-phonon relaxation. However, also an interplay between $c_e(T_e)$ and the non-linear temperature dependence of $M(T_s)$ may explain the effect, as well as a different diffusion. In the following part we will look at structures that show a very slow diffusion and a high absorption. The latter enhances non-linear effects in the fluence dependence, simplifying the interpretation.

Fig. 4.30: External fluence dependence of the dynamics on Cu(001)/Ni(10)/Cu. (a) Ellipticity transients at external fluences $f$ of 1.8, 1.4 and 1.2 mJ/cm$^2$. The transients are normalized on $f$ in mJ/cm$^2$. (b) Pump induced change in ellipticity, $\Delta \psi''$ and (c) rotation $\Delta \psi'$ versus fluence for various delay times $\Delta t$. 

\[ \text{Equation} \]
Fig. 4.31: External fluence dependence of the spin dynamics, Si/Si$_3$N$_4$(60)/Ni(10). (a) Ellipticity transients, normalized on fluence, at different fluences. Higher fluences result in larger normalized effects. (b) The same data, but converted to fluence-normalized spin temperatures. After the correction for the non-linear $M(T_s)$ dependence one finds during the first 0.5 ps reduced effects at larger fluences. The solid lines represent smoothed versions of the lowest fluence transient.

4.9.2 Si$_3$N$_4$/Ni structure

As was shown in Chap. 3, the absorption in the Si$_3$N$_4$/Ni(10) structure is about a factor of two larger compared to that of the Cu(001)/Ni(10) sample. Furthermore, in Sect. 4.8 the MO effect on this structure was calibrated against temperature. The larger absorption will enhance non-linear effects in fluence while the calibration allows us to convert the MO transients directly to a spin temperature. The insulating substrate will suppress heat diffusion.

Figure 4.31(a) shows experimental ellipticity transients on the Si$_3$N$_4$/Ni(10) structure measured at different external fluences $f$. The data show that the pump-induced change $\Delta \psi''/f$ is larger at higher fluences, indicating a non-linear dependence of $\Delta \psi''$ on $f$. Using the $M(T_s)$ relation from Fig. 4.25(b) the transients can be converted to spin temperatures, as plotted in Fig. 4.31(b). During the first 0.5 ps $\Delta T_s(\Delta t)/f$ is lower at higher fluences. The increase of $\Delta \psi''/f$ with fluence observed in Fig. 4.31(a) is therefore caused by the non-linear $M(T_s)$ relation. In Fig. 4.31(b) also the slower relaxation at higher fluences is reproduced, as was previously observed in the Cu(001)/Ni structure.

The fluence dependence of the spin temperature transients, reproduced in Fig. 4.32(a), can nicely be described with the 2TM. The solid lines in the figure are simulations using values for the electron and lattice heat capacity as given in Sect. 4.4.4. The position of the peak in spin temperature is observed to be increasingly delayed for higher fluences, c.f. Eq. 4.32. Therefore the magnetic time constant $\tau_M$ was varied from 70 to 100 fs with increasing fluence. In combination with the temperature dependence of $c_e$ this correctly reproduces the non-linear behavior in peak temperature observed in Fig. 4.31(b).
Fig. 4.32: (a) Spin temperature transients at indicated external fluences. The solid lines are results of a S3TM using $c_s = 2.8 \cdot 10^6 \text{J/m}^3/\text{K}$, $\gamma = 3.76 \cdot 10^3 \text{J/m}^3/\text{K}^2$ and $g_{ep} = 180 \cdot 10^{16} \text{W/m}^3/\text{K}$. The absorption at a fluence of 1.8 mJ/cm$^2$ is taken as $0.34 \cdot 10^9 \text{J/m}^3$. Values at other fluences are directly obtained by scaling. The magnetic response is delayed by 100, 90, 80 and 70 fs for fluences from 1.8 to 0.45 mJ/cm$^2$. The dashed line is a simulation using $g_{ep} = 160 \cdot 10^{16} \text{W/m}^3/\text{K}$. The dotted line is a convolution of the pump-probe crosscorrelation with a step function, showing that the observed response is delayed. (b) Transient Kerr and reflectivity data at different fluences. The open symbols are the as-measured reflectivity traces (scaled linearly with a constant factor to obtain a temperature), the dotted lines represent the electronic contribution separated using a fit to Eq. 4.37. The solid lines are simulations using $g_{ep} = 170 \cdot 10^{16}$ and $180 \cdot 10^{16} \text{W/m}^3/\text{K}$ at 1.6 and 0.8 mJ/cm$^2$, respectively. The reflectivity transients are obtained without an additional delay. For the spin temperature transients $\tau_M = 95$ and 75 fs was used.

It must be noted that before electron thermalization, i.e. $\Delta t < \sim 0.2 \text{ ps}$, a description in terms of an electron temperature is not valid. The $\tau_M$ quoted must therefore be seen as a delay with respect to an effective ‘electron temperature’ $T_e$ that before thermalization can be thought of representing the excess energy in the electron system. It is also important to realize that the electron thermalization is fluence dependent. Experiments [16, 17, 68] and theory [6, 24] show that the electron system thermalizes more rapidly with increasing fluence. The increase in $\tau_M$ with fluence can therefore not be explained by a slower thermalization of the electron system.

The electron-phonon coupling constant $g_{ep}$ was fixed at 180 $\cdot 10^{16} \text{W/m}^3/\text{K}$. Experimentally we observed a slightly decreased e-p relaxation with increasing fluence. The dotted line in Fig. 4.32(a) represents a simulation using $g_{ep} = 160 \cdot 10^{16} \text{W/m}^3/\text{K}$, better describing the high fluence measurement. The values for $g_{ep}$ compare reasonably well with Regensburger et al. [60], who used $g_{ep} = 100 \cdot 10^{16} \text{W/m}^3/\text{K}$. Beaurepaire et al. [5] employed a 3TM with $g_{ep} = 80$ and $g_{es} = 60 \cdot 10^{16} \text{W/m}^3/\text{K}$. In the 3TM, energy is removed from the electron system both by coupling to the spin as well as to the lattice system. If the spin and lattice heat capacities $c_s$ and $c_l$ are of the same order, the energy transport to both systems will be similar. In that case the two coupling constants combine to an effective coupling constant...
\[ g_{e \rightarrow sl} \approx g_{es} + g_{el} = 140 \cdot 10^{16} \text{ W/m}^3/\text{K}. \] It must be noted that in both Refs. [5, 60] \( \gamma \) was chosen \( 6 \cdot 10^3 \text{ J/m}^3/\text{K}^2 \), overestimating the experimental temperature dependence of \( c_{es} \) and therefore also \( c_{el} \) itself. The figures used here exactly describe the experimental heat capacity.

To calculate the spin temperatures Eq. 2.27 was used, correcting for the equal size of pump and probe spot. In the derivation of this equation, a Gaussian temperature profile was assumed. However, this is not strictly valid as \( c_e \) increases with temperature, ‘flattening’ the profile. A detailed calculation shows a maximum effect of 5\% on the peak temperature at the highest fluence. As the accuracy of the deduced spin temperatures is limited, with an estimated error of 15 K, no extra correction is applied.

Interestingly, also the reflectivity data show a non-linear fluence dependence. In Fig. 4.32(b) the transient reflectivity data are plotted together with the corresponding MO traces, indicated by the solid circles. The open squares represent the measured reflectivity transients that contain both electron and lattice contributions. Upon doubling the fluence to 1.6 mJ/cm\(^2\), the peak change in reflectivity only increases with a factor of 1.85. In Sect. 4.6 a procedure was described to estimate the lattice contribution to \( \Delta R/R \), c.f. Eq. 4.37. The dotted lines in the figure represent reflectivity transient where the estimated lattice contribution is removed.

The solid lines represent simulated curves using the 2TM. The MO transients are well described using similar parameters as in Fig. 4.32(a), their values given in the caption of the figure. This procedure neglects electron thermalization, and the simulated curves therefore rise faster than the measured transients. The simulation does indeed correctly predict a non-linear increase of the electron temperature with fluence. However, on a longer time scale the calculated \( T_e \) transients deviate from both the as-measured reflectivity data and the assumed electronic contribution. This suggests that the lattice contribution to \( \Delta R/R \) is overestimated, resulting in an apparently faster electron-phonon relaxation. The simulated temperature transients yield \( \tau_E = 0.6 \text{ ps} \), more in line with the literature values reported in Sect. 4.6.

### 4.9.3 Pt/Co/Pt structure

The fluence dependent behavior is not only restricted to Ni, but is also observed on the Pt/Co/Pt structure. Figure 4.33 shows two (normalized) transient ellipticity measurements taken at contrasting fluence. From static and dynamic Kerr measurements we found that in this sample \( M'(T) \) is constant in the temperature range considered. Therefore \( \Delta \psi'' \) is directly proportional to the change in spin temperature \( \Delta T_s \). Like the Ni structures, c.f. 4.31(b), also the Pt/Co/Pt sample shows a decrease of the normalized peak temperature with increasing fluence. Since \( M'(T) \) is constant, the effect is directly visible in \( \Delta \psi'' \).

### 4.9.4 Conclusions

The magnetization dynamics during the first picoseconds shows a non-linear fluence dependence that can be explained by the temperature dependence of the electronic heat capacity. The non-linear behavior is both observed in Ni and Pt/Co/Pt structures, and thus appears general. Using a realistic set of parameters and a linear relation between \( c_e \) and \( T_e \), the fluence dependence of the spin temperature transients can be well described. Note that a different fluence dependence may be ob-
Fig. 4.33: Fluence dependence of spin temperature on the Pt/Co/Pt structure. For this structure $M'(T)$ is found to be temperature independent in the temperature range considered. The pump-induced change in ellipticity, $\Delta \psi''$ can therefore simply be converted to a spin temperature by multiplying with a suitable constant $c$.

served in the as-measured MO transients due to the non-linear $M(T_s)$ relation. The measurements furthermore show a slower response of the spin system and a reduction of the electron-phonon coupling constant with fluence. This is in line with the temperature-dependent measurements, which show a similar behavior with increasing ambient temperature.

A non-linear fluence dependence was also observed in the transient reflectivity data. Although the magnitude of the effect follows correctly from the model, the simulated and measured curves deviate on a longer time scale. This is most likely caused by lattice contributions to $\Delta R/R$ that are difficult to correct for in the structures considered.

Concluding, the fluence dependence of the magnetization dynamics is well explained by a demagnetization process that is driven by the electron temperature. Specifically, $T_s$ follows $T_e$, with $T_s$ obtained from the magneto-optic transients by assuming the equilibrium $M(T_s)$ relation.

### 4.10 Instantaneous versus delayed response

In the previous sections, focusing on the dynamics after thermalization, experimental evidence was presented showing that the ultrafast demagnetization is driven by the electron temperature $T_e$. In this section we will specifically discuss the dynamics during the first hundreds of femtoseconds. Since the experiments of Beaurepaire et al. [5] it has been a matter of debate whether or not the spin response is delayed with respect to optical excitation at $t = 0$. More precisely, we can discern three scenarios:

1. The spin response is (nearly) instantaneous, reaching a minimum in the magnetization before electron thermalization.
2. The spin temperature directly follows $T_e$, i.e. $T_s = T_e$ and $\tau_M \sim \tau_{th}$. 


3. The spin temperature follows the electron temperature with a delay, i.e. $\tau_M > \tau_{th}$.

Note that $\tau_M$ describes a delay with respect to $T_{e,E}$, i.e. the excess energy in the electron system. Therefore, for $\tau_M = \tau_{th}$ a spin temperature transient closely similar to $T_{e,\text{dist}}$ is found. In this section we will examine the MO response during the first picosecond in detail. Before going to the experimental results a summary is given of results published on this subject.

