Doctoral Thesis

Ultrafast demagnetization
An electronic point of view

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ULTRAFAST DEMAGNETIZATION:
AN ELECTRONIC POINT OF VIEW

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(Dr. sc. ETH Zurich)

presented by

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# CONTENTS

Summary vii  
Zusammenfassung ix  

## 1 Introduction 1  
1.1 From navigation to mass storage .................................... 2  
1.2 The quest for speed .................................................. 3  
1.3 Ultrafast demagnetization ............................................. 6  
  1.3.1 Theoretical and experimental findings ......................... 6  
  1.3.2 Methods .......................................................... 8  

## 2 Time and spin resolved photoemission 13  
2.1 The experimental setup: a mobile end-station ..................... 14  
  2.1.1 The magnetic sample ............................................. 14  
  2.1.2 Sample holder and magnetic coils ................................ 15  
  2.1.3 Measuring the spin polarization: Mott detector ............... 16  
  2.1.4 Electrostatic lens system ....................................... 19  
2.2 Requirements for the probe pulse .................................. 20  
2.3 The Free Electron Laser in Hamburg (FLASH) ....................... 20  
  2.3.1 Timing .......................................................... 22  
  2.3.2 Finding temporal overlap ....................................... 24  
  2.3.3 FEL fluctuations ................................................ 25  
  2.3.4 Data storage and analysis ...................................... 25  
2.4 FEL experiments ..................................................... 26  
  2.4.1 FEL intensity resolved measurements .......................... 26  
  2.4.2 Time resolved reflectivity experiments ....................... 33  
  2.4.3 Time- and spin-resolved experiments .......................... 33  

## 3 Imaging spin filter detector 41  
3.1 The physics of a SPLEED detector ................................. 42  
3.2 Imaging SPLEED Detector .......................................... 43  
  3.2.1 The setup ..................................................... 45  
  3.2.2 Analyzer crystal preparation ................................... 47
3.2.3 Sherman factor determination ........................................ 49
3.2.4 Image processing ....................................................... 49
3.2.5 Efficiency comparison between the SPLEED and the Mott de-
tector ................................................................. 53
3.2.6 Azimuthal orientation and balancing .............................. 54
3.2.7 Oxygen covered surface ............................................. 54
3.3 FLASH ................................................................. 56
  3.3.1 Delay line detector ................................................... 56
  3.3.2 Measuring the asymmetry ........................................... 58

4 Ultrafast demagnetization; an interface- and transport effect 61
  4.1 Hypothesis .............................................................. 62
  4.2 Interface versus bulk demagnetization ............................. 62
  4.3 Thickness dependence of the demagnetization time ............ 64
  4.4 Spin transport .......................................................... 65
  4.5 Demagnetization on insulators ....................................... 66
  4.6 Resistivity dependence ................................................ 67

5 Modeling ultrafast demagnetization 69
  5.1 Spin caloritronics ....................................................... 70
  5.2 The chemical potential ............................................... 71
  5.3 Ultrafast temperature- and chemical gradients .................. 74
    5.3.1 Laser absorption ............................................... 74
    5.3.2 Electron gas thermalization .................................. 76
    5.3.3 Surface- temperature and chemical potentials .............. 78
  5.4 Spin currents and ultrafast demagnetization: The R-model .... 80
    5.4.1 Implications of the R-model .................................. 86
  5.5 Implication on x-ray absorption spectroscopy .................... 88

6 Kerr Experiments 91
  6.1 Does MOKE measure the true magnetization? .................... 92
  6.2 The Kerr setup ....................................................... 93
    6.2.1 Sample .......................................................... 95
  6.3 Pump power and its influence on the remagnetization .......... 96
    6.3.1 Method .......................................................... 96
    6.3.2 Results and discussion ....................................... 96
  6.4 Pump pulse's length influence on the demagnetization ........ 98
    6.4.1 Method .......................................................... 98
    6.4.2 Results and discussion ....................................... 99
  6.5 Double pulse experiment ........................................... 101
It is known from thermodynamics that a ferromagnet heated above its Curie temperature looses its macroscopic magnetization. However, thermodynamics does not describe the velocity of this process. It was long believed that the time it takes for the magnetization of transition ferromagnets to react on a sudden temperature increase is limited by the weak spin-orbit interaction to the 100 ps time scale. Therefore, it was a big surprise when Beaurepaire et al. showed in 1996 that the magnetization of nickel can be reduced on the sub-picosecond time scale when heated by a femtosecond laser pulse. Since this discovery, the mechanisms responsible for ultrafast demagnetization are still highly debated.

The most often employed technique to access the ultrafast magneto dynamics is the magneto optical Kerr effect. However, it has been argued that the strong laser excitation might induce state blocking effects such that the observed ultrafast demagnetization is mimicked by optical artifacts. Furthermore, most optical methods rely on the spin-orbit interaction which has been shown to be altered during the demagnetization.

In this thesis, a method is described which overcomes these problems by measuring the time evolution of the spin polarization of the cascade electrons by time- and spin resolved photoemission. Photon pulses (40/180 eV), generated by the free electron laser (FEL) in Hamburg, provide enough energy to release electrons from everywhere within the valance band. These photo-electrons represent, therefore, an average magnetic signal of the sample. With this technique, we could show that the demagnetization time in iron is indeed ultrafast and comparable with values measured by the magneto optical Kerr effect. In addition, it was found that the FEL pulses alone can reduce the measured spin polarization. This effect is, however, not caused by an FEL induced demagnetization. The reason is space charge – the vast number of electrons released start to repel the low energetic but highly spin polarized electrons and reduce therewith the measured spin polarization. This finding will help to design forthcoming photoemission experiments at free electron laser based sources.

Photoemission has in general a low electron yield. This complicates spin resolved photoemission experiments as the widely employed Mott spin polarimeters have additionally a low detection efficiency. In collaboration with Prof. Schönhense’s Group (Mainz, Germany), a high efficiency spin polarimeter was developed. An
iridium crystal acts as a spin selective electron mirror and allows, in conjunction with a hemispherical energy analyzer, the simultaneous measurement of the spin polarization, the energy, and the electron’s emission angels. This multidimensional detection scheme has the potential to allow for future time-, angle-, energy-, and spin-resolved photoemission experiments.

In search for the mechanisms at play responsible for the ultrafast demagnetization, two important correlations were discovered and are presented in this thesis: The demagnetization time scales with magnetic film thickness and electrical resistivity. Based on these two observations, a semi-classical thermodynamical model is developed explaining ultrafast demagnetization as a spin transport effect with localized spin-flips at the ferromagnet/substrate interface. We propose the spin currents to be caused by a chemical potential gradient generated by the absorption of the infrared pump pulse. The localized spin-flips solve the dilemma of how spin transport can also induce ultrafast demagnetization in a ferromagnet deposited on an insulator. The model gives realistic values of the demagnetization time and amplitude for the transition ferromagnets without any fit parameter. Moreover, the model predicts that laser pulses of equal energy, but longer pulse length, should result in a reduced demagnetization and that the ultrafast demagnetization should be slower for a hot sample than for a cold one. Both propositions are shown to hold experimentally for the case of nickel. Therewith, the experiments provide evidence that the Elliott-Yafet spin-flip mechanism is unlikely to be the main cause for the ultrafast demagnetization in nickel. The proposed model provides an intuitive mechanism for ultrafast demagnetization based on spintronics fundamentals.
ZUSAMMENFASSUNG

Es ist aus der Thermodynamik bekannt, dass ein Ferromagnet, der über seine Curie-Temperatur aufgeheizt wird, seine makroskopische Magnetisierung verliert. Die Thermodynamik kann aber die Zeitskala der Entmagnetisierung nicht vorhersagen. Es wurde lange vermutet, dass die schwache Spin-Bahn-Wechselwirkung in den Übergangsferromagneten die Zeit mit der die Magnetisierung einem kurzen Aufheizen folgen kann, auf etwa 100 ps limitiert. Deshalb war es eine grosse Überraschung, als Beaurepaire et al. 1996 zeigen konnten, dass die Magnetisierung von Nickel auch auf einer sub-Picosekunden Zeitskala mit einem ultraschnellen (100 fs) Laserpuls reduziert werden kann. Bis heute ist jedoch unklar, was genau die mikroskopischen Ursachen für diesen Effekt sind.