4.10.1 Other work

The first ultrafast demagnetization experiments on Ni by Beaurepaire et al. [5] showed a magnetic response that was delayed by 2 ps with respect to electron thermalization. This initial result was based on a measurement with just nine points during the first four picoseconds. Later measurements on the same structure showed a response that was $\sim 200$ fs delayed with respect to the convolution of the pulse envelope with an exponential decay [7]. In both experiments the minimum in magnetization was found after electron thermalization. The spin response was therefore delayed with respect to that of the electron system, i.e. consistent with scenario (3).

However, detailed investigations of the Ni dynamics at the Freie Universität Berlin using SHG showed convincing examples of a breakdown of the MO signal before electron thermalization [36] and even within the pump-probe crosscorrelation of 60 fs [35], i.e. scenario (1). Only on other materials evidence for a delayed response is reported. In Ref. [34] the magnetic breakdown of GdFeCo shows a delay of $\sim 500$ fs with respect to the transient reflectivity, and in [48] a temperature dependent demagnetization time is observed in the half-metal Sr$_2$FeMoO$_6$. In the latter case $\tau_M$ was found to increase strongly when approaching $T_c$, reaching values close to 200 ps.

4.10.2 Experimental results

In this work a number of Ni samples has been investigated at various ambient temperatures and fluences. By combining these measurements we will try to give an answer to the question whether or not the spin response is delayed with respect to electron thermalization.

In Fig. 4.34 measured ellipticity transients on the Cu(001)/Ni and Si$_3$N$_4$/Ni structure are plotted, zooming in on the first 0.7 ps after pump excitation. The dashed curves represent the convolution of the pump-probe crosscorrelation with a step function, describing the effect of measuring an instantaneous (step) response with a limited experimental resolution. Comparing these curves with the measured transients one sees that on the Cu(001)/Ni sample the MO response is instantaneous within the experimental resolution, c.f. Fig. 4.34(a). On the other hand, the MO transients measured on the Si$_3$N$_4$/Ni structure, depicted in Fig. 4.34(b), show a clear delay. In the latter figure also the transient reflectivity is plotted. The maximum electron temperature as given by the extremum in $\Delta R/R$ is reached at $\Delta t_{\text{ex}} \approx 200$ fs. The MO transients reach their minimum values after 200 fs, indicating a delayed spin response. A similar result is found on the SiO$_2$/Ni structure.

In Fig. 4.34 MO transients are plotted for different ambient temperatures. Raising the temperature is expected to accelerate the thermalization of the electrons, see e.g. Eq. 4.6. The MO transients do however show a clear shift of their minima.
to a longer delay time, i.e. from 160 to 210 fs for the Cu(001)/Ni and from 270 to 390 fs for the Si$_3$N$_4$/Ni structure. The fact that for both structures the MO response slows down while the electron thermalization accelerates shows that also in the Cu(001)/Ni structure there is no direct relation between electron thermalization and demagnetization.

The fluence dependent measurements on Si$_3$N$_4$/Ni, reproduced in Fig. 4.35(a), can be analyzed along the same line. Increasing the laser fluence reduces the electron thermalization time since the maximum electron temperature is increased [6, 16, 33]. However, the spin temperature transients plotted in Fig. 4.35(a) show an increasingly delayed response with fluence. At an external fluence of 0.45 mJ/cm$^2$ an extremum is reached after 180 fs, while at the highest fluence it takes 270 fs to reach the maximum reduction of the magnetization. Fits using Eq. 4.15 for $|\Delta t| > 100$ fs yield $\tau_M$ varying from 70 to 100 fs going from 0.45 to 1.8 mJ/cm$^2$, c.f. Fig. 4.32. During temporal overlap of the pump and probe pulse Eq. 4.15 poorly describes the data. This was also observed in the reflectivity transients, see e.g. Fig. 4.12(b), an effect that was attributed to a coherent contribution. In Fig. 4.35(b) the as-measured ellipticity transient at 1.8 mJ/cm$^2$ is fitted with the sum of Eq. 4.15 and a Gaussian centered at $\Delta t = 0$ to attribute for coherent effects. This removes most of the discrepancies around $\Delta t = 0$, while the magnetic relaxation time $\tau_M$ remains 100 fs. From transient reflectivity measurements at 1.8 mJ/cm$^2$ a thermalization $\tau_{th} = 80$ fs is derived, see e.g. Fig. 4.12.

This fluence dependency can be obtained in a different way by varying the Ni thicknesses. In Sect. 3.3.2 it was found that with increasing Ni thickness the absorption per unit volume decreases. In Fig. 3.8(a) magneto-optic transients are plotted for various Ni thicknesses. The extremum of the transients clearly shows a shift to
Fig. 4.35: (a) Spin temperature transients measured on Si\textsubscript{3}N\textsubscript{4}/Ni as a function of fluence. Increasing the fluence shifts the peak in spin temperature to a longer time delay. Solid lines are a fits to Eq. 4.15, showing an increase of $\tau_{th}$ from 0.06 to 0.1 ps. (b) As-measured ellipticity transient at a fluence of 1.8 mJ/cm\textsuperscript{2}. The solid line is a fit to Eq. 4.15 ($\tau_{th} = 0.1$ ps), including an additional Gaussian contribution centered at $\Delta t = 0$. In the dashed curve the Gaussian is removed.

longer $\Delta t$ for thinner films, i.e. for higher excitation densities.

In Sect. 4.4.1 it was argued that spin-lattice interactions are required to reduce the magnetization. It is of interest to make a crude estimate of the number of spin flips and phonons emitted by the cooling electron gas. Here we will use the known number of spins in the excited volume to convert the transient loss of magnetization to the number of effective spin flips. Also, the number of emitted phonons is estimated from the electron-phonon energy scattering rate.

Figure 4.36(a) shows a transient ellipticity trace on Si\textsubscript{3}N\textsubscript{4}/Ni(10) at an external fluence of $\sim$ 1.8 mJ/m\textsuperscript{2}, corresponding to the highest fluence curve in Fig. 4.35(a). The solid line is a fit with a broadened version of Eq. 4.15, the dashed line shows the effect of using an impulse excitation. In the experiment, a volume $\pi r^2 d$ is heated, with $r \approx 5$ $\mu$m and $d \approx 10$ nm. With $0.6 \mu_B$ per atom for Ni at $T = 0$ K, the volume contains $4 \cdot 10^{10}$ spins. This allows us to convert the loss of magnetization to the (effective) number of flipped spins, as is shown by the curve labeled $N_{\text{spin}}$ in Fig. 4.36(b). In a similar manner, the number of emitted phonons $N_{\text{phonon}}$ can be derived. The excess energy in the electron system is found to decay with a time constant $\tau_E \approx 0.4$ ps after excitation, c.f. Figs. 4.4(a) and 4.15. Using the absorbed energy of $\sim 0.4$ nJ and assuming only zone-edge phonons of energy $k_B \Theta_D = 40$ meV are emitted, one obtains the curve labeled $N_{\text{phonon}}$ in Fig. 4.36(b). We emphasize that the number $N_{\text{phonon}}$ thus calculated will underestimate the number of e-p scattering events, since (i) we used the maximum phonon energy available and (ii) phonon absorption processes were completely neglected. Despite the long energy relaxation time $\tau_E = 0.4$ ps compared to the demagnetization time $\tau_M = 0.1$ ps, and even in this
Fig. 4.36: (a) Transient ellipticity trace corresponding to the highest fluence trace of Fig. 4.35(a). The solid line represents a fit with a pulse-broadened version of Eq. 4.15 for $|\Delta t| > 100$ fs, yielding $\tau_{M} = 0.1$ ps. Without broadening, the dashed line is obtained. (b) The number of effective spin flips $N_{\text{spin}}$ as derived from panel (a) and the number of emitted 40 meV phonons $N_{\text{phonon}}$ using $\tau_{E} = 0.4$ ps and an absorption of $0.3 \cdot 10^{9}$ J/m$^3$. For all $\Delta t$, $N_{\text{phonon}} > N_{\text{spin}}$.

‘worst case’ scenario, $N_{\text{phonon}}$ is at all time larger than $N_{\text{spin}}$. This is directly related to the large number of 40 meV phonons needed to transport the excess energy from the electron to the phonon system. The transients show that during demagnetization less than one spin flip is required per (net) emitted phonon. Therefore, a possible role of the phonon system in the demagnetization process can not be excluded.

4.10.3 Discussion

Magneto-optic transients measured on the Si$_3$N$_4$/Ni and SiO$_2$/Ni structures show a non-instantaneous response. The delay time at which the maximum reduction of the magnetization is reached, a quantity related to the demagnetization time, depends on temperature and fluence. The data suggest a slower magnetic response at elevated temperatures. This is also as found for the half-metal Sr$_2$FeMoO$_6$ [48], although there relaxation times of hundreds of picoseconds are observed. Similar measurements on the Cu(001)/Ni structure that we presented here do show an instantaneous response. However, also here the minimum in the Kerr response does shift to longer delay times with increasing ambient temperature. These results therefore present the same ambiguity that is also found in literature.

Interestingly, in reviewing published results on Ni it is found that only on insulator/thin film samples a delayed response is observed, i.e. the glass/Ni(22) structure of Beaurepaire et al. [5, 7] and the polycrystalline films used here. In work showing an instantaneous response (within the experimental resolution) or a minimum in the magnetization before the maximum in the electron temperature, either thick Ni films [57], bulk Ni crystals [36, 60] or Cu/Ni samples [11, 26] were used. This may be a
coincidence, but could also point at the importance of transport effects, or possibly magneto-optic artifacts.

It must be noted that magneto-optic techniques may not yield the true magnetization dynamics on the time scale of electron thermalization. In Sect. 4.7 it was shown that within the crosscorrelation of the pump and probe pulse coherent effects can contribute to the magneto-optic signal. In Ref. [27] it was furthermore shown that during electron thermalization ellipticity and rotation transients on a CoPt$_3$ alloy showed strongly contrasting dynamics.

Concluding, all experimental evidence so far points at an extremely rapid demagnetization within several hundreds of femtoseconds, i.e. on the time scale of electron thermalization. Results on the precise time scale of the effect are, however, contradictory. In this work measurements on Si$_3$N$_4$/Ni samples showed a minimum in the magnetization after 390 fs (393 K). This minimum is clearly delayed with respect to the extremum in the transient reflectivity ($\Delta t = 200$ fs), and most likely also with respect to the electron thermalization time. On the other hand, the magneto-optic response of a Cu(001)/Ni structure was found to be instantaneous within the experimental resolution. The contradicting results may be related to different material properties, but one can also doubt if magneto-optic techniques can unambiguously probe the magnetization dynamics during the thermalization process.

### 4.11 Conclusions

In this chapter the ultrafast pump-induced demagnetization of ferromagnetic materials was investigated using magneto-optic techniques. It was found that

1. The MO-signal is not always a good measure of the magnetization dynamics. Experiments on epitaxial Cu/Ni structures showed coherent contributions to the MO-signal within the crosscorrelation of pump and probe pulse, and also long-term effects were observed that may be related to strain. One should therefore be extremely careful directly relating transient MO experiments to magnetization dynamics, especially during electron thermalization when the system is in a highly non-equilibrium state.

2. At elevated temperatures the pump-induced rise in spin temperature decreases. This effect is in agreement with a magnetization dynamics driven by the electron temperature, since the electronic heat capacity increases with temperature. However, calculations on the magnitude of the effect underestimate the experimental results.

3. When increasing the pump fluence the pump-induced rise in spin temperature decreases. Also this effect is in agreement with a magnetization dynamics driven by the electron temperature. Direction and magnitude of the effect are in good quantitative agreement with the temperature dependence of the electronic heat capacity.

4. The pump-induced demagnetization occurs within hundreds of femtoseconds. The magnetization dynamics on polycrystalline Si$_3$N$_4$/Ni and SiO$_2$/Ni structures show a response that is delayed with respect to electron thermalization, while experiments on epitaxial Cu/Ni structures display an instantaneous effect. The demagnetization time is found to depend on ambient temperature, and for
the polycrystalline structures also on fluence. In general, a slower relaxation is found at higher fluences and temperatures.

4.12 Outlook

Beaurepaire and co-workers [5] were the first to suggest a relation between the spin- and electron-temperature to describe the ultrafast demagnetization. Later, Hohlfeld et al. even suggested the relation $T_s(\Delta t) = T_e(\Delta t)$. Since the electronic (and spin) heat capacity depend on temperature, this implies a fluence and ambient temperature dependence of the dynamics. In this thesis these dependencies were for the first time observed, and a reasonable agreement with variations in the (estimated) electronic heat capacity was found. However, still some open issues remain.

The variation in $c_e(T_e) = \gamma T_e$ is not sufficient to explain the ambient temperature dependence of the dynamics, as shown in Fig. 4.26. In this work already a larger value of $\gamma$ was chosen than obtained from (low-temperature) heat capacity measurements. This was justified as the inclusion of magnetic contributions to $c_{tot}$, i.e. assuming a fast equilibration of $T_s$ and $T_e$. Experimental or theoretical information on $c_e(T)$ would however be helpful.

Also, the transient reflectivity measurements did not show a temperature dependent behavior. It must be noted that the transient reflectivity data presented in this report are strongly affected by lattice contributions, although this is not expected to play an important role during the first hundreds of femtoseconds. In general, the interpretation of reflectivity data on 3d-metals is based more on the assumption of a linear relation with $T_e$ than on actual model calculations. Alternative methods to measure the electron dynamics, e.g. time-resolved photoemission spectroscopy, could provide complementary information to validate this approach and to interpret the magneto-optic data.

In all reports on pump-probe measurements on 3d-ferromagnets an extremely fast demagnetization is observed. The exact response does however vary from instantaneous to some hundreds of femtoseconds delayed, i.e. after electron thermalization. Part of this ambiguity may be related to magneto-optic effects. A direct way to test this is by varying the wavelength of the probe beam, for example by frequency doubling. The latter method will greatly change the sensitivity to the non-thermal electron distribution, directly revealing state-filling effects to the MO signal.

At this point pump-probe demagnetization experiments do show an ultrafast demagnetization that is related to the electron system, but a thorough theoretical understanding of the interactions involved is still missing. From the experimental side one could work to obtain more information. It has for example been suggested that at the photon energies currently used ($\sim 1.6$ eV) one can directly create Stoner excitations [39], requiring excitation energies of $\sim 0.1 - 0.6$ eV for Ni [47]. By reducing the energy of the pump photons it is experimentally possible to test this hypothesis.
5. PRECESSIONAL DYNAMICS

5.1 Introduction

In pump-probe experiments on ferromagnetic materials, the magnitude of the magnetization can be changed on a sub-picosecond time scale by laser heating. In this chapter we will show that also the direction of the magnetization can be changed by sudden laser-heating. By exploiting the temperature dependence of the magnetic anisotropy, the pump excitation can be used to launch a coherent precession of the magnetization. The precession can be followed in time by a delayed probe pulse with a sub-picosecond resolution. This allows for an all-optical study of the precessional dynamics of magnetic materials, thus revealing information on their dynamic magnetic properties.

Because of the all-optical character of the technique, it enables a local, non-contact measurement of structured magnetic layers as for example present in magnetic readheads, Magnetic Random Access Memories (MRAMs) and spintronic devices in general [59, 80]. The approach works in the time domain and therefore allows for a direct determination of the damping. This is a great advantage over frequency domain techniques such as FerroMagnetic Resonance (FMR) or Brillouin light scattering where information on damping is only indirectly obtained. Magnetic damping is one of the crucial though poorly understood phenomena that greatly affects the fast magnetic switching behavior in spintronic devices.

The first section of this chapter briefly introduces the basic theory needed to understand precessional phenomena in ferromagnets. The precession of an isolated magnetic moment in an applied field is readily described. However, in a ferromagnetic solid the precession of the magnetic moments is also influenced by for example the shape of the material and the orientation of neighboring spins. These effects can be accounted for by introducing a fictitious effective magnetic field in which the moments precess.

After the introduction of the theory, the mechanism of the optical excitation is explained, and its general applicability is demonstrated in a qualitative way. Next, the approach is validated by a quantitative comparison with microwave FMR measurements. The remaining part is dedicated to applications of the technique to different structures, proving the existence of a canted state in epitaxial Cu/Ni/Cu wedges, showing standing spin-waves in polycrystalline Ni-layers, and demonstrating the local character of the technique by characterizing microstructured Ni\textsubscript{80}Fe\textsubscript{20} elements.

5.2 Magnetic anisotropy and precessional phenomena

This section briefly describes the basic theory needed to understand precessional phenomena in ferromagnets. In a semi-classical approach, the precession of the mag-
netization vector is driven by a torque exerted on the magnetization by an effective magnetic field. In the context of this thesis, the effective magnetic field is composed of the applied field, the anisotropy fields and the exchange field,

$$\mathbf{H}_{\text{eff}} = \mathbf{H}_{\text{applied}} + \mathbf{H}_{\text{anis}}(\mathbf{M}) + \mathbf{H}_{\text{exch}}(\mathbf{x}), \quad (5.1)$$

with $\mathbf{x}$ the spatial coordinates. The exchange contribution $\mathbf{H}_{\text{exch}}$, which is only present when the magnetization is spatially varying, will be accounted for in a mean-field approximation.

In the next parts the different anisotropy contributions to the effective field are discussed. Then the Landau-Lifshitz-Gilbert equation, describing the dynamic behavior of the magnetization, is introduced and solved for a thin magnetic layer using a linearization technique. Finally, different experimental techniques to measure precessional phenomena are discussed.

### 5.2.1 Magnetic anisotropy

When a magnetic field is applied to a ferromagnetic material, its magnetization will generally not align itself with the direction of the external field. Instead, the magnetization will be inclined towards preferential axes that are caused by the magnetic anisotropy of the material. This anisotropy can have a number of different origins, for example the shape of the sample (shape anisotropy), the crystal structure (magneto-crystalline anisotropy) or even stress in the layer (magneto-elastic anisotropy).

Formulated in terms of energy, the free enthalpy density of a ferromagnetic material in an external field $\mathbf{H}$ can be written as

$$E(\mathbf{M}, \mathbf{H}) = E_{\text{anis}}(\mathbf{M}) + \mu_0 \mathbf{M} \cdot \mathbf{H}, \quad (5.2)$$

i.e. the sum of the anisotropy energy and the Zeeman energy. In the Stoner-Wohlfarth model, see e.g. Ref. [43], the orientation of the magnetization as a function of field follows a (local) minimum in Eq. 5.2. This approach is valid in the single domain regime where domain wall motion does not enter the energy function. Since the systems gains energy when rotating the magnetization away from minima in $E_{\text{anis}}(\mathbf{M})$, these minima will appear as preferential or ‘easy’ axes of the magnetization.

In modeling the magnetization dynamics it is convenient to use a fictitious field, the anisotropy field $H_{\text{anis}}$, to describe the effect of anisotropy. $H_{\text{anis}}$ can directly be derived from $E_{\text{anis}}$ using

$$\mathbf{H}_{\text{anis}} = -\frac{1}{|\mathbf{M}|} \nabla E_{\text{anis}}(\mathbf{M}). \quad (5.3)$$

**Shape anisotropy**

One of the most important sources of magnetic anisotropy in thin films and nanostructures is the shape anisotropy, Fig. 5.1(a). Its origin lies in the long range magnetic dipolar interaction that senses the outer boundaries of the sample. The dipolar interaction makes it unfavorable for a thin magnetic film to have its magnetization pointing out-of-plane (OOP) due to the energy involved with the large stray fields. For an ellipsoidal ferromagnet, the effect of the shape anisotropy is given by:

$$\mathbf{H}_{\text{shape}} = -\mathbf{N} \mathbf{M}, \quad (5.4)$$
with \( \mathbf{N} \) the shape-dependent demagnetization tensor. For a thin film in the \( xy \)-plane, all elements are zero except \( N_{zz} \), which is 1. Applying an out-of-plane field to a thin film, which tends to increase \( M_z \), will thus induce a demagnetizing field with the opposite direction. The energy per unit volume associated with this effect can be derived by calculating the magnetostatic energy. For a thin film, it follows that

\[
E_{\text{shape}} = \frac{1}{2} \mu_0 |M|^2 \sin \theta_M^2, \tag{5.5}
\]

with \( \theta_M \) the angle of the magnetization with respect to the film plane.

**Magneto-crystalline anisotropy**

In crystalline materials, spin-orbit and dipole-dipole interactions add an extra anisotropy term to the magnetization that reflects the symmetry of the lattice, as schematically depicted in Fig. 5.1(b). For cubic lattices, as for example in nickel, the magneto-crystalline energy can be written as:

\[
E_{\text{cryst}} = K_0 + K_1 (m_x^2 m_y^2 + m_y^2 m_z^2 + m_z^2 m_x^2) + K_2 m_x^2 m_y^2 m_z^2 + \ldots \tag{5.6}
\]

\[
m_i = \frac{M_i}{|M|}, \tag{5.7}
\]

with \( x, y \) and \( z \) the crystal axes. For bulk nickel, with \( K_1 < 0 \), the crystalline anisotropy will tend to align the magnetization along the diagonals of the cubic lattice to minimize the energy.

**Magneto-elastic anisotropy**

When a crystalline layer is put under stress, its lattice will deform, see e.g. Fig. 5.1(c). This changes the magneto-crystalline anisotropy, which can be expressed by...
an additional strain-anisotropy term. In the epitaxial Cu/Ni/Cu wedges the strain in
the Ni layer adds a uniaxial OOP anisotropy contribution described by

\[ E_{\text{strain}} = K_u m_z^2. \] (5.8)

**Exchange interaction**

The exchange field, the last term in Eq. 5.1, is due to the exchange interaction that
is responsible when there is a spatial variation in the orientation of the magnetization,
and it causes spinwave phenomena in ferromagnets. For small excitations, \( H_{\text{exch}} \) is given by

\[ \vec{H}_{\text{exch}} = \frac{D}{M} \nabla^2 \vec{M}, \] (5.9)

with \( D \) the exchange stiffness. For cubic lattices, \( D \) is given by

\[ D = 2JSa^2, \] (5.10)

with \( J \) the exchange integral, \( \hbar S \) the spin angular momentum and \( a \) the lattice con-
stant [49].

5.2.2 **Equilibrium magnetization**

The anisotropy energy terms, i.e. Eqs. 5.5, 5.7, and 5.8, in combination with the
Zeeman energy due to the applied field \( (\mu_0 \vec{H} \cdot \vec{M}) \) can be used to determine the equi-
librium orientation of the magnetization. For a thin film with only shape anisotropy
the total energy can be written as

\[ E(\theta_M) = \frac{1}{2} \mu_0 |M|^2 \sin(\theta_M)^2 - \mu_0 |H||M| \sin(\theta_M - \theta_H) \] (5.11)

with \( \theta_M \) and \( \theta_H \) the angle of the magnetization and the external field with respect to
the film plane, respectively. In equilibrium, \( E(\theta_M) \) corresponds to a (local) minimum
and thus

\[ \frac{dE}{d\theta_M} = 0 \] (5.12)

\[ \frac{d^2E}{d^2\theta_M} > 0. \]

From this it follows that for an out-of-plane applied field \( \theta_M \) is given by

\[ \theta_M = \arcsin \left( \frac{|H|}{|M|} \right) \] (5.13)

For more complex energy-functions a solution can only be obtained numerically.