Die Photoemission hat generell eine geringe Elektronenausbeute. Zudem werden


INTRODUCTION
EVERYONE experienced the mysterious and seemingly unconnected interaction two magnets can exert on each other. This effect has also captivated many scientists and engineers. Their work to understand and exploit magnetic effects has presumably advanced our way of life, unlike any other technology.

1.1 From navigation to mass storage

One of the first technological applications of magnetism was the usage of magnetized materials by Chinese sailors as compass needles “... some time in the 9th or the 10th century would be a very probable guess.” [1, p. 101] (secondary source).

Since then, technology based on magnetism has dramatically changed our lifestyle. One of the most influential developments was presumably the industrial production of electric power with generators starting at the end of the 19th century. Also at that time, in 1889, Valdemar Poulsen [2] observed that steel wire can be magnetized by a coil fed with an electrical current generated by a microphone. Employing this effect, he built the first working sound recorder. By doing so, he started the area of magnetic data storage, featuring infinite read-write cycle life and long data retention.

Since then, a great amount of research in the field of magnetism has been devoted to the technological aspects of data storage. Magnetic materials are especially suited for that purpose: the magnetization of a magnetic domain can be aligned by an external magnetic field along an anisotropy direction. Thus, to each magnetic domain an orientation state “up” or “down” a boolean ‘0’ or ‘1’ can be attributed – storing one bit of information.

The ever increasing demand for data storage capacity downsized a single magnetic domain into the sub-100 nm scale. Yet, reducing the domain size is not the only technological challenge. Also the sensitivity of the reading device (read head) has to cope with the shrinking magnetic moment inherent to the smaller domains. The discovery of the giant magneto-resistance effect in magnetic hetero-structures made it eventually possible to keep up with the downsizing. Read heads could be produced, based on this effect, sensitive enough to still detect these tiny bits. The Nobel prize in physics was awarded to A. Fert and P. Grünberg in 2007 for this discovery.

Still, sequential magnetic recording as performed in modern commercial hard drives has one drawback: the data transfer is slow compared to the speed of electronic components. A state of the art hard drive can stream data at a rate\(^1\) of about 210 MB/s. Yet, random access memory (RAM) can be accessed at rates\(^2\) up to 48’000 MB/s; more than two orders of magnitude faster than possible with mag-

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\(^1\) Seagate website, retrieved 30th of October 2013.
\(^2\) Corsair website, retrieved 30th of October 2013.
netic hard drives!

1.2 THE QUEST FOR SPEED

It is imperative for data storage devices to keep up with the ever increasing data processing speed and the amount of data production. Thus, a storage device not only needs to have a big capacity, it also has to process the data at a high speed. The speed limit is governed by the time it takes to switch the magnetization of one bit. This promotes the scientific interest to find the quickest way to deliberately alter the magnetization.

One of the fastest way to do so is called precessional or “ballistic” switching [3, 4]. We have to look at the magneto dynamics to understand the underlying speed limit. The physics of a magnetic moment in a magnetic field astonishingly resembles the dynamics of the classical gyroscope. Therefore, torque and angular momentum are key ingredients in magneto dynamics.

The reason for this similarity is of quantum mechanical origin. Quantum mechanics links the angular momentum $\vec{L}$ of a particle to a magnetic moment $\vec{m}$ by the gyromagnetic ratio $\gamma$ as

$$\vec{m} = \gamma \vec{L}.$$  (1.1)

The gyromagnetic ratio is not a constant per se. It depends on the particle and the quantum mechanical state it is in. For a free electron, it is $\gamma = eg\mu_0/2m_e$, where $e \approx -1.602 \cdot 10^{-19}$ C is the charge of an electron, $g \approx 2$ the Landé g-factor of an electron, $\mu_0 \approx 4\pi \cdot 10^{-7}$ Vs/Am the vacuum’s permeability, and $m_e \approx 9.109 \cdot 10^{-31}$ kg the electron mass. It is known form electrodynamics (and experience with compass needles) that a magnetic moment placed in a magnetic field $\vec{H}$ will experience a torque trying to align the magnetic moment with the magnetic field as

$$\vec{T} = \vec{m} \times \vec{H}.$$  (1.2)

Since the torque is nothing but the temporal derivative of the angular momentum, equation 1.2 together with equation 1.1 describe the dynamics of a magnetic moment without damping:

$$\frac{d\vec{m}}{dt} = \gamma \vec{m} \times \vec{H}.$$  (1.3)

This equation already contains the essence to understand the limits of the switching time. Let’s suppose the magnetic moment is aligned along the x-direction (see Figure 1.1 (a)). If we switch on a magnetic field of strength $H$ along the z-direction, the magnetic moment will start to precess in the x-y plane with a frequency of $|\gamma H|/2\pi = 28$ GHz/T, see Figure 1.1 (b). We can switch off the magnetic field after
the magnetic moment has precessed 180°, and we have reversed the direction of the magnetic moment as depicted in Figure 1.1 (c). The time it takes a free electron’s magnetic moment to be inverted in such a process is \( \approx 18 \text{ ps} \) in a magnetic field of 1 T. This implies that the switching time depends solely on the applied magnetic field. However, experimentally the induction of the coil, producing the magnetic field, introduces a reciprocal trade off between achievable field strength and pulse length.

So far, we have treated the magneto dynamics of one single electron. In a solid, however, the situation is more difficult as in fact there are \( \sim 10^{23} \text{ electrons/cm}^3 \), and the interaction between them can not be neglected! The most dominant interaction mechanism is called the exchange interaction which is responsible for spontaneous magnetic order. The exchange interaction has a typical energy scale of \( \sim 1 \text{ eV} \) [5, p. 492] which corresponds\(^3\) to a tremendous built-in magnetic field \( \mu_0 H_{ex} \) of several thousand teslas [5, p. 487]. Accordingly, this energy needs to be provided to switch a single electron’s spin from the majority- to the minority band.

Interestingly, the precession induced by the exchange field could indeed be measured in a beautiful experiment by Weber et al. [6]. Spin polarized electrons were shot through a ferromagnetic thin film, and the processional rotation induced by the exchange field during the passage was measured. Even though the exchange field is very strong, it is completely isotropic and hence does not bind the magnetization to a certain crystallographic direction. There are other fields which produce such anisotropies:

The crystal’s ligand field orients the orbital angular momentum \( \vec{L} \) to a specific crystal direction. Subsequently, the relativistic effect of spin-orbit coupling orients the spins along the direction of the angular momentum. This mechanism was first de-

\(^3\)The Zeemann energy \( E_Z = -\vec{m} \cdot \vec{H}_{ex} \) relates the energy of electron’s magnetic moment with the magnetic field.
scribed by van Vleck [7]. In the bulk of transition ferromagnets, the spin-orbit coupling has a relatively weak interaction energy of $E_{so} \sim 10 \mu eV$ because the orbital angular momentum is vastly quenched by the ligand field. Nevertheless, it defines together with the demagnetization field ($\vec{H}_d$) the axis along which the magnetization will spontaneously orient (easy axis). In fact, the spin-orbit coupling is the most important coupling pathway between the spin system and the crystal. Therefore, the spin system in these materials is only weakly coupled to its surrounding. This loose coupling enables for example ferromagnetic resonance experiments. The resonance line width in high quality transition ferromagnet films is typically $\sim 10 \mu eV$ – in agreement with $E_{so}$ [5, p. 684]. By applying Heisenberg’s uncertainty principle, the relatively slow spin lattice relaxation rate of $\tau_{so} \approx 100 \text{ ps}$ is found.