5.2.3 **Magnetization dynamics**

In the previous section the equilibrium orientation of the magnetization was calculated.
However, to describe the dynamics of magnetization processes the equation of
motion is needed:

\[ \frac{d\vec{M}}{dt} = -\gamma \mu_0 \left( \vec{M} \times \vec{H}_{\text{eff}} \right) + \frac{\alpha}{M} \left( \vec{M} \times \frac{d\vec{M}}{dt} \right). \] (5.14)
The first term of this Landau-Lifshitz-Gilbert (LLG) equation states that the change of the magnetization is given by the torque on the magnetization ($\vec{M} \times \vec{H}_{\text{eff}}$) induced by the effective magnetic field (Eq. 5.1). $\gamma$ is the gyromagnetic ratio and is determined by the Landau splitting factor $g$ of the precessing electrons,

$$\gamma = \frac{g\mu_B}{h}. \quad (5.15)$$

In equilibrium $d\vec{M}/dt = 0$ and thus $\vec{M} \times \vec{H}_{\text{eff}} = 0$, which is another way of stating the equilibrium condition Eq. 5.12.

The second term on the right-hand side is the (phenomenological) Gilbert damping term, proportional to a dimensionless damping parameter $\alpha$. After a sudden change of the applied field the damping leads to a gradual alignment of the magnetization with the effective field. For $\alpha^2 \ll 1$ the magnetization relaxes exponentially to its equilibrium orientation on a typical time scale $\tau$ given by

$$\tau = \frac{1}{\alpha \omega}, \quad (5.16)$$

with $\omega$ the precession frequency. $\alpha = 1$ represents a critically damped precession.

When the magnetization is far from equilibrium, numerical methods will generally be needed to calculate the trajectory of the magnetization. However, for small excitations the trajectory can be approximated by an elliptical precession around the equilibrium orientation, allowing for a linearization of the LLG equation. With $\vec{M}_0$ the equilibrium orientation and $\delta \vec{M}$ the displacement, the motion of the magnetization can be approximated by

$$\vec{M} = \vec{M}_0 + \delta \vec{M}(t), \quad (5.17)$$

$$\delta \vec{M}(t) = \text{Re}(\delta \vec{M} \exp[i(\omega t + k z)]). \quad (5.18)$$

$\omega$ is the precession frequency and the extra phase-term $kz$ allows for spin-waves in the $z$-direction. Considering a thin layer with only shape anisotropy and including exchange interactions, the effective field can be written as

$$\vec{H}_{\text{eff}} = \vec{H}_{\text{applied}} - N \vec{M} + D \nabla^2 \vec{M}. \quad (5.19)$$

Applying Eqs. 5.18 and 5.19 to the LLG equation, ignoring damping and higher-order terms in $\delta \vec{M}$, one finds

$$i \omega \delta \vec{M} = \gamma \mu_0 \delta \vec{M} \times \left( \vec{H} - N \vec{M}_0 \right) - \gamma \mu_0 \vec{M}_0 \times \left( D \delta \vec{M} + k^2 D M \delta \vec{M} \right). \quad (5.20)$$

For a thin layer only $N_{zz}$ is non-zero and furthermore the $x$- and $y$- directions are equivalent. In this case Eq. 5.20 can be solved by writing it in cartesian components and putting the determinant of the coefficient matrix to zero. This results in the solution for $\omega$,

$$\omega = \gamma \mu_0 \left[ \left( H_x + k^2 D M \right) \left( H_x + \left[ k^2 D + N_{zz} \right] M_x \right) + \left( H_z + \left[ k^2 D - N_{zz} \right] M_z \right) \right]^{1/2}, \quad (5.21)$$
where $M_y$ and $H_y$ were chosen zero to profit from the symmetry. Equation 5.21 has the familiar limits

$$\omega = \gamma \mu_0 \left[ (H - N_{zz} M) + Dk^2 \right]$$

(5.22)

for $H_x = M_x = 0$, i.e. the situation with the magnetization and applied field completely out-of-plane, and

$$\omega = \gamma \mu_0 \sqrt{(H + Dk^2)(H + Dk^2 + N_{zz} M)}$$

(5.23)

for $H_z = M_z = 0$, the completely in-plane equivalent.

### 5.2.4 Measuring precessional phenomena

In equilibrium the magnetization of a ferromagnetic material is aligned with $\vec{H}_{\text{eff}}$. To excite a precessional motion $\vec{H}_{\text{eff}}$ or $\vec{M}$ need to be changed on a time scale that is short compared to the precession time, Eq. 5.16.

In FerroMagnetic Resonance (FMR) experiments [18] an electromagnetic field in the microwave frequency range is applied to a ferromagnetic sample, see e.g. Fig. 5.2(a). Its magnetic component $H(\omega)$ can excite a precession of the magnetization if the frequency of the microwave field matches the precession frequency. In this situation the microwave absorption is resonantly enhanced, an effect that can accurately be measured when the ferromagnetic sample is placed in a microwave cavity. In FMR experiments the microwave frequency is generally fixed, and the external field is swept to obtain resonance conditions. Since FMR measures the absorption of the complete sample it is essentially a non-local technique, and therefore the experiments have to be performed on uniform layers. In this work a comparison with FMR data is used to validate the all-optical technique presented in the next section.

Besides applying a rapidly oscillating field one can also abruptly change the applied magnetic field. This alters the equilibrium orientation of the magnetization and thereby starts a precession. The rise time of the field pulse should be sufficiently
short, since damping works to align the magnetization with the changing equilibrium orientation. To apply a short field pulse the ferromagnetic material is generally put on top of a strip line, i.e. a conductor optimized for the transport of high frequency signals [10, 22], or inside a coil of µm dimensions [1, 32]. As shown in Fig. 5.2(b), sending a short current pulse through such structures will generate a magnetic field with a fast rise time in the ferromagnetic film. The excited precession can be followed in time, either by an optical measurement with a delayed probe pulse [21] or by an electronic detection scheme using the induction voltage generated in the strip line by the precessing magnetization [65]. This pump-probe technique works in the time-domain, contrary to FMR which maps the frequency response of the ferromagnetic system.

In Fig. 5.2(c) the Brillouin Light Scattering (BLS) [12] method is schematically depicted. In BLS, a monochromatic laser beam is incident on the magnetic structure. Light that is scattered from the sample is collected and spectrally analyzed. Inelastic scattering processes, e.g. absorption and emission from magnons, will introduce spectral intensities that are offset with respect to the original laser frequency. Analysis of the optical spectrum yields information (in the frequency domain) on the magnetic excitations.

5.3 All-optical pump-probe technique

In this section a novel, all-optical technique is presented to launch and detect a precession of the magnetization. In our approach, the temperature of a ferromagnetic material is suddenly altered by an intense laser pulse, generating a short-lived change of the anisotropy field. This ‘anisotropy field pulse’ subsequently launches a precession of the magnetization. The induced precession is measured by a second, time delayed laser pulse. As in the magnetic pump-optical probe technique, c.f. 5.2.4, the precession is measured directly in the time-domain. However, with the optical excitation method no strip line or miniature coil is needed.

After discussing the experimental setup and a typical measurement the excitation mechanism and the applicability of the technique will be addressed. Then different scenarios for the pump-induced change of the anisotropy will be investigated, followed by conclusions.

5.3.1 Experimental setup

One of the experimental configurations employed is schematically depicted in Fig. 5.3(a). A sample with in-plane magnetization is mounted between two magnet poles that generate a nearly out-of-plane field and pull \( \vec{M} \) to a canted orientation. The excitation is created by an intense laser pulse that is focused on the sample using a lens mounted inside one of the poles of the electromagnet. After a variable time delay \( \Delta t \) a second, much weaker pulse is used to probe the resulting change in magnetization by measuring the polarization state of the reflected laser pulse. In the polar configuration employed here, mainly the out-of-plane component of the magnetization, \( M_z(\Delta t) \), is measured.

Figure 5.3(b) represents a typical measurement on a Si/SiO\(_2\)(5)/Ni(7) structure, showing the relative change \( \Delta M_z/M_z \) as a function of pump-probe delay \( \Delta t \). For \( \Delta t < 0 \) (region I), the magnetization is probed before excitation and therefore \( \Delta M_z = \ldots \)
Fig. 5.3: (a) Schematic pump-probe setup. The pump pulse locally heats the sample, the magnetization dynamics is subsequently measured by the polarization state of the reflected probe pulse. Due to the rotation of the sample a finite in-plane component of the applied field is present. (b) Typical room temperature measurement on a 7 nm Ni film (open circles: data, thick line: fit) displaying the perpendicular component of the magnetization, $M_z$, as a function of delay time $\Delta t$. The different stages are indicated by numbers. (c) The stages of the excitation process: I. $\Delta t < 0$, the magnetization $\vec{M}$ points in equilibrium direction (dotted line), IIa. $\Delta t = 0$, the magnitude of $\vec{M}$ and the anisotropy change due to heating, thereby altering the equilibrium orientation, IIb. $0 < \Delta t < 10$ ps, $\vec{M}$ starts to precess around its new equilibrium, III. $\Delta t > 10$ ps, heat has diffused away, the magnitude of $\vec{M}$ and anisotropy are restored, but the precession continues because of the initial displacement of $\vec{M}$.

0. When the pump pulse heats the sample at $\Delta t = 0$ an almost instantaneous decrease of the magnetization is observed, followed by a rapid recovery due to electron-phonon relaxation and heat diffusion into the substrate (region II). The ultrafast demagnetization phenomena observed during these first picoseconds were discussed in detail in Chap. 4.

Strikingly, in some cases the MO-response is found to increase again after equilibration. A persistent response is observed that remains visible even after hundreds of picoseconds, e.g region III in Fig. 5.3(b). We will demonstrate that this effect is not related to changes in the magnitude of the magnetization, as during the first picoseconds, but to its orientation, i.e. a precessional effect. The polar MO-configuration that was used for the experiment is mainly sensitive to $M_z$. An optically triggered precession of the magnetization will thus indeed show up as an oscillation in the MO-signal.
5.3.2 Excitation mechanism

To launch a precession of the magnetization, the equilibrium orientation of the magnetization needs to be momentarily altered. In the specific case of a film with a preferential in-plane magnetization, the excitation mechanism is depicted in Fig. 5.3(c). By applying an appropriate external field $\vec{H}$, the magnetization is canted out-of-plane. The canting angle $\theta_c$ is determined by the subtle balance between the external field and the anisotropy field of the film. Upon sudden heating by the pump pulse, not only the magnetization decreases but also the anisotropy of the film changes. This results in a change of the equilibrium orientation from $\theta_c$ to $\theta'_c(\Delta t)$ (IIa), triggering an initial precession of the magnetization around its new time-dependent equilibrium orientation (IIb). The initial precession is not visible in Fig. 5.3(b), region II, since its displacement $\Delta \vec{M}$ is approximately parallel to the surface, and the small effect on $M_z$ is completely masked by the strong change in magnitude of $\vec{M}$. Heat diffusion into the film quickly removes the excess heat, restoring the original equilibrium angle. However, at this point the magnetization is still not in equilibrium due to its initial displacement, and will continue to precess around the rigid equilibrium angle $\theta_c$ for hundreds of picoseconds (III). The solid line in Fig. 5.3(b) is a fit to the data, yielding a precession frequency $f = 9.98$ GHz and a phenomenological Gilbert damping parameter $\alpha = 0.05$.

5.3.3 Applicability

In the previous section a first demonstration of the technique on a thin film with in-plane magnetization was presented. The method described here is, however, applicable to a much wider range of systems that show different magnetic configurations. The external field should simply be applied such as to create a canted configuration of the magnetization. The canted orientation is the result of the balance of different torques on the magnetization. Since laser heating will affect the various torques differently, the laser pulse can trigger a precession in such a system.

Figure 5.4 demonstrates the general applicability by showing measured precessional phenomena in three systems showing a contrasting magnetic ground state. The case of a thin film with an in-plane orientation of the magnetization, most commonly encountered, is depicted in Fig. 5.4(a). An efficient generation of precessional effects is achieved by applying an out-of-plane field to cant the magnetization. In some films the equilibrium orientation is already canted without applying an external field, as for example in the Cu(111)/Ni structure used in Fig. 5.4(b). In this case no additional fields need to be applied to launch a precession of the magnetization. In fact, it is found that the precession can even be quenched by pulling the magnetization completely out-of-plane, as shown by the 0.25 T curve in the figure. Finally, if the easy-axis is oriented out-of-plane, an in-plane external field can be used to create a canted configuration. This situation is depicted in Fig. 5.4(c). The difference between the 0.05 and 0.25 T curve nicely shows the necessity of canting the magnetization.

As is clear from the examples given above, the all-optical excitation method can be applied to a wide range of structures. The optical nature of the technique does, however, also impose some limitations on the structures under study. The samples used should for example be reflecting, and the magnetic layer can not be buried under thick, optically absorbing layers. This means that metallic top layers should be less than $\sim 10$ nm thick. Restrictions on much more transparent insulators and
semiconductors are less severe. The thermal nature of the excitation also requires that the system should be reasonably well heat conducting to ‘sink’ the incoming laser energy.

It is of interest to compare this technique to an analogous method introduced by Ju et al. [44]. In their work a ferromagnetic layer was exchange biased to an anti-ferromagnetic film. By laser heating above the blocking temperature the coupling between the layers could suddenly be broken, resulting in a precession of the unpinned layer. Although this technique also results in a laser-induced precession of the magnetization, its application is strictly confined to coupled multilayer systems.

5.3.4 Pump-induced anisotropy changes

To launch a precession of the magnetization, the anisotropy field of the ferromagnetic material has to be momentarily altered. There are several scenarios that result in a change of \( H_{\text{eff}} \) upon pump heating.

First, the crystalline anisotropy is temperature dependent. In some cases this dependence even leads to a reorientation of the easy axis as a function of temperature. In magnetic structures that show a canted orientation of the magnetization, the canting angle is generally found to be temperature dependent [53, 64]. In the epitaxial Ni structures that show a canted regime, the temperature dependence of the canting angle is expected to be the main excitation mechanism.

When in a thin film the magnetization is canted by an external field and neglecting the crystalline anisotropy, the equilibrium orientation is set by a balance between the Zeeman energy \( \mu_0 \vec{M} \cdot \vec{H} \) and the shape anisotropy, Eq. 5.5. Because of their different magnetization dependencies, the equilibrium canting angle \( \theta_c \), given by Eq. 5.13, is
Fig. 5.5: (a) Precessional phenomena in a Si/SiO$_2$(5)/Ni(37) film as a function of laser fluence. Independent of fluence the same dynamics is found, i.e. damping and precession frequency remain constant. This can be seen by the solid lines that represent a single fit to the data. The curves are normalized on fluence and shifted for clarity, the rich response of this structure is discussed in Sect. 5.6. (b) Unscaled data of the $1.8$ mJ/cm$^2$ curve from panel (a) including the first picoseconds after excitation. The oscillations occur on a background, indicated by the dashed line, showing that the heated volume has not yet reached thermal equilibrium with the rest of the sample.

A function of $|M|$. Upon laser heating $|M|$, and therefore also $\theta_c$, change, starting a precession of the magnetic moment.

The localized heating of the magnetic layer also generates uniaxial strain in the film. Since the film is only heated to a (optical penetration) depth of 13 nm, lateral expansion is inhibited by the underlying material. Therefore the material has to expand perpendicular to the film plane. This generates a unidirectional magneto-elastic strain contribution that can trigger a precession of the magnetization. Evidence for this mechanism comes from differences observed between SiO$_2$/Ni and Si$_3$N$_4$/Ni films. We found experimentally that in the SiO$_2$/Ni structure the external field has to be applied almost perpendicular to the film ($\pm 30^\circ$) to allow for a detectable excitation. In contrast, the Si$_3$N$_4$/Ni structure already shows sizable precessional effects for an almost in-plane field configuration. At the same time transient reflectivity measurements on this structure, shown in Figs. 4.12(c) and (d), show large strain wave and lattice expansion effects that are not present in the SiO$_2$/Ni sample. It therefore seems likely that strain-induced effects do play an important role in the excitation, as the magnetic properties of both structures are almost identical.

Independent of the excitation mechanism one may expect the same long-term behavior, since the disturbance mainly works on a short time scale. This is confirmed by the observed fluence dependence of the excited precession. Figure 5.5(a) shows results of measurements on a Si/SiO$_2$/Ni film taken at three different fluences. The complicated nature of the response is due to the excitation of standing spinwaves, a phenomenon that is described in Sect. 5.6. Comparing the curves one sees that the
precession frequency and damping are independent of fluence. This confirms that the pump excitation mainly changes the anisotropy during the first picoseconds, i.e. the initial excitation merely determines the amplitude and phase of the following precession. In fact, after scaling on fluence the measurements are found to overlap, showing that in the present case the excitation is linear in fluence.

In the Si/SiO$_2$/Ni sample the thermal conductivity is not as high as in fully metallic structures and therefore the precession occurs on a background due to the reduced magnitude of the magnetization. This can be seen in Fig. 5.5(b). The sharp spike around $\Delta t = 0$ corresponds to the ultrafast demagnetization described in Chap. 4. In this structure the heat diffusion is not fast enough to cool the heated volume within some tens of picosecond. The precession therefore appears on a background due to the time-dependent amplitude, and possibly angle $\theta_c(\Delta t)$, of $\vec{M}$. This is indicated by the dashed line in the figure. At the highest fluence the long-term temperature rise is $\sim 40^\circ$C, an effect that does not seem to affect the precessional dynamics. In the analysis of the data the slow diffusion is accounted for by a linear background.

5.3.5 Conclusions

The temperature and strain dependence of the anisotropy allow for the optical excitation of a precession in a wide range of magnetic structures. As a prerequisite, the equilibrium orientation of the magnetization should depend sensitively on temperature or strain, a situation that can be achieved by canting the magnetization with an external field. As confirmed by fluence dependent measurements, the optical excitation mainly affects the first picoseconds. The measured precession therefore occurs in the original anisotropy field, revealing the equilibrium magnetic properties. The exact excitation mechanism determines the amplitude and phase of the precession, but is not of importance for the interpretation of the dynamics on a longer time scale. This is confirmed by a comparison with FMR measurements, which will be described in the next section.

5.4 Comparison to conventional FMR

In the previous section the all-optical technique was introduced and results were qualitatively discussed for a number of configurations. To unambiguously demonstrate the precessional nature of the oscillation and the quantitative character of the technique, a comparison has been made with FerroMagnetic Resonance (FMR) measurements.

In FMR, the sample is placed in a microwave-cavity and the absorption of microwave radiation is measured as a function of field. For a certain field the precession frequency matches the fixed microwave frequency and an increased absorption is observed. Since FMR measures the absorption of the complete sample, it is essentially a non-local technique, and the experiments have to be performed on uniform layers.

For the thin polycrystalline films used in the experiments, shape anisotropy is expected to be the dominant contribution. Fig. 5.6(a) shows calculated values for the precession frequency as a function of applied field, assuming only a shape contribution characterized by the field $H_\text{a}$. With $N_{zz}$ equal to one, the anisotropy field $H_\text{a}$ is simply equal to $M/\mu_0$. The precession frequency $f$ shows an angular dependence that is most strong for the OOP orientation, labeled 90° in Fig. 5.6(a). For an exactly OOP field, no precession is observed until $H_{\text{app}} > H_\text{a}$, since then the demagnetization field is
no longer sufficient to cancel the applied field. For these fields the magnetization is oriented fully OOP. In the all-optical approach, however, the magnetization needs to be canted, and to have a finite precession frequency the direction of the applied field can thus not be completely OOP. As is evident from Fig. 5.6(a) this results in a strong dependence of $f$ on the angle of the applied field for near-perpendicular configurations.

Figure 5.6(b) shows the optically measured dependence of $f$ on applied field in a Si/SiO$_2$/Ni(30) film, represented by the solid squares. The film has an in-plane anisotropy, and the field is applied nearly OOP. On the same sample FMR measurements were performed to determine $H_a$. Since the microwave frequency is fixed it is not possible to directly determine $f(\vec{H})$. Instead, the angular dependence of the resonance field is measured, as shown in the inset of Fig. 5.6(b). Using Eqs. 5.13, 5.21 and the microwave frequency of 9.45 GHz a $\mu_0 H_a$ of 0.46 T can be deduced. The lines in Fig. 5.6(b) are calculated field dependencies of $f$ using the above value for $H_a$. The optically measured field dependence is reasonably well described by the 87° curve (dotted line).

The current setup supports only a limited control of field angle. It is therefore preferable to work in an (almost) in-plane field configuration, as it follows from Fig. 5.6(a) that in the 0° regime the precession frequency only weakly depends on angle. Experimentally it is found that even for very small field angles a sizeable precession
can be excited in Si/Si₃N₄/Ni layers. Therefore a 30 nm thick layer of polycrystalline Ni was grown on top of a Si(001)/Si₃N₄(60) substrate and covered by a 3 nm layer of Cu to prevent oxidation. The inset of Fig. 5.7 shows a FMR measurement on the structure, plotting the absorption of the 9.45 GHz microwave radiation versus in-plane field. A clear resonance is observed at an applied field of 0.18 T. In the all-optical FMR experiment the frequency is directly measured as a function of field, this time applied under a ∼ 10° angle. In Fig. 5.7 the optically determined precession frequency is plotted versus applied field. The 9.45 GHz microwave frequency falls nicely in the measurement range. Therefore the FMR result, represented by the single black square, can directly be compared to the optical measurement, indeed showing a very good agreement.

Since shape anisotropy is the dominant contribution to the film anisotropy, the field dependence of \( f \) should be well described by Eq. 5.23 (with \( k = 0 \)). The solid line in Fig. 5.7 is a fit to the data using \( g = 2.12 \), resulting in an anisotropy field \( \mu_0 H_a \) of 0.42 T. There is an excellent correspondence with the measured data, which clearly show a square root-like behavior at lower fields. From angle-resolved FMR measurements we found \( \mu_0 H_a = 0.39 \) T, slightly lower than, but in reasonable agreement with, the all-optical result.

**Fig. 5.7:** Optically determined precession frequency versus in-plane field for a Ni layer, the solid line is a fit to the data. Inset: Microwave FMR measurement on the same layer, yielding a resonance field of 0.18 T at 9.45 GHz, depicted by the solid square in the main diagram.
Fig. 5.8: (a) In-plane FMR measurement showing \( \frac{dA}{dH} \), i.e. the derivative of the absorption with respect to the applied field, versus field. The solid line is a fit to the data yielding a line width \( \mu_0 \Delta H \) of 0.145 T, corresponding to \( \alpha = 0.054 \). (b) Optically measured damping parameter \( \alpha \) as a function of field. The results for low fields are unreliable as the relaxation time becomes long compared to the 600 ps scan range. An average over the higher fields yields \( \alpha = 0.052 \).

Using Eq. 5.23 it is also possible to relate the width of the FMR resonance (\( \Delta H \)) to the damping parameter \( \alpha \), which can be measured directly with the all-optical technique. When the precessional motion is damped the spectral width of the absorption peak increases. The resulting absorption profile,

\[
A(f) = \frac{A_0}{(f-f_0)^2 + \Delta f^2},
\]

characterized by a central frequency \( f_0 \) and a width \( \Delta f \), is directly related to the damping parameter by

\[
\alpha = \frac{\Delta f}{f}.
\]

However, in the FMR experiment the frequency is fixed and the field is varied. In the linear regime the width of \( A(H) \), \( \Delta H \), can be related to \( \Delta f \) by

\[
\Delta f = \frac{df(H)}{dH} \Delta H,
\]

with \( f(H) \) given by Eq. 5.23. Figure 5.8(a) shows the as-measured in-plane FMR response, which is actually \( dA(H)/dH \) and thus corresponds to the derivative of \( A(f) \), Eq. 5.24. The solid line represents a fit to the data, yielding \( \mu_0 \Delta H = 0.145 \text{ T} \). With Eqs. 5.25 and 5.26, this results in a damping of \( \alpha = 0.054 \). Figure 5.8(b) shows the optically determined damping parameter as a function of field. For low fields the damping time was too long for an accurate determination of \( \alpha \) since the delay time...
range is limited to $\sim 600$ ps in our current setup. An average over the higher field values yields an $\alpha$ of $0.052 \pm 0.009$, in close agreement with the FMR result.