Based on this discussion, we can extend equation 1.3 also for solids. The magnetic field $\vec{H}$ is replaced by an effective magnetic field $\vec{H}_{\text{eff}} = \vec{H}_{\text{ex}} + \vec{H}_{so} + \vec{H}_d + \vec{H}_{\text{ef}}$, where $\vec{H}_{\text{ef}}$ is an external field and $\vec{H}_{so}$ the field associated with the spin-orbit interaction. Since energy can be transferred out of the spin system, we need to add a frictional term $\frac{a}{m} \vec{m} \times \frac{d\vec{m}}{dt}$ aligning $\vec{m}$ towards $\vec{H}_{\text{eff}}$, where $a$ is a phenomenological damping constant. The new equation is called the Landau-Lifshitz-Gilbert (LLG) equation [5, p. 88]:

$$\frac{d\vec{m}}{dt} = \gamma \vec{m} \times \vec{H}_{\text{eff}} + \frac{a}{|\vec{m}|} \vec{m} \times \frac{d\vec{m}}{dt}. \quad (1.4)$$

This equation is widely, and very successfully, employed in micro magnetic simulations in the nano- and picosecond time scale. As we are interested in the temporal limit of magnetization manipulation, the following question is obvious: Does equation 1.4 still provide useful results in the femtosecond time scale? Gamble et al. [8] performed an experiment were they shot a 70 fs long relativistic electron bunch through a magnetic thin film. Indeed, the femtosecond short action of the electric and magnetic field of the electron bunch imprints a magnetization pattern markedly good described by a modified LLG equation. It is important to note here that the LLG equation 1.4 describes the magnetodynamics only in the limit of a constant magnitude of the magnetization $|\vec{m}(t)| = \text{const.}$ [5, p. 89]. However, it is evident from heating a ferromagnet to its Curie temperature that also the magnitude of the magnetization can be changed ($|\vec{m}(t)| \neq \text{const.}$) over time and equation 1.4 can, in this case, not be applied.

What happens if we use a short ($< 100 \text{ ps}$) laser pulse to heat up a ferromagnet? We would expect, based on the above general considerations, that the fastest way to transfer spin angular momentum out of the spin system is dominated by the spin-orbit interaction, leading to a demagnetization time scale of $\tau_{so} \sim 100 \text{ ps}$. Thus, the magnetization should not change during the action of a laser pulse shorter than $\tau_{so}$. 
Indeed, experiments by Vaterlaus et al. [9] showed that during a $30 \text{ ps} < \tau_{\text{so}}$ long laser pulse an iron thin film does not demagnetize even though it is heated above the melting point and rendered to a paramagnetic state. In contrast, during a laser pulse of $20 \text{ ns} > \tau_{\text{so}}$ length, the electron spins have enough time to equilibrate with the lattice, and the iron film demagnetizes.

Therefore, it was a big surprise to the magnetism community, when Beaurepaire et al. [10] showed in 1996, that the magnetization of a nickel film can be reduced (quenched) even by a 60 fs infrared laser pulse within less than 1 ps. This observation contradicted the understanding of magnetodynamics gained up to then. And his discovery started a new field, called femtomagnetism [11]. Even though the discovery was made nearly two decades ago, the underlying microscopic processes at play, responsible for the magnetic quenching, are still poorly understood.

1.3 Ultrafast Demagnetization

This section is intended to give a coarse view on both the theoretical and experimental aspects of ultrafast demagnetization.

A generic feature of all the ultrafast experiments is the usage of ultrashort laser pulses. Typically, a magnetic sample is excited (pumped) by an intense and ultrashort ($\sim 100 \text{ fs}$) 800 nm infrared laser pulse. The temporal evolution of the magnetization $\vec{M}(\Delta t)$ is measured stroboscopically, in a so-called pump-probe experiment. Time delayed by $\Delta t$ to the first pump pulse, a second pulse samples the magnetization $\vec{M}(\Delta t)$, called probe pulse. The scheme is repeated for various $\Delta t$ until the full trace $\vec{M}(\Delta t)$ is recorded. Necessities for a pump-probe experiment to work are: 1) the system has to be prepared always in the very same state before the arrival of the pump pulse, 2) the system needs to fully relax between the pump pulses, and 3) the system has to react always in the same manner on the pump pulses.

1.3.1 Theoretical and Experimental Findings

It is known that when an infrared laser pulse hits a solid, it will be primarily absorbed by the electron gas. Then, by energy equilibration, also the spin- and the phononic system will be heated up [10]. In this way, one looks at the problem in a thermodynamical picture. However, thermodynamics does not provide deeper insights into the microscopic processes responsible for the demagnetization.

It has been suggested that already during the action of the laser pulse, the coherent excitation of the electrons can induce ultrafast demagnetization. Theoretically this mechanism has been proposed by Zang et al. [12]. And, experimentally Bigot et al. [11] interpreted their findings based on a such an effect. However, as exper-
ments by Eschenlohr et al. [13] showed, ultrafast demagnetization can be caused by hot electrons alone. Therefore, the presence of a laser field is not a necessity for ultrafast demagnetization. Moreover, the possibility of a direct spin angular momentum transfer from the photons to the electron spins could be ruled out by experiments performed by Dalla Longa et al. [14]. Thus, a coherent light matter interaction seems not to explain the observed ultrafast demagnetization. The spin lattice coupling is the most important pathway of spin angular momentum transfer to the lattice as discussed above. However, its time scale is limited to \(\sim 100\) ps. It is, hence, difficult to understand why the spin-orbit interaction, in a ferromagnet heated by femtosecond laser pulse, can account for a thousand times shorter ultrafast demagnetization.

A possible way out this dilemma was proposed by Koopmans et al. [15]. They suggested that after the excitation by an ultrafast laser pulse the dampened precession in the exchange field governs the demagnetization time. Furthermore, models on the stochastic Landau-Lifshitz-Bloch equation [16, 17] have been proposed where also a damping parameter is included. However, experiments by Walowski et al. [18] showed that the damping parameter does not influence the demagnetization time.

Ultrafast demagnetization is often described in the framework of the Elliott-Yafet interaction. In the presence of spin-orbit coupling, the spin- and the orbital angular momentum operators do not commute. Therefore, a single electron wave function is always a superposition of a spin up (\(|↑⟩\)) and a spin down (\(|↓⟩\)) state. It was Elliot [19] who realized that these superposition states possess a finite spin-flip transition rate involving a lattice perturbation (phonon). Later on, Yafet [20] extended the phononic transition term by a spin-orbit interaction component. In their theory, Fermi’s golden rule is applied to calculate the spin-flip transition rate. However, the validity of Fermi’s golden rule to the ultrafast time scale (<100 fs) is not ensured. It has been pointed out by Fähnle et al. [21, p. 11] that Fermi’s golden rule can in principle not be applied to the case of ultrafast demagnetization since it demands energy conservation. However, energy conservation can not be achieved when the electrons demagnetize faster (<100 fs) than an oscillation period of a phonon mode (\(\sim 1\) ps). As the electrons can not “know” yet the energy of the phonon. However, this approach is often used due to it’s successful application in aluminum [22] in the 1-100 ns timescale – where the application of Fermi’s golden rule is valid.

Recent ab-initio studies [23, 24] on the Elliott-Yafet interaction indicate that the effect is too small to explain the observed ultrafast demagnetization alone. Moreover, other scattering mechanisms have been proposed. For example the Coulomb electron-electron scattering [25, 26]. It was thought that this mechanism could be an other ultrafast demagnetization pathway as electron-electron scatter-
ing by far outnumbers electron-phonon scattering events [21, p. 13]. Still, it is obvious that an electron-electron scattering event alone can not reduce the spin moment of the electron system as the angular momentum is conserved. Therefore, the strong assumption needs to be made that during the scattering the spin angular momentum can be transported efficiently to the lattice, regardless through which pathway [21, p. 13].

In summary, we can state that bulk spin-flip theories do not convincingly explain how the weak spin-orbit coupling can account for the \( \sim 100\,\text{fs} \) demagnetization time observed for example in Fe, Ni, and Co [27, 28]. These difficulties lead to the speculation that the ultrafast demagnetization is not caused by bulk spin-flip scattering events. In fact, Malinowski et al. [29] observed, in 2008, that the action of the laser pulse on a ferromagnet generates spin currents. Two years later, Battiato et al. [30] presented a model based on this idea. Spin currents deplete the ferromagnet of its majority spins, causing a demagnetization without the need for spin-flips. Indeed, the predicted spin currents have been observed experimentally [31–33]. Nevertheless, their theory can not realistically account for the ultrafast demagnetization of ferromagnetic thin films deposited on insulators [14, 34].

In this thesis, the interface between the ferromagnet and the substrate is proposed as the location where the spin-flips can happen on a femtosecond timescale, see chapter 4. Based on this new Ansatz, a semiclassical model is introduced in chapter 5 explaining the ultrafast demagnetization as a spin transport effect caused by a chemical potential gradient. Since spin-flips are included in the model, also ultrafast demagnetization of thin films deposited on insulators can be explained. In addition, the model’s implications are shown in chapter 6 to hold also experimentally. Namely that longer pump pulses should result in a less efficient demagnetization and that the demagnetization of a hot sample is slower than for a cold one.