Concluding, the good agreement between FMR and the optical technique confirms the idea that for the long-term dynamics the impact of the laser pulse equals that of a picosecond magnetic field pulse, i.e. the all-optical method is capable of locally and quantitatively probing equilibrium magnetization dynamics. It must be stressed that this good agreement is not self-evident. First of all, since the optical excitation creates a highly excited material, a deviating frequency and/or damping might be anticipated. The resemblance with the microwave results means that at the laser fluencies applied, the system relaxes to near equilibrium soon enough not to affect dynamics appreciably on a 100 ps time scale. Secondly, spin waves laterally moving out of the irradiated area might enhance the damping. However, this was not experimentally observed with the current focus diameter of 10 $\mu$m ($k_{\text{max}} \approx 0.1 \cdot 10^6$ m$^{-1}$) and a typical damping time in the order of 0.1 ns.

5.5 Canted spin-state in Cu/Ni/Cu wedges

In Sect. 5.3 it was shown that canting the magnetization by an external field allows for the optical excitation of a precessional motion. For magnetic systems that naturally show a canted spin configuration by the interplay of different anisotropy contributions, one can expect that no external field is required to optically launch a precession. The observation of precessional effects in absence of an external field therefore is a strong indication of the existence of a canted spin-state. In this section epitaxial Cu(001) and Cu(111)/Ni/Cu wedges are studied that show a change of easy axis, i.e. a Spin Reorientation Transition (SRT), with Ni thickness. Using the all-optical technique it will be shown that the SRT from the out-of-plane (OOP) to the in-plane (IP) configuration proceeds through a canted state.

As described in Sect. 3.2, for a small Ni thickness the magnetization of the Ni layer in epitaxial Cu/Ni/Cu structures is preferentially oriented in-plane (IP). With increasing thickness the easy-axis changes to out-of-plane (OOP) and upon further increase again back to IP. The SRTs can be identified in Fig. 5.9(a), reproduced from Sect. 3.2, which shows the OOP remanence and coercive field for a Cu(001)/Ni/Cu structure as measured with polar MOKE. The region with 100% remanence corresponds to the fully OOP region. In the Cu(111)/Ni/Cu sample, Fig. 5.9(b), the transitions are also present, although less sharp and a 100% OOP remanence is not achieved.

The origin of the SRTs lies in a changing balance between surface and volume anisotropy contributions, where the surface contribution is the dominant term at small film thickness while the volume contribution is most important for the thicker films. The difference between surface and volume anisotropy arises through the reduced symmetry at the interface, changing the magnetic properties. In epitaxially grown films also strain effects can result in a spin reorientation. For thicker layers strain relaxes by misfit formation [45], resulting in a thickness-dependent strain contribution to the anisotropy of the film.

For a single-domain film, the SRT can occur in a number of different ways. For example, an intermediate canted state may exist, or a phase with both in-plane and out-of-plane easy-axes. In a multi-domain case also coexisting IP, OOP and canted domains are possible. It is experimentally difficult to separate the different reorien-
Fig. 5.9: Remanence and coercive field as measured with MOKE in the polar configuration.
(a) Cu(001)/Ni/Cu wedge (also the in-plane remanence is shown) and (b) Cu(111)/Ni/Cu wedge.

tation types when only one magnetization component is measured. For example, the gradual decrease in remanent OOP magnetization with increasing thickness in Fig. 5.9(a) can be caused by a canting of the magnetization towards the IP orientation. However, also a multi-domain state is possible that shows a pattern of oppositely oriented OOP domains, i.e. stripe domains. In the latter case zero remanence corresponds to equally sized up- and down-domains in the absence of an external field. Also the finite remanence in both the IP and OOP configuration observed in Fig. 5.9(a) is no unambiguous sign of a canting state, as a multi-domain state may exist with both IP and OOP oriented domains [71].

Using torque magnetometry [29] or FMR [18] one can determine the anisotropy of homogeneous samples. The MOKE provides a locally sensitive technique, but one needs to combine measurements taken in different configurations to extract the vector components of the magnetization. Also, in the analysis of the magnetization loops obtained by MOKE one should take care to separate domain- and anisotropy-related effects. Using the all-optical FMR technique, a SRT through a canting state can easily be identified. As described in Section 5.3.2, the optical excitation of a magnetic precession requires a temperature dependent orientation of the magnetization. This situation is met in the canting regime, where the orientation depends sensitively on the relative magnitude of the different anisotropy contributions, which will generally show a different temperature dependence [53].

Figures 5.5(a) and (b) show series of transient MOKE measurements on respectively the Cu(001)/Ni/Cu and the Cu(111)/Ni/Cu wedge structures as a function of Ni thickness. The data were taken in the polar configuration without external field, and represent the relative change in the OOP component of the remanent magnetization. Following the ultrafast demagnetization phenomena at $\Delta t = 0$ ps the magnetization almost completely recovers due to the rapid heat diffusion in the metallic
system. However, after about 20 ps a much slower magnetization dynamics sets in. \(\Delta \epsilon/\epsilon\) again drops, reaching a minimum around 100 ps followed by a gradual recovery. In the next part of this section we will show that the slower dynamics is caused by an optically launched precession of the magnetization, directly showing the existence of a canted spin configuration in the Ni layer.

The orientational nature of the effect can readily be shown by looking at its field dependence. In Fig. 5.11 the usual MOKE loop (open circles), i.e. a measurement of \(\epsilon\) versus OOP field \(H\), is compared with the pump-induced effect \(\Delta \epsilon(H)\) for two delay times. The ‘dynamic’ MOKE loop at 0.3 ps (dashed line) shows the same field dependence as the ‘static’ loop, i.e. \(\Delta \epsilon/\epsilon\) is constant. This is to be expected since the response shortly after laser heating is dominated by changes in the magnitude of \(M\). For a fixed orientation of the magnetization \(|\Delta \vec{M}|/|\vec{M}| = \Delta M_z/M_z = \Delta \epsilon/\epsilon\). The latter ratio therefore simply reflects the relative change in magnitude of \(M\), and since the pump-induced demagnetization is found to be field-independent this ratio is constant.

The field dependence of \(\Delta \epsilon\) at \(\Delta t = 100\) ps, near the second minimum in the transient, shows a completely different behavior. For high OOP fields the pump-induced effect is quenched, in striking contrast with the static response. In Fig. 5.4(b) the transient response for this sample was plotted both in remanence and at high fields, again showing the reduction of the long-term effect with applied field. The observed field dependence is well-explained by an orientational effect. The applied field stabilizes the magnetization in the OOP direction, thereby preventing the optical excitation of a precessional motion of the magnetization vector.

The magnitude of the precessional effect shows a strong correlation with the measured remanence, i.e. with the magnetic configuration during the SRT from OOP to IP. The transients plotted in Fig. 5.5 show an increasing precessional contribution with Ni thickness. The curves are however normalized to the remanent value of the Kerr ellipticity. Since the remanence drops to zero this greatly enhances the effect

\[\Delta \epsilon = \Delta \epsilon / \epsilon \]

\[\Delta t = [\text{ps}]\]

\[\Delta \epsilon/\epsilon\]

\[3.6 \text{ nm}\]

\[4.6 \text{ nm}\]

\[5.6 \text{ nm}\]

\[6.5 \text{ nm}\]

\[7.5 \text{ nm}\]

\[13 \text{ nm}\]

\[\text{Fig. 5.10: (a) TRMOKE measurements on a Cu(111)/Ni/Cu wedge as a function of Ni thickness. (b) Same, but on a Cu(001)/Ni/Cu wedge.}\]
Fig. 5.11: Open circles: ‘static’ MOKE loop ($\epsilon(H)$) as measured on the Cu(111)/Ni/Cu structure in the canted regime. Dashed line: ‘dynamic’ MOKE loop, i.e. the pump-induced change of the Kerr effect versus applied field ($\Delta\epsilon(H)$), taken at $\Delta t = 0.3$ ps. The shape is identical to the static loop, indicative of an effect scaling with the magnitude of the magnetization. Solid circles: dynamic MOKE loop measured at $\Delta t = 100$ ps. Applying an OOP field quenches the pump-induced effect $\Delta\epsilon$.

Fig. 5.12: (a) Open circles: remanence of the Cu(001)/Ni/Cu structure as a function of Ni thickness. Closed squares: amplitude of the precessional effect (defined as $\Delta\epsilon(100 \text{ ps}) - \Delta\epsilon(550 \text{ ps})$) normalized on the saturation Kerr ellipticity. The amplitude is maximum near 50% remanence. (b) Same, but for the Cu(111)/Ni/Cu structure. The solid lines are a guide to the eye.
at larger thickness. In Fig. 5.12 the amplitude of the precessional effect is normalized on the saturation Kerr effect, yielding a measure of $\Delta M_z/|\vec{M}|$. In the figure the amplitude, defined as $|\Delta \epsilon(100\text{ ps}) - \Delta \epsilon(550\text{ ps})|/\epsilon_{sat}$, is plotted as a function of Ni thickness. The $\epsilon(550\text{ ps})$ term corrects partially for a changing heat diffusion, but does otherwise not affect the result. Figure 5.5(a) shows that for the Cu(001)/Ni/Cu structure the precession amplitude is minimal for thin layers that show an OOP easy axis, as evidenced by their 100% remanence. With increasing Ni thickness the amplitude of the precession shows a steep rise while the remanence drops. At a remanence of $\sim 60\%$ the amplitude peaks and upon further increase of film thickness, i.e. going to an in-plane configuration, decreases again. A similar result is found on the Cu(111)/Ni/Cu wedge, Fig. 5.12(b).

These observations are in good qualitative agreement with a SRT through a canted state. For the stable OOP and IP configurations no precession can be excited. On the other hand, the precession amplitude peaks during the SRT when laser heating can sharply change the equilibrium orientation of the canted magnetization vector. It must be noted that a mixture of OOP and IP domains can not explain the observations. The negative sign of $\Delta \epsilon$ at 100 ps indicates that the precessional motion decreases $M_z$. If laser heating could temporarily change the easy-axis orientation of an OOP domain to IP the initial precession would indeed decrease $M_z$. However, after cooling down ($\sim 10\text{ ps}$) the magnetization vector would precess around the OOP easy axis, a process that does not further change $M_z$.

In principle it is possible to derive the anisotropy of the Ni film from the measured precession. However, the precession is heavily damped ($\alpha > 0.5$) and only half a cycle is discernible. This greatly hinders a direct determination of the precession frequency and therefore of the anisotropy parameters. The large damping may be caused by inhomogenities in the SRT region. In the transition region the strain in the Ni layer relaxes by misfit formation, a process that is likely to be responsible for the SRT since the strain relaxation alters the magneto-elastic contribution to the magnetic anisotropy, Eq. 5.8. The stochastic nature of this process can create a spatial variation in the anisotropy, resulting in a distribution of precession frequencies that will appear as extra damping.

In Ref. [73] we modeled the excitation and following precession for the Ni(111) film and derived values for the crystalline anisotropy $K_1$ and the uniaxial anisotropy $K_u$, Eqs. 5.7 and 5.8, from the position of the second minimum in $\Delta \epsilon$. The values reported there do reproduce the observed ‘static’ and ‘dynamic’ behavior. However, the positive value reported for $K_1$ is somewhat unexpected as for bulk Ni $K_1$ is found to be negative. Also, a positive $K_1$ results in (100),(010) and (001) easy axes. The latter would exclude a canted state in the Cu(001)/Ni film as these axes are either parallel or perpendicular to the uniaxial axis.