1.3.2 Methods
Experimentally, the easiest way to measure the ultrafast demagnetization is undoubtedly by a photon in – photon out experiment. In such an experiment, the magnetic state of the sample (\( \vec{M}(\Delta t) \)) is contained in the change of the properties of the incoming to the outgoing photon beam:

The magneto optical Kerr effect [35–37] (MOKE) is probably the most convenient technique to access the femtosecond evolution of the magnetization [10, 11, 38, 39]. In a MOKE experiment, a polarized, ultrashort laser pulse is directed onto a magnetic sample. The change of polarization of the reflected compared with the incoming beam is in first order proportional to the magnetization of the sample. Most femtosecond laser systems operate at a wavelength of 800 nm. Thus, em-
deploying this wavelength, the technique can access electronic states about ±1.5 eV above and below the Fermi level. There is a controversial discussion if MOKE can still faithfully reflect the magnetization of an excited sample or if it breaks down in this limit. In principle, it is well possible that state blocking effects [40–42] alter the MOKE signal of the excited sample. The topic is discussed in more detail in chapter 6.

Another way to optically access the magnetization makes use of frequency doubling or second harmonic generation (SHG). The yield of the frequency doubled photons depends in first order on the magnetization of the sample. The technique [43] is very surface sensitive for centrosymmetric media because frequency doubling is symmetry forbidden for the bulk but allowed at the surface [44, p. 495]. Moreover, it has been observed that during ultrafast demagnetization, according to electrodynamics, the temporal change of the magnetization emits electromagnetic radiation [45]. The spectrum lies in the THz region. Even though the techniques allows to conclusively show that the magnetization changes upon an ultrafast pump pulse, it only accesses the temporal derivative of the magnetization, convoluted with the bandwidth of the detector. Thus, the time resolution of this technique is limited to ~ 1 ps.

The most generic of all the optical methods is x-ray magnetic circular dichroism (XMCD). Circularly polarized x-rays induce transitions from the occupied $L_2/M_2$ or the $L_3/M_3$ states either to the unoccupied majority or minority d-states in the valance band [46, 47]. Every element has its characteristic $L$ or $M$ levels, thus, the method provides element specific access to the magnetization state [48–50]. In addition, XMCD is unique in the sense that both the spin- and the orbit angular momentum can be measured independently. It could be shown, for example, that the spin-orbit coupling is altered during the ultrafast demagnetization [48].

All the optical methods rely on the electronic density around the Fermi level and, despite the THz emission experiments, also on the spin-orbit coupling. After the interaction with an intense pump pulse the electronic occupation and the spin-orbit coupling can be changed [48]. Therefore, it is possible that the optical methods are impaired by the hot electron gas.

Time- and spin polarized photoemission provides a way to overcome these ambiguities by directly measuring the spin polarization. The technique is thus unaffected by state filling processes and does also not rely on spin-orbit coupling within the solid.

The ultimate goal in a time- and spin resolved photoemission experiment is to gather information about the temporal evolution of the density of the occupied states, individually resolved for the majority (↑) and minority (↓) spins. Photoe-
mission can be understood on the basis of Fermi’s golden rule:

\[ w_{i\rightarrow f} = \frac{2\pi}{\hbar} \left| \langle \Psi_f \phi | \Delta | \Psi_i \rangle \right|^2 \rho_f. \tag{1.5} \]

Here, \( w_{i\rightarrow f} \) is the transition rate, \( \Delta \) is the time dependent perturbation caused by the electromagnetic field [51], \( \rho_f \) is the density of final states, and \( \Psi_{i,f} \) are the initial- and final state wave functions, respectively. The absorption of a photon removes an electron from the initial \( N \) electron wave function \( \Psi_i(N) \) and promotes it to a \( (N-1) \) state \( \Psi_f(N-1) \). The photo excited electron is assumed to propagate as a free-electron state \( \phi(E, \vec{k}) \) in vacuum\(^5\) with energy \( E \) and wave vector \( \vec{k} \). By the use of an energy analyzer, we can select electrons with a specific energy \( E \) and wave vector \( \vec{k} \). The intensity recorded in such a channel reads then [51]

\[ I(E_f, \vec{k}_f) \sim \left| \langle \Psi_f(N-1) \phi(E_f, \vec{k}_f) | \vec{A} \cdot \vec{p} | \Psi_i(N) \rangle \right|^2 \delta(E_f - E_i - \hbar \omega), \tag{1.6} \]

where \( \hbar \omega \) is the energy of the absorbed photon, \( \vec{A} \) the vector potential of the electromagnetic field, \( \vec{p} \) the momentum operator, and \( E_{i,f} \) are the energies of the initial and final states, respectively. The final state \( \Psi_f(N-1) \) is expected to be close to the ground state of the initial wave function \( \Psi_i(N) \) when the influence of the hole in the final state can be efficiently screened [51, p. 472]. In this limit, which is mostly fulfilled in metals due to their itinerant electrons, \( I(E_f, \vec{k}_f) \) represents a meaningful measure of the density of states in the one-electron band picture [51].

By the usage of a spin polarimeter, we can further split the intensity into their spin resolved components

\[ I(E_f, \vec{k}_f) = I_{\uparrow}(E_f, \vec{k}_f) + I_{\downarrow}(E_f, \vec{k}_f), \tag{1.7} \]

which are likewise a measure for the spin resolved density of states. This derivation assumes continuous monochromatic photons of energy \( \hbar \omega \). The measurement of the ultrafast temporal evolution of the density of states, however, relies on short probe pulses. Photon pulses of a length \( \tau \) are not monochromatic anymore. Their spectral width is given by \( \sim \hbar / \tau \) which also governs the achievable energy resolution. A 10 fs long pulse, for example, has a spectral width of \( 6.58 \cdot 10^{-16} \text{eVs/10fs} \approx 70 \text{meV} \). This is much smaller than the typical valance band width of \( \sim 10 \text{eV} \) in a transition ferromagnet. Therefore, the temporal dynamics of the valance band can still be accurately resolved.

\(^4\)The assumption of the three step model.

\(^5\)For the sake of clarity, the effect of the surface scattering is omitted, for a detail treatise see for example [51].
It is important to note that electronic transitions conserve the spin angular momentum. However, this should not deceive that spin polarized electrons can still be very well generated from non magnetic materials. As pointed out by Heinzmann et al. [52] this happens when the spin-orbit splitting is resolved somewhere in the measurement process. This would in principle allow the measurement of the evolution of the magnetization and the spin-orbit coupling by time-, spin-, and angle-resolved photoemission spectroscopy.

Up to now, a full temporal-, spin-, angle-, and energy resolved measurement could not be performed as spin polarimeters suffer form a low figure of merit (discussed in chapter 3). Either the experiments could access the evolution of the spin integrated density of states [53–55], or, when spin analysis was employed, the low yield of the spin polarimeter inhibited energy resolution [56, 57]. Moreover, spin resolved experiments employed up to now, based on threshold photoemission, could only resolve the top most $\sim 1$ eV of the valance band. Thus, it was not possible to track the magnetic evolution of the valance band as a whole. This lack, clearly demands for further experimental investigations. In the next chapter, a method based on the measurement of the cascaded electrons excited with photons of sufficient energy (40 eV) is presented. These electrons can stem from every-where within the valance band and provide thus a valance band integrated measure of the magnetization without the need of the spin-orbit coupling.
The spin analysis of photo-electrons can provide a direct measure of the magnetization. In this chapter, time and spin resolved photoemission is examined with free electron laser (FEL) radiation. A short introduction to the properties of a FEL and its radiation characteristics is provided. It was generally thought that angular momentum conservation dictates the spin polarization of photo-electrons to be conserved. However, we show in experiments that space charge effects can reduce the spin polarization without the violation of the conservation law. Furthermore, time resolved measurements show that the average valence band magnetization of an iron thin film can be quenched with an infrared pump pulse on a sub-100 fs time scale which is in line with magneto optical measurement methods.
2.1 **THE EXPERIMENTAL SETUP: A MOBILE END-STATION**

The experiments are performed in a ultrahigh vacuum (UHV) system to allow for the study of uncontaminated surfaces. The UHV system consists of a preparation- and measurement chamber, see Figure 2.1 (a). The chamber layout makes it possible to simultaneously measure and prepare samples. This is important for light sources such as Free Electron Lasers (FEL) where only little beamtime is granted.