Concluding, the observation of an optically excited precession of the magnetization in zero field unambiguously demonstrates a canted configuration of the magnetization in the transition region from IP to OOP in the Cu(111)/Ni/Cu and Cu(001)/Ni/Cu structure, confirming observations with torque magnetometry [29] and Brillouin light scattering techniques [25]. The precessional motion is heavily damped, hampering a quantitative determination of anisotropy parameters. The large damping is possibly caused by an inhomogeneous structure of the film in the region of the SRT, resulting in a distribution of precession frequencies within the laser spot.
5.6 Standing spin waves

The analysis so far has been based on a homogeneous precession of the magnetization. It can be understood, however, that the approach is oversimplified if the thickness of the film is no longer negligible compared to the penetration depth of light, typically 10-15 nm for ferromagnetic transition metals. In that case, spins within the optical skin-depth of the film are more intensely excited and also more efficiently detected by the delayed probe pulse. This property will be shown to provide an intriguing additional possibility of the all-optical technique: the investigation of standing spin waves in magnetic films.

Figure 5.13(a) shows the measured magnetization change for a 52 nm thick polycrystalline Ni layer versus pump-probe delay. Instead of a single oscillation, we find a much richer response that is well described by the sum of two damped oscillations at frequencies $\omega_0$ and $\omega_1$, indicated by the drawn curves in the figure. Measurements on a wedge structure, see Fig. 5.13(b), show that the precession at $\omega_0$ is thickness independent. In contrast, the oscillation at $\omega_1$ shows a strong thickness dependence, approximately falling off as $1/L^2$ to $\omega_0$, with $L$ the thickness of the layer.

This behavior is perfectly explained in terms of a fundamental and first-order excited mode of a standing spin wave within the thickness of the layer. The fundamental mode, shown graphically in Fig. 5.14, bottom surface, is the normal precession of the magnetization that is uniform within the thickness of the layer. With open boundary conditions, the first order standing wave is expected to have a single node in the middle of the layer and to be free at the surfaces, as depicted in Fig. 5.14, middle. The full precession is given by the sum of the fundamental and first-order mode, Fig. 5.14, top. In the time-resolved experiments the magnetization is sampled within the optical penetration depth ($\sim 13$ nm). The measured data, indicated by the full circles, therefore are drawn at $d = 0$. The thickness dependence of $\omega_1$ can qualitatively be understood by looking at the (quadratic) magnon dispersion relation for the out-of-plane situation, Eq. 5.22 and Fig. 5.13(b), inset. Due to the finite

---

**Fig. 5.13**: (a) Measurement on a 52 nm polycrystalline Ni layer (open circles). The measurement is fitted with two damped sines, as shown in the decomposition (top). (b) Fundamental ($\omega_0$) and first-order ($\omega_1$) spinwave frequency in Ni versus layer thickness. Inset: schematic magnon dispersion relation.
thickness of the film the allowed $k$ values are discrete. At $k = 0$ we find the uniform precession at $\omega_0$, whereas $k = \pi/L$ gives the first order standing spin wave at a frequency $\omega_1 = \omega_0 + D(\pi/L)^2$, with $D$ the spin wave exchange constant. However, for the configuration studied here with the applied field under an angle of $\sim 80^\circ$ with respect to the film plane and a canted orientation of the magnetization, the complete description of Eq. 5.21 is needed. As one can see in Fig. 5.6(a), for applied field angles near the out-of-plane orientation the (fundamental) precession frequency sensitively depends on angle. This fact is used to calibrate the exact field angle (which is difficult to define in the current setup) by using the shape-anisotropy field $H_{az}$ known from conventional FMR measurements and the magnitude of the applied field of 0.25 T. With the angle thus obtained ($75^\circ$) and Eq. 5.21 a spin-wave stiffness $D = 440$ meV Å$^2$ is found. This number compares well with reported literature values obtained by FMR and neutron diffraction, ranging from 350 to 500 meV Å$^2$ [30].

So far no modes with $k \geq 2\pi/L$ have been observed. This can be attributed to the small, but finite, penetration depth of light: due to their shorter wavelength, higher order modes are less efficiently excited and measured since one averages over a skin-depth of $\sim 13$ nm. An estimate of the relative excitation efficiency of the different

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Fig. 5.14: Observation of standing spin waves. Because of the nonuniform heating by the pump pulse both the fundamental precession ($\omega_0$), which is uniform in the depth $d$ of the layer, and the first-order standing spin wave ($\omega_1$) are excited. From the resulting precession (sum) only the magnetization near the surface is optically measured. The measured data is thus shown at $d = 0$ as solid dots.
Fig. 5.15: Efficiency of detecting mode $n$ relative to the fundamental mode $n = 0$. $A_n$ is the amplitude of the $n$-th Fourier component describing the initial exponentially decaying excitation, $\sum_{n=0}^{\infty} A_n \cos(n\pi/Lx) / \int_0^L \cos(n\pi/Lx)^2 dx = \exp(-x/d_{ext})$.

The excitation efficiency of mode $n$ is given by its amplitude $A_n$. Since also the probe pulse decays exponentially in the material the detection scales with $A_n$, too. The overall sensitivity to a particular mode $n$ therefore becomes $A_n^2$. Figure 5.15 shows a plot of $A(n)^2/A(0)^2$ for the first- and second-order standing mode, together with the measured relative contribution of the first-order mode. The model correctly predicts the increasing contribution of the first-order mode with thickness and the calculated values are in fair agreement with the measured data. For the 60 nm film, a sizable contribution of 25% is predicted for the second-order mode. However, at this point the fundamental- and first-order mode are very close in frequency and amplitude, so its actual contribution ($A_2^2/[A_0^2 + A_1^2]$) is only 12.5%. Moreover, due to the higher frequency (18 GHz) the decay-time of the second-order mode is expected to be short compared to the fundamental- and first-order mode (assuming a constant $\alpha$), complicating its detection.

An interesting aspect of the all-optical technique is that the anti-symmetric mode observed in the optical experiment cannot be measured by microwave FMR. In uniform thin films FMR selection rules only allow excitations with a net magnetic moment.
5.7 Characterization of microstructured layers

An attractive aspect of the optical technique is its spatial resolution. The local character is demonstrated in Fig. 5.16(a) where an individual 10 $\mu$m permalloy element is addressed out of a lithographically defined array. For permalloy the cubic crystalline anisotropy is negligible and since the layer was not grown in field no in-plane uniaxial anisotropy is present. However, still a clear precession is observed. We conjecture that the precession is excited by the different magnetization dependence of the shape anisotropy ($E \sim M^2$) and the Zeeman energy in the applied field ($\vec{H} \cdot \vec{M}$). In general, also strain, induced by the rapid heating of mainly the top 10-15 nm of the layer, may contribute to the excitation. However, for permalloy this contribution is expected to be small due to its low magnetostriction.

The spatial resolution allows for the determination of the dynamic properties of individual elements. In Fig. 5.16(b) the measured precession frequency is plotted when focusing the laser beams on elements of the same size, but of a different shape. The difference in shape is expected to influence the demagnetization field and might thus be visible in the precession frequency. However, the low precession frequency in combination with measurement noise and a restricted delay time range ($\sim 600$ ps in the current setup) results in a reduced accuracy. So far no significant difference in precession frequency is observed between the elements. The experiments do however show the new possibilities this technique offers in studying structured materials.

5.8 Discussion

In this chapter a novel all-optical technique was presented to measure the dynamic magnetic properties of microstructures. The key element of the approach is the temperature dependence of the anisotropy, which allows us to use the heat from an absorbed laser pulse to generate an anisotropy field pulse that excites a precession of the magnetization. This approach has some distinct advantages over existing techniques for (dynamic) magnetic characterization.
First of all, it is a local technique that allows for non-contact measurements. This is convenient for the characterization of small devices since the structure needs not to be disturbed, and selecting an element simply means focusing two laser beams. Currently a spatial resolution of $\sim 10\mu m$ is used. However, a (sub-)µm resolution is readily obtainable before being limited by the wavelength ($\approx 800$ nm) of the pulses used. For frequency doubled pulses (400 nm) a spatial resolution of less than 0.5µm has been demonstrated, see for example Ref. [1]. To obtain an even higher spatial resolution, liquid immersion lenses and near field methods can be used. As to the latter, the development of hybrid MO/SPM (Scanning Probe Microscopy) techniques is currently intensively studied at a number of institutes to obtain sub-micron magneto-optical resolution.

Another advantage is the direct time domain character of the technique. When studying damping phenomena using FMR or other frequency domain techniques the width of peaks in the frequency domain has to be converted to a damping time, see e.g. Eq. 5.25. In a time domain technique the precessing magnetization is followed in real time, greatly simplifying the interpretation. Also, FMR can not be used to characterize inhomogeneous media as for example magnetic tape used in recording, since inhomogenities will just show up as extra broadening and will thus be interpreted as damping. Depending on the scale of the inhomogeneity, the optical technique can still be used.

As a final point, the local excitation with the all-optical technique allows for a direct study of spinwave phenomena. As was shown in section 5.6, standing spinwaves can be excited within the thickness of the layer using the limited penetration depth of the laser light. Since only a small area is heated, it can be expected that for a sufficiently small laser spot also spinwaves with a finite $k_\parallel$ are excited. In Ref. [66], Silva et al. observed spinwaves propagating from the edge of a strip line. At the edge a sharp drop in the transverse magnetic field is present, allowing for a non-uniform excitation of the magnetization using short field pulses. For the large-angle (80°) excitation, a group velocity of $150$ km/s was observed. This fast transport of magnetic flux away from the strip line was proposed as a cause for the observed increase in damping at the center of the stripline. With the current 10 µm resolution no lateral spinwaves could be observed in the optical experiment. Also, the good agreement with the damping obtained from the FMR experiments suggests that lateral spreading of the excitation is not yet affecting the observed damping. Using the spot radius of 5 µm and a damping time of 1 ns, this would mean a lateral group velocity of $\ll 5$ km/s.

The method also has several drawbacks. Due to the optical nature, the sample under investigation should be reflecting and the magnetic layer can not be buried under thick, optically absorbing layers. This means that metal top layers should be less than 10 nm thick, restrictions on the more transparant insulators and semiconductors are less severe. The system should also be reasonably well heat conducting to ‘sink’ the incoming laser energy. To excite the precession, a canted state is required with the magnetization at an angle with the applied field. This means that the applied field can not saturate the sample and a multi-domain state may exist.

The all-optical measurements in this chapter were performed in the ‘small perturbation’ limit where the anisotropy and damping parameters that determine the switching process are measured, but the layer itself is not actually switched. However, the optical technique is not necessarily restricted to this regime. For example, one can think of a magnetic film with an in-plane magnetization but a strong strain...
dependence of the anisotropy. After laser heating strain effects may temporarily change the easy axis to an out-of-plane orientation, starting a precession that rotates and possibly switches the magnetization in the film plane. Such a process may be thought of as a candidate for new hybrid recording schemes.
A. DEFINITIONS

A.1 Temperature definitions

<table>
<thead>
<tr>
<th>label</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{e,\text{dist}}(t)$</td>
<td>Temperature derived from a least-squares fit of the Fermi-Dirac distribution to $n(E)$</td>
</tr>
<tr>
<td>$T_{e,\text{slope}}(t)$</td>
<td>Temperature corresponding to the slope of $n(E)$ at the Fermi level</td>
</tr>
<tr>
<td>$T_{e,E}(t)$</td>
<td>Temperature corresponding to the excess energy $E_E$ in the electron system</td>
</tr>
<tr>
<td>$T_e(t)$</td>
<td>Temperature of the electron system, well defined for $t \gg \tau_{th}$</td>
</tr>
<tr>
<td>$T_l(t)$</td>
<td>Temperature of the lattice (phonon) system</td>
</tr>
<tr>
<td>$T_s(t)$</td>
<td>Temperature of the spin system. $T_s$ is the temperature at which the magnetization versus temperature curve yields the measured magnetization.</td>
</tr>
</tbody>
</table>

Tab. A.1: Definition of the different temperatures used. The electron distribution as a function of energy $E$ is represented by $n(E)$. Note that after thermalization, $T_{e,\text{dist}}$, $T_{e,\text{slope}}$, and $T_{e,E}$ yield identical values, i.e. $T_e$.