Both chambers are equipped with ion- and titanium-sublimation pumps. Pressures are as low as $< 10^{-10}$ mbar in the preparation chamber and $2 \cdot 10^{-10}$ mbar in the measurement chamber. The preparation chamber is additionally pumped with a turbo molecular pump.

The speciality about the setup is its compact design. Its size is only 90 cm in width, 240 cm in length, and 160 cm in hight. It is build on wheels to allow easy transportations. The system has been used as a mobile end-station at the free electron laser in Hamburg (FLASH), and at the Swiss Light Source in Villigen.

2.1.1 **THE MAGNETIC SAMPLE**

The photoemission studies were carried out on 8/15 monolayer (ML) iron films deposited on W(110). This magnetic system has been chosen since it is very well...
investigated [58–64] and can be grown reproducibly. Beneficial are its properties: the spin polarization depends only weakly on the film thickness, it can be magnetized in a single domain state, and posses a small coercive field allowing for switching by small magnetic fields [65]. Below 43 ML of iron coverage [66], the film has its easy-axis along the [1\bar{1}0] direction. Nevertheless, the growth mode is complicated [60] due to the big lattice mismatch between iron and tungsten of $\approx 34\%$.

**Sample preparation**

The magnetic thin films are grown on polished W(110) crystals in the UHV preparation chamber. The W(110) surface is cleaned by annealing the crystal at 1400°C for 5 min in a $4 \cdot 10^{-8}$ mbar oxygen atmosphere. After this initial procedure, the crystal is flash-annealed three times; the crystal is heated to 2000°C for 10 s. Between each flash cycle, the crystal cools down during 30 s. After the surface cleaning, the crystal is allowed to cool down for 30 min. Iron is evaporated from a Knudsen cell type evaporation source. Small iron pieces\textsuperscript{1}, within a tungsten crucible, are heated by electron bombardment. The cell is pre-heated during 10 min to allow for a stable temperature. The deposition rate is calibrated with a quartz balance. A typical evaporation rate is 0.5 ML per minute. During evaporation, the pressure rises from $2 \cdot 10^{-10}$ mbar to $3 \cdot 10^{-10}$ mbar [65]. The whole sample preparation procedure – from cleaning the substrate to iron evaporation – is computer controlled\textsuperscript{2} resulting in a high- repeatability and quality of the produced samples.

**2.1.2 Sample holder and magnetic coils**

To switch the magnetization of the sample, typically Helmholtz coils are being used. However, in photoemission experiments, it is important not to perturb the electric fields around the sample. Hence, the use of Helmholtz coils, which would alter the electrical fields around the sample, are undesirable. To avoid this problem, we build a special planar coil type, see Figure 2.2. The arrangement of the coils can be understood as a Helmholtz coil pair where each coil is tilted outwards with respect to the other one by 90 degrees, thus generating a large magnetic stray field. The sample is placed in the middle of the two coils, where the field is most homogeneous. The two coils are placed behind a metallic shield. This allows for electrical biasing of the sample. Star shaped cut-outs in the shield minimize eddy currents and minimize interference with the magnetic field, generated by the coils. Each coil consists of only five windings to minimize inductance which allows a fast switching of the magnetic films. A 15 ML iron film on W(110) can be reliably evaporated from a Knudsen cell type evaporation source.

\textsuperscript{1}Iron lumps from GoodFellow with a purity of 99.99+ %.

\textsuperscript{2}The open source TANGO control system is being used, http://www.tango-controls.org/.
switched by this coil geometry along the easy axis within 3 $\mu$s [67]. The small number of turns$^3$ needs to be compensated by high coil currents to reach the necessary switching fields. We developed and built a high current pulser, being able to deliver bipolar currents of up to 1000 A at 1000 V. The pulser can deliver pulses at a repetition rate of up to 10 kHz and as short as 2 $\mu$s. This is ideal for measurements with commercial amplified laser systems because of the similar repetition rates. The design and performance of the pulser are described in detail in Ref. [67].

### 2.1.3 Measuring the spin polarization: Mott detector

The spin polarized photo emitted electrons are collected by the use of an electro static lens and focused into a spin-polarimeter. Such polarimeters work primarily on the principle of spin dependent scattering. We used a Mott spin-polarimeter (Mott detector) [68] to measure the spin polarization of the photo emitted electrons where the electrons are scattered on a 80 nm thick gold film. For the detector to work, the electrons are accelerated to 50 keV.

---

$^3$The wiring from the current generator is 1.5 m long – despite bifilliarly wound – produces a larger inductance than the coil itself.
2.1. The experimental setup: a mobile end-station

A mobile end-station 17

Figure 2.3: Working principle of a Mott detector: The incoming electrons are scattered depending on their spin orientation. As an example, the incoming electron (highlighted in cyan) will be predominantly scattered upwards, where the created charge \( C_1 \) or the number of “clicks” \( N_4 \) will be registered in an electron detector. The large black arrows indicate the spin orientation which has a scattering surplus in the respective detector. The detector pairs measuring \( P_x \) and \( P_y \) are highlighted in light blue or red, respectively.

which is already a tenth of their rest mass. Thus, the electrodynamics starts to become relativistic. The strong electric field generated by the gold nuclei is partly transformed in the rest frame of the electrons to a magnetic field. It asserts a force on the magnetic moments of the electrons depending on their spin orientation. This generates a left/right counting asymmetry in a detector pair collecting the back scattered electrons, see Figure 2.3. The counting asymmetry is a measure for the spin polarization component perpendicular to the scattering plane. Hence, two perpendicularly mounted detector pairs allow for the measurement of the spin polarization \( P_x, P_y \) along the x- and y- direction, respectively. The coordinate system is defined in Figure 2.2 (b). The spin orientation along these directions can be computed by the counting asymmetries

\[
P_x = \frac{1}{S} \frac{N_2 - N_4}{N_2 + N_4}, \quad P_y = -\frac{1}{S} \frac{N_1 - N_3}{N_1 + N_3}.
\]

Here, \( N_i \) are the number of electrons counted in each detector \( i = 1 - 4 \), and \( S \) is the Sherman factor describing the spin selectivity of the detector. For an ideal spin detector it would be \( S = 1 \) and for a detector with no spin selectivity \( S = 0 \). In our case \( S = 0.17 \). The determination of \( P_x \) and \( P_y \) by equation 2.1 works only if the electron flux is low enough to count each electron individually. For time resolved measurements, this counting technique is unsuitable: The FEL probe pulse can release hundreds of electrons within only a few 10fs, and they can not be individually
Figure 2.4: The detection chain: The signal from each electron detector is amplified, shaped, and digitized on the 50 kV potential. An optical fiber transmits the data to a computer on ground potential. The trace shows a test scan where the detector was excited by stray light from an ultrafast infrared laser pulse.

counted anymore. Still, the amount of charge reaching the detector is an equally good measure of the number of electrons. Hence, equation 2.1 can be adapted by replacing the number of electrons by the amount of deposited charge per pulse \( C \) as \( N_i \rightarrow C_i \), and we get

\[
P_x = \frac{1}{S} \frac{C_2 - C_4}{C_2 + C_4}, \quad P_y = -\frac{1}{S} \frac{C_1 - C_3}{C_1 + C_3}.
\]

(2.2)

Experimentally, misalignments and varying detection efficiency lead to apparatus asymmetries in the determination of the spin polarization. By measuring two magnetization directions of the sample (\( C_i^{↑,↓} \) for an up (↑) or down (↓) in saturation magnetized sample), it is possible to totally cancel out apparatus asymmetries under the condition that the beam of photo electrons does not move upon switching [69, p. 1228]:

\[
P_{x,y} = \frac{1}{S} \frac{\sqrt{C_{2,3}^{↑}C_{4,1}^{↓}} - \sqrt{C_{2,3}^{↓}C_{4,1}^{↑}}}{\sqrt{C_{2,3}^{↑}C_{4,1}^{↓}} + \sqrt{C_{2,3}^{↓}C_{4,1}^{↑}}}.
\]

(2.3)

Unless otherwise noted, equation 2.3 is used to calculate the spin polarization. Figure 2.4 explains the detection scheme: the current pulse from the detector is amplified by a charge sensitive amplifier\(^4\). This amplifier produces sharp voltage

\(^4\)The gain of the amplifier was adjusted for optimal resolution. We could choose from the whole pallet of Cremat, Inc. amplifiers providing gains of: 1.4 V/pC (CR-110), 0.13 V/pC (CR-111), 13 mV/pC (CR-
spikes, where the spike-height is proportional to the deposited charge in the detector. These spikes are further conditioned by a pulse shaper, producing Gaussian like pulses\(^5\). The pulse height of these pulses is proportional to the charge deposited in the detector. Therefore, the sampling window of the digitizer is tuned on the maximum of these pulses. The effective signal reads then \( C = C_{\text{Max}} - C_{\text{Base}} \), the difference between the maximum and the base line, see inset in Figure 2.4. During the experiments, the baseline value is automatically remeasured at least every 100 ms to account for baseline drifts. The resolution of this acquisition system is sufficient to detect single electrons. All the detection electronics is floated on 50 kV, and the digital signals are transferred to a computer by insulated optical fibers. This acquisition system was developed in-house and became a commercial product.

The Mott detector is distinguished for its robustness, as it does not rely on atomically clean surfaces. Hence, no down-time is caused by tedious surface preparations before it can be operated. This is an important aspect as available beam-time at FELs is very limited. As discussed later in the text, the price to pay for the robustness is the low detection efficiency. In the used Mott detector, only about 1\% of the incident electrons reach an electron detector. In general, the performance of a spin-polarimeter is described by a value called figure of merit (FoM) which is defined as

\[
\text{FoM} = \frac{I}{I_0} S^2.
\]

Here, \( S \) is the Sherman factor\(^6\), \( I_0 \) is the incoming electron current, and \( I \) is the current on the electron detectors. An ideal spin-polarimeter has a FoM = 1. The employed Mott detector has a FoM \( \approx 10^{-5} - 10^{-4} \).

2.1.4 Electrostatic Lens System

The photo emitted electrons are collected by an electrostatic lens system directing the electrons to the Mott detector. Two different lens systems have been used during the experiments at FLASH:

Deflector lens

Figure 2.1 (b) shows the Mott detector together with a 20° deflector. The electron detectors in the Mott spin-polarimeter are also very sensitive to infrared light. To

\(^5\)Cremat, Inc. shapers of either 1 \( \mu \)s or 250 ns FWHM where used. Note that the slower shapers introduce less noise.
inhibit stray light from the infrared pump pulse reaching the detectors, a blackened\(^6\) \(20^\circ\) deflector was installed between the sample and the Mott detector. The deflector suppressed infrared radiation so well that no signal in the Mott detector could be observed from the infrared pump pulses alone. The lens system did not provide energy analysis and was designed to pass the photo emitted secondary electrons up to \(100\) eV energy from the sample. The working distance from the first lens element to the sample was \(40\) mm.

Energy analyzer
The Mott detector was mounted at the output of a hemispherical energy analyzer\(^7\), see Figure 2.1 (c). Also in this setup, the working distance to the sample was \(40\) mm and no stray light could reach the Mott.

2.2 Requirements for the probe pulse
In the first chapter, I have motivated the need for an experiment being able to measure the ultrafast demagnetization not only through states close to the Fermi level but by measuring the magnetization state of the hole valence band. Hence, we need radiation which has sufficient energy to overcome the work function of the sample \(W_{\text{Fe(110)}} = 5.1\) eV [70, p. 40] and can still probe the width of the valance band, about \(\Delta E_V \approx 10\) eV. Therefore, we need at least photons with an energy of \(\hbar \omega > W_{\text{Fe(110)}} + \Delta E_V \approx 15\) eV. Furthermore, to employ an ultrafast pump-probe measurement, the photon pulses need to be ultra-short (~\(100\)fs). Radiation pulses with this characteristic can nowadays be generated by high harmonic generation, where an intense laser pulse is focused in a rare gas jet [71]. At the start of my thesis such sources had not enough power to be used in a photo emission experiment in conjunction with the low yield of a Mott detector. Hence, we conducted our experiments at the free electron laser (FEL) in Hamburg (FLASH) [72] providing both, short, and intense pulses of sufficient energy.

2.3 The Free Electron Laser in Hamburg (FLASH)
Laser radiation in the vacuum ultraviolet (VUV) regime (10-200 eV) can not be produced in an active medium. The absorption in any possible gain material is too high due to the large ionization cross section. Hence, an other technique needs to

\(^6\)All the lens elements of the electron optics are covered by graphite powder. It provides a homogenous work function and reduces the generation of secondary electrons. Furthermore, the graphite powder minimizes infrared reflection.

\(^7\)SPECS\textsuperscript{TM} Phoibos 150 hemispherical energy analyzer
be employed: Abandoning an active medium means to make use of the electromagnetic radiation emitted from accelerated electrons, called synchrotron radiation. Synchrotron radiation is produced by sending a relativistic electron beam through a magnetic undulator. Such a device consist of a periodic arrangement of magnets. Their magnetization direction is transversal to the flight direction of the electrons and the magnets are mounted with alternating magnetization direction. The Lorentz force acting on the electrons in the undulator forces them on an oscillatory trajectory and they start to emit narrow band electro-magnetic radiation around the center wavelength of

\[
\lambda_{ph} = \frac{\lambda_u}{2\gamma^2} \left(1 + \frac{K^2}{2}\right).
\]  

(2.5)

Here, \( \gamma = \frac{E}{m_e c^2} \), \( K = \frac{q B_u \lambda_u}{2\pi m_e c} \), \( \lambda_u \) is the undulator period, \( B_u \) the undulator peak magnetic field, \( E \) the electron energy, \( q \) the elementary charge, \( m_e \) the electron rest mass, and \( c \) the speed of light.

The undulator installed at FLASH [75] is a 30 m long device, has a magnetic periodicity of \( \lambda_u = 27.3 \) mm, and a peak magnetic field of \( B_u = 0.47 \) T. Note that despite it’s length, such an undulator is a precision device; the total position error of a single undulator magnet is only about 30–40 \( \mu \)m [75] over the whole undulator length to provide lasing. From equation 2.5, we see that the emitted wavelength can be easily tuned by varying the energy of the electrons \( E \).

Since decades, synchrotron radiation is widely used to produce x-rays of varying wavelength and polarization. A free electron laser, however, has the advantage over a synchrotron facility that the spectral intensity is orders of magnitudes larger and that VUV or x-ray pulses of sub-100 femtosecond length can be produced. The high intensity is achieved by letting the electrons interact with their already produced synchrotron radiation. When this interaction is made sufficiently strong, by a long enough undulator and a sufficiently large bunch charged density, it will induce an electron density modulation of the photon wavelength \( \lambda_{ph} \) within the
electron bunch, called “micro-bunching”. Once this process has been initiated, the electrons start to emit coherent radiation with $\lambda_{ph}$ as the center wavelength and amplify it in an exponential manner. At a certain undulator position, the process of “micro-bunching” is fully completed and the amplification saturates. This is the optimal working point of a free-electron laser, since it produces the least amount of intensity variations and produces maximal radiation power. The short light pulses from a FEL are a consequence of the lasing activity; which can only be reached by making a sub-100 femtosecond charge spike in the electron bunch.

A schematic layout of FLASH is depicted in Figure 2.5. The generation of an FEL pulse starts at the electron injector, in the RF (radio frequency) gun. The gun is designed to deliver electron bunches separated by $1\,\mu s$ and can form charge pulse trains of up to 800 pulses [76]. The repetition rate of these pulse trains (macro-bunches) is 10 Hz. Within the gun, an ultraviolet laser produces pulses of 4 ps rms duration [77] which release photo-electrons from a Cs$_2$Te cathode. These electrons are immediately accelerated by the first cavity running at 1.3 GHz to relativistic energies of 4 MeV [76], resulting in bunches of $\approx 2\,\text{mm}$ [76] length. The pulses cannot be shorter, as otherwise space charge effects would start to rip them apart. Hence, it is important for the beam quality to bring the electrons as quickly as possible to relativistic energies, suppressing effectively space charge effects by increasing the average distance of the electrons in their rest-frame. Once the electrons are at relativistic energies, their bunch length can be further compressed by magnetic bunch compressors (BC1/2 in Figure 2.5). Starting from a typical bunch charge of 0.5-1 nC, the peak current after the compressors is in the order of 1-2 kA within only a 50 fs long charge spike [77] – just enough to render the electron-radiation interaction strong enough to induce lasing.