A.2 Time-constant definitions

<table>
<thead>
<tr>
<th>label</th>
<th>description</th>
<th>typical value</th>
<th>reference</th>
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<tbody>
<tr>
<td>$\tau_{ee}$</td>
<td>hot electron lifetime</td>
<td>fs’s at 1 eV</td>
<td>Eq. 4.2</td>
</tr>
<tr>
<td>$\tau_{th}$</td>
<td>characteristic electron thermalization time</td>
<td>$\sim 80$ fs</td>
<td>Eq. 4.10, Figs. 4.4 and 4.12</td>
</tr>
<tr>
<td>$t_{th}$</td>
<td>thermalization time ($T_{e,\text{dist}}$ at 90% of thermalized value)</td>
<td>$\sim 2.3\tau_{th}$</td>
<td>Eq. 4.11</td>
</tr>
<tr>
<td>$\tau_E$</td>
<td>characteristic time of electron-lattice energy exchange</td>
<td>0.25-0.45 ps</td>
<td>Eqs. 4.23 and 4.37, Figs. 4.4 and 4.15</td>
</tr>
<tr>
<td>$\tau_M$</td>
<td>characteristic delay between spin- and electron ($T_{e,E}$) temperature</td>
<td>up to 100 fs</td>
<td>Figs. 3.8, 4.34 and 4.35</td>
</tr>
<tr>
<td>$t_{ex}$</td>
<td>time at which the maximum electron temperature ($T_{e,\text{spin}}$) is reached</td>
<td>200 fs</td>
<td>Fig. 4.12</td>
</tr>
<tr>
<td>$t_{ex}$</td>
<td>time at which the maximum spin temperature ($T_s$) is reached</td>
<td>up to 390 fs</td>
<td>Figs. 3.8, 4.34 and 4.35</td>
</tr>
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Tab. A.2: Definition of the different time-constants used. Also characteristic values for Ni, and references to related equations and figures, are given.
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This thesis focuses on the magnetization dynamics of ferromagnetic metals. Materials as nickel and cobalt show a spontaneous magnetization at room temperature, which is characterized by a direction and a magnitude. When these ‘magnets’ are gradually heated, the magnitude of their magnetization decreases. Upon reaching the Curie temperature, all long-range order is lost and the material is no longer magnetic. In this work, ferromagnetic thin films are suddenly excited by an ultrashort laser pulse, and the resulting magnetization dynamics is measured on a sub-picosecond (1 ps = 10^{-12} s) time scale. These dynamics include both transient changes in the magnitude, Chap. 4, as well as in the direction of the magnetization, Chap. 5.

To access the dynamics on such short time scales, a pump-probe technique is employed. Using an intense, \( \sim 100 \text{ fs (} 100 \cdot 10^{-15} \text{ s}) \) ‘pump’ laser pulse the ferromagnetic film is abruptly heated. After a variable delay, a much weaker ‘probe’ laser pulse samples the resulting change in magnetization. The magnetization is optically detected using the magneto-optical (MO) Kerr effect, i.e. by recording the polarization of the reflected probe pulses. The pump-probe technique and the different modulation schemes used to detect the small polarization changes are discussed in Chap. 2.

Chapter 4 discusses the ultrafast loss of magnetization following pulsed laser excitation. Upon absorption of a laser pulse, the electron system suddenly gains an amount of energy. Subsequent relaxation processes thermalize the electron distribution, heat the lattice and change the magnitude of the magnetization. Using pump-probe experiments, the electron and spin dynamics can be followed in time, allowing for the identification of the mechanisms leading to the laser-induced demagnetization. It must be noted, however, that the use of magneto-optic techniques to measure the magnetization is only validated in equilibrium. In this work, the use of MO-techniques in the highly non-equilibrium situation after pulsed laser excitation is scrutinized. It is indeed found that in some structures the transient MO Kerr measurements do not yield the magnetization dynamics. During pump-probe coincidence, coherent processes can produce artifacts in the magnetic measurement. These artifacts, which are well described by a coherent oscillator model, are discussed in Sect. 4.7.3. Moreover, on a longer time scale differences are found between MO ellipticity and MO rotation transients, Sect. 4.7.2, showing that at least one of the transients is not representative of the magnetization dynamics. A preliminary scheme to filter out the true magnetization dynamics from these data is presented in Sect. 4.8.5.

Measurements on suitable thin film Ni and Co-Pt structures show that the magnetization decreases within hundreds of femtoseconds after laser heating. Comparison with measurements of the electron dynamics, Sect. 4.6, show strong similarities, suggestive of the electron temperature as the driving force of the demagnetization. In Sects. 4.8 and 4.9 the temperature and fluence dependence of the magnetization dynamics is investigated. The observed trends can be well-explained by the temperature
dependence of the electronic heat capacity. A comparison of the dynamics during the first hundreds of femtoseconds, Sect. 4.10, does however reveal differences between the electron and spin dynamics, showing that the laser-induced demagnetization is not an instantaneous process.

In Chap. 5 it is shown that heating with an ultrashort laser pulse does not only alter the magnitude, but also the direction of the magnetization. This results in a precessional motion of the magnetization that lasts for hundreds of picoseconds. In the chapter results of this new, all-optical technique are compared with existing methods. It is shown that the all-optical method yields quantitative information on anisotropy, damping and spin-spin interaction. Results are obtained locally, i.e. within the laser spot, and in the time-domain. Due to the limited penetration depth of the light, $\sim 13$ nm for Ni at 1.6 eV, the excitation is also confined in the depth of the film. The non-uniform heating results in the excitation of standing spin waves, allowing for the determination of the spin wave exchange constant. The lateral confinement of the excitation is also expected to lead to lateral spin waves. However, with the current resolution (10 nm FWHM) lateral spin waves could not be observed.
SAMENVATTING

Het onderzoek dat in dit proefschrift wordt beschreven, is gericht op het dynamisch gedrag van magnetische metalen. Materialen als ijzer, cobalt en nikkel zijn ferromagnetisch bij kamertemperatuur. Ze hebben een zekere magnetisatie, die gekenmerkt wordt door een grootte (‘sterkte’) en een richting ('noord-' en 'zuidpool'). De richting van de magnetisatie is te veranderen door een magnetisch veld aan te leggen. Dit gebeurt bijvoorbeeld bij het beschrijven van een hard disk, waar de digitale informatie is opgeslagen in de magnetisatie-richting van kleine gebiedjes op de disk. De grootte van de magnetisatie is te beïnvloeden door de ferromagneet te verwarmen. Boven de zogenaamde Curie temperatuur is de magnetisatie zelfs volledig verdwenen.

In dit werk wordt specifiek gekeken naar het dynamische gedrag van de magnetisatie. De dynamische eigenschappen bepalen bijvoorbeeld de minimale tijd die nodig is om informatie op een hard disk te schrijven. Ook levert de bestudering van de dynamica informatie over fundamentele interacties in de ferromagneet. Omdat de tijdschalen waarop de processen plaatsvinden bijzonder kort zijn, in de orde van 100 femtoseconde (0.0000000000001 s), wordt een zogenaamde ‘pump-probe’ techniek gebruikt.

In de hier beschreven pump-probe experimenten wordt een magnetisch materiaal plotseling geexciteerd door een intense en zeer korte laserpuls, de ‘pump’. Na een instelbare tijdsvertraging volgt een veel zwakkere ‘probe’ laserpuls, waarmee de magnetisatie bepaald wordt. Een optische meting van de magnetisatie is mogelijk door het magneto-optische Kerr effect, het verschijnsel dat na reflectie van een magnetisch materiaal de polarisatie van een lichtbundel op een magnetisatie-afhankelijke manier is veranderd. Door nu bij een serie tijdsvertragingen te meten, kan de magnetisatie als functie van de tijd na excitatie bepaald worden. De tijdsresolutie van de techniek wordt bepaald door de lengte van de laserpulsen, in dit werk ~ 85 fs. Een uitgebreide beschrijving van de techniek is te vinden in hoofdstuk 2.

Het onderzoek in hoofdstuk 4 is gericht op de processen die leiden tot de afname van de grootte van de magnetisatie na ‘verwarming’ door een laserpuls. Onze metingen laten zien dat deze laser-geinduceerde demagnetisatie razendsnel is: al binnen een paar honderd femtoseconde na excitatie bereikt de grootte van de magnetisatie een minimum waarde. Deze snelle tijdschaal levert informatie over de processen die verantwoordelijk zijn voor de demagnetisatie. Bij verwarming door een laserpuls wordt namelijk alleen energie aan de elektronen overgedragen; het rooster (de positie van de atomen) en de magnetisatie blijven in eerste instantie onveranderd. Uit niet-magnetische pump-probe metingen blijkt dat de temperatuur van het rooster over een periode van een tot twee picoseconde, dus relatief langzaam, oploopt. Dit toont aan dat de verandering van de magnetisatie voornamelijk gedreven wordt door de toestand van het elektronische systeem. Ook temperatuur- en vermogens-afhankelijke

Fig. A.1: Precessiebeweging van de magnetisatie. De magnetisatie, voorgesteld door een pijl, beschrijft een cirkelbeweging om zijn evenwichtsstand. Door demping neemt de uitwijking steeds verder af en zal de magnetisatie uiteindelijk in zijn evenwichtsstand terechtkomen.

metingen, beschreven in hetzelfde hoofdstuk, wijzen op een verband met de elektron-temperatuur. In het hoofdstuk wordt ook de interpretatie van de metingen kritisch belicht. Met de optische pump-probe techniek wordt de magnetisatie indirect gemeten door te kijken naar de polarisatie van de probe puls. Dit zogenaamde Kerr effect is in wijd gebruik voor statische metingen van de magnetisatie. De interpretatie van het Kerr effect in een niet-evenwichts situatie, zoals kort na excitatie door een intense laser puls, is echter niet triviaal. Het wordt aangetoond dat in verschillende situaties het Kerr effect geen direct verband houdt met de magnetisatie dynamics.

In hoofdstuk 5 wordt aangetoond dat een laserpuls niet alleen de grootte, maar ook de richting van de magnetisatie kan veranderen. Dit leidt tot een precessiebeweging van de magnetisatie, waarbij de magnetisatie cirkelbanen beschrijft rond een evenwichtsrichting, zie Fig. A.1. Deze laser-geinduceerde precessie dynamica is met een tijdschaal van honderden picoseconden (1 ps = 1000 fs) een stuk trager dan de eerder beschreven demagnetisatie dynamica. Door vergelijking met andere meetmethoden wordt aangetoond dat de volledig optische techniek in staat is om quantitatieve uitspraken te doen over parameters als demping, spin-spin interactie sterkte en magnetische anisotropy. De demping parameter bepaalt hoe snel de magnetisatie zich uitlegt met de nieuwe evenwichtsrichting, dus hoe snel de tolbeweging van Fig. A.1 is beëindigd. Deze parameter is van direct belang voor toepassingen als hard disk. Wanneer data zeer snel op een disk geschreven dient te worden, is het namelijk niet gewenst dat de magnetisatie lang precedeert. Met de optische excitatie is het mogelijk de magnetisatie-richting van slechts een klein deel van het materiaal te veranderen. Door de koppeling tussen naburige elektronen, de spin-spin interactie, leidt dit tot golf-achtige verschijnselen die zich uitbreiden vanaf de randen van het geexciteerde gebied. Deze golfverschijnselen zijn inderdaad waargenomen, waardoor ook de spin-spin interactie sterkte volledig optisch kon worden bepaald.
DANKWOORD

Hier moet dus het dankwoord komen! Een pagina zou genoeg moeten zijn...