### 2.3.1 Timing

In ultrafast time resolved measurements it is of outermost importance to know the time delay between the pump and the probe pulse precisely (sub-100 fs resolution). At FLASH, this timing is impaired by either slow drifts or by a pulse to pulse time jitter. Slow drifts – for example caused by temperature expansion of the accelerator structure – are measured at FLASH by a so-called “streak camera”. The pulse to pulse time jitter [73] – mostly produced by field variations in the first accelerator module – is measured in a device called “beam arrival monitor”. In the following, the different timing devices are briefly discussed.

---

8 Space charge describes undesired effects based on Coulomb repulsion, originating from a too high electron density.

9 Order of minutes.
**2.3. The Free Electron Laser in Hamburg (FLASH)**

**Figure 2.6:** Schematic setup of the pump-probe timing at FLASH: The time delay between the pump and the probe beam is changed by the delay stage. The time jitter between the probe beam and the reference clock is measured with the beam arrival monitor (BAM). The difference between the pump pulse and the probe beam is measured by a streak camera. The sum of the BAM, the streak camera, and the delay stage gives the jitter corrected pump-probe delay.

*The delay stage*

To deliberately change the timing between the infrared pump- and the FEL probe beam, there is a 3 ns long delay stage installed, \( \Delta t_{\text{Delay}} \). During the experiments, the delay stage is scanned continuously over the time range of interest. For every probe pulse the position of the delay line is read out and saved in the data acquisition system (DAQ) of FLASH.

*Pump laser and streak camera*

The pump laser provides 800 nm infrared pulses of about 120 fs FWHM length [78]. Its repetition rate matches the pulse structure of the FEL, so that pulse trains of 1-800 pulses (separated by 1 \( \mu \)s) with a repetition rate of 10 Hz can be delivered. The pump laser is synchronized to the 1.3 GHz master oscillator. The signal is distributed to the laser hutch over a 300 m long coaxial cable [78]. Such a long coaxial cable cannot maintain femtosecond resolution over longer times\(^{10}\). Hence, the time difference of the pump pulses before the delay stage is compared to the arrival time of the electron bunches after the undulator. After the electrons have passed the undulatory, they are deflected into a beam dump by a bending magnet. The generated synchrotron radiation emitted during the deflection can be used as a precise electron arrival marker [78]. This is done by measuring the time difference between the synchrotron light arrival and the pump pulse (before the delay

\(^{10}\)Order of minutes.
line) in a streak camera [78]. The streak camera can measure the difference with a resolution of < 0.7 ps FWHM [78] on a pulse to pulse basis. However, by averaging the signal, slow drifts can be measured with a resolution of ≈ 50 fs [78].

**Beam arrival monitor**

The pulse to pulse time jitter is measured in front of the undulator with a beam arrival monitor (BAM 2 in Figure 2.5). This device picks up the electrical pulses from a small metal plate placed closely to the location of the electron bunch passage. These electrical signals, with a bandwidth of 10 GHz [73], are sampled in a Mach-Zehnder type electro-optical modulator by the reference laser pulses transported over length stabilized fibers [73]. The light intensity after the modulator is a measure for the arrival time. Even though the pick-up signal has “only” 10 GHz bandwidth, it is remarkable that the arrival time of the electron bunch can be measured with a root mean square deviation of only 6 fs rms [73]. The BAM 1 can further be used to actively stabilize the arrival time of the electrons by tuning the phase of the accelerating cavities [73]. This is necessary for experiments which can not resolve each FEL pulse separately.

**Jitter corrected timing**

Figure 2.6 summarizes how the time jitter correction is achieved at FLASH. The beam arrival monitor (BAM 2 in Figure 2.5) measures the time jitter between the FEL radiation and the reference clock, $\Delta t_{BAM}$. The streak camera captures the time difference between the FEL radiation and the pump pulse $\Delta t_{streak}$, before the delay line. Therefore, the total jitter corrected time delay between the pump- and the probe beam is the sum of all these time deviations $\Delta t = \Delta_{Delay} + \Delta t_{BAM} + \Delta t_{streak}$.

### 2.3.2 FINDING TEMPORAL OVERLAP

Before a time resolved experiment can start in the sub-picosecond timescale, we need to find the coarse (few picoseconds precision) temporal overlap between the infrared (IR) pump and the FEL probe pulses. Once we are in the proximity of time zero\textsuperscript{11}, the actual experiments are used to find the precise sub-picosecond temporal overlap.

In our case, the temporal overlap was searched with an antenna (the pin of a male SMA connector) within the vacuum chamber. The FEL and the pump beam were focused onto the antenna. Both beams will create photoelectrons which generate a brief current pulse in the coax cable attached to it, a marker for their arrival time. This signal is amplified\textsuperscript{12} and sampled with an oscilloscope with more than 4 GHz.

\textsuperscript{11}“Temporal overlap” is synonymously also called “time zero”.

\textsuperscript{12}Two KUHNE electronics (KU LNA BB 0180 A-SMA) amplifiers (7 GHz bandwidth) in series, providing each $23 \pm 3$ dB amplification.
bandwidth. The oscilloscope is triggered by a fast photodiode picking up the timing of the infrared pump pulses. This diode is placed behind a dielectric mirror before the laser shutter. To find time zero, first, the infrared laser shutter is closed. Then, the FEL shutter is opened and the voltage pulse is saved as a reference trace in the oscilloscope. Now, only the IR laser shutter is opened, and the delay stage is moved until the electrical signal from the IR pulses overlap the saved FEL trace. With this procedure time zero can be found to a precision of ±10 ps.

### 2.3.3 FEL fluctuations

We have already discussed time jitter at FLASH. It can be compensated by measuring the beam arrival times. FLASH not only jitters in time, but basically in every parameter one can imagine, such as: Intensity, spectrum, beam position, and lasing mode [79]. The physical origin is that lasing at FLASH is initiated by a spontaneous, random photon emission at the beginning of the undulator. Hence, every pulse from the FEL is started by a random fluctuation. To overcome such inconveniences, the same principle as for the timing needs to be applied: every parameter needs to be tracked for each pulse and sorted during data analysis.

**Intensity fluctuations**

For our spin resolved measurements, the most discomforting of the above variations is the intensity. It varies up to 100 % from pulse to pulse. This introduces a significant noise level to the measured spin resolved signal. However, in performing an intensity resolved measurement, the fluctuations can even be beneficial as the fluctuations already span a certain intensity region. To make use of this feature, we only need to be able to track the FEL intensity on a pulse to pulse basis. The energy of an FEL pulse, before the monochromator, can be measured by a gas ionization meter. However, its energy before and after the monochromator are generally not correlated. Because the spectral fluctuations of the FEL pulses result in an unknown transfer function through the monochromator. To circumvent this problem, the end station PG2 [80] is equipped with a fine gold mesh with a pitch of 0.31 mm [77]. It can be inserted into the FEL beam. A fraction (35 %) of the VUV photons are scattered off into a multichannel plate detector (MCP), where the generated photo-current is proportional to the FEL intensity $I_{FEL}$ [81].

### 2.3.4 Data storage and analysis

As already mentioned, each FEL pulse (event) at FLASH is described by its own beam diagnostic data. Furthermore, data measured by the experiment needs to be aligned to these diagnostic data. This task is solved at FLASH by their own data acquisition system (DAQ) [82] which can handle and consolidate the generated
data\textsuperscript{13}. Our measurements produced terabytes of raw data. These raw files were downloaded to a local computer in Zurich. These files could be accessed by a C++ code provided by FLASH. The code extracts the relevant data, performs average calculations, and saves the processed raw data to a binary file of only a few tens of megabytes in size which can be conveniently loaded and analyzed in MATLAB\textsuperscript{TM}.

\section*{2.4 FEL experiments}

All our FEL based experiments were performed at the PG2 beam line \cite{80, 83} at FLASH. The FEL and infrared radiation impinged under 45° to the surface normal along the tungsten’s $[11\overline{2}]$ direction onto the sample. The FEL beam size on the sample was $A_0 = 130 \times 150 \ \mu m^2$, and the pulse length was $\approx 50$ fs FWHM, as estimated from the FEL beam’s spectrum and the transmission properties of the beamline. The magnetic orientation of the iron films was switched in a quasi-random sequence\textsuperscript{14} with a $12 \mu s$ FWHM long field pulse, 300 $\mu s$ before the FEL macro-bunch.

Figure 2.7 shows the layout of the FEL photoemission experiments. The FEL probe beam produces photo electrons which are analyzed in the Mott detector. The absorption of FEL photons generates holes. These are filled at first by Auger processes. Plasmon excitations followed by electron-electron scattering events, eventually generate a secondary electron cascade \cite{84}. The formation of the cascade is depicted in the inset of Figure 2.7. Moreover, the cascade is superimposed by directly emitted photo electrons ($n'l'$) originating from the electronic levels $nl$, as indicated in the inset, here $n = 3, 4$ and $l = s, p, d$. Their kinetic energy is $E_{n'l'} = E_{nl} + \hbar \omega - E_{\text{vac}}$, where $\hbar \omega$ is the photon energy, and $E_{\text{vac}} = 5.1$ eV \cite[p. 40]{70} the work function of the iron (110) surface. By the use of an energy analyzer (energy filter) one can choose electrons with a certain energy for further analysis in the Mott detector. Cascade electrons are easy to detect, since they are emitted in large numbers. It would be desirable to compare their demagnetization behavior with those of the valance band ($4s'/p', 3d'$).

To start, we need to examine whether the intense FEL pulses themselves could alter the magnetization of the iron film. Then, in the second part of this section, the time resolved experiments are presented.

\subsection*{2.4.1 FEL intensity resolved measurements}

Due to the conservation of angular momentum in electronic transitions, we expect the spin polarization of an ensemble of electrons released by an ultrashort

\textsuperscript{13}See also http://tesla.desy.de/doocs/doocs.html.

\textsuperscript{14}The quasi-random sequence had a period of 1024 steps and was implemented on FPGA board (also reading out the digitizer from the Mott detector). This implies that after 102.4 s of measurement time, the same magnetic sequence starts again.
2.4. FEL experiments

Figure 2.7: Schematic view of the FEL experiments. The inset shows the energy diagram of bulk iron and in red the expected photo emitted electron intensity $I$. The Fermi energy is denoted as $E_F$. First, an intense IR pump pulse perturbs the magnetization of the iron film, then time delayed, the FEL probe beam produces photo electrons who’s polarization is analyzed in the Mott detector. The voltage of the fist lens element is $V_0$. 

<table>
<thead>
<tr>
<th>Electron Cascade</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe: 4s/p, 3d'</td>
<td>-10</td>
</tr>
<tr>
<td>Fe: 4s'/p', 3d'</td>
<td>-10</td>
</tr>
<tr>
<td>W(110)</td>
<td>50 kV</td>
</tr>
<tr>
<td>Au foil</td>
<td></td>
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FEL pulse neither to depend on the number of electrons within the ensemble, nor on the FEL pulse intensity. However, the experiment shows surprisingly exactly the opposite: from a certain FEL intensity onwards, the measured spin polarization is reduced. The effect is going to be identified as a space charge effect. In addition, a space charge simulation (see section 2.4.1) was performed and provides quantitative agreement with the observations.

The photo emission setup consisted of the 20° deflector in conjunction with the Mott detector, as shown in Figure 2.1 (a) and (b). The FEL photon energy was tuned to 182 eV. The sample (15 ML thick iron film) was on ground potential and the first lens element on \(V_0 = 890\) V in order to attract most of the photo emitted electrons. For the determination of the spin polarization \(P\) the detector pair for \(P_y = P\) is used where \(P_y\) is given by equation 2.3.

The FEL macro-bunches were each filled with 30 FEL pulses, separated by 10 µs.

**Attenuating the FEL**

The intensity of the FEL pulses can be deliberately attenuated by making use of a krypton gas attenuator, varying the width of the exit slit in the beam line, and by a 200 nm thick aluminum absorber before the monochromator. The gas attenuator, pressurized with \(5 \cdot 10^{-3}\) mbar Kr, changes the FEL pulse intensity by approximately a factor of two. Opening the exit slit width from 10 µm to 100 µm only changed the FEL pulse intensity on the sample by about 30%. With the aluminum filter, however, the intensity could be changed by two order of magnitudes. Due this big effect, the aluminum filter is used to change between the low and high intensity regime (< 5 µJ/cm², or > 5 µJ/cm²) depicted in Figure 2.8 (a).

**Results and discussion**

Figure 2.8 (a) shows the measured change of the spin polarization as a function of the FEL pulse intensity \(I_{FEL}\). Above \(I_{FEL} > 10\) µJ/cm² the measured spin polarization starts to decrease. It is reduced to 40% of its initial value at a FEL intensity of 300 µJ/cm². For two reasons this reduction is surprising: First, angular momentum conservation dictates that a cloud of photo electrons can not alter its total spin polarization. And second, the FEL intensity is, compared to infrared induced demagnetization experiments [86], 1-2 orders of magnitude too small to induce a sizable demagnetization. This renders the assumption of a FEL induced demagnetization very unlikely. Resonant x-ray holography on Co/Pd multilayers [87] showed that the magnetization is not altered up to an FEL intensity of 25 mJ/cm².
2.4. FEL EXPERIMENTS

Figure 2.8: Space charge effects: (a) The measured polarization is reduced for higher FEL flux (data). The simulation (black line) explains this reduction as a space charge effect. (b) The relative yield $\frac{Y(I_{\text{FEL}})}{I_{\text{FEL}}}$ (data) is described nicely by a power law fit, indicating a space charge effect. The asymptotic behavior is well reproduced by the simulation. Note, as the transmission through the electro-optical lens system is unknown, the relative yield of the simulation has been scaled to match the asymptotic behavior of the measurements for best comparability. (c), (d) Measured polarization and electron yield as a function of kinetic energy. The arrow and the blue area indicate the electrons being lost for increasing FEL flux by space charge. Graph adopted from Ref. [85].
For the experimental analysis, the FEL intensity normalized electron yield, defined as
\[ \hat{Y} := \frac{Y(I_{\text{FEL}})}{I_{\text{FEL}}} \] (2.6)
can provide deeper insights. Here, \( Y(I_{\text{FEL}}) \) is the sum over the signals from all the four electron detectors within the Mott for both magnetization directions. This quantity gives us a hint of what could be the reason for this apparent demagnetization effect (see Figure 2.8 (b)). The photoemission yield \( Y \) is generally highly linear on laser intensity. At very high intensities though, it has been observed by Ferrini et al. [88] that the photoemission yield can grow in a superlinear manner. Therefore, we would expect \( \hat{Y} \) being constant, or at least increasing on FEL intensity – but certainly not decreasing. However, our experiment shows that \( \hat{Y} \) decreases, in good agreement with a power law, \( \hat{Y} \propto I_{\text{FEL}}^{-0.6} \) (see Figure 2.8 (b)).
The observed electron loss might be caused by a space charge effect. When enough electrons are emitted at once, the Coulomb interaction can push them apart such that not all of them can reach the detector anymore. And possibly, space charge might also explain the observed polarization reduction. To quantify this idea, we performed a space charge simulation.

**Space charge simulation**
A space charge simulation\textsuperscript{15} was performed to analyze the conjecture that the reduction of the polarization and intensity normalized yield can be caused by space charge effects. This was done by employing the particle tracking code Astra\textsuperscript{16}.
The simulation bases on two secondary electron distributions\textsuperscript{17}: The initial spin polarization \( P(E) \) and the electron yield \( Y(E) \) in dependence of the kinetic energy \( E \) of the emitted electrons, see Figure 2.8 (c) and (d). These distributions were measured on a 15 ML iron film on W(110), excited by a continuous electron beam of 4 keV kinetic energy. Energy analysis was provided with the hemispherical energy analyzer Phoibos 150.
Let us briefly discuss the possible influence of the excitation mechanism on the secondary electron cascade, whether it is by a continuous beam of high energetic electrons, or by short-, VUV laser pulses; both excitations have energies far above the plasmon frequency. Hence, we can expect that the same processes, either Auger decays, or plasmon excitations dominate the initial stage of the formation of the cascade as pointed out by Yu et al. [84]. Both processes occur on a time scale shorter than one femtosecond and are thus much faster than the length of the FEL pulse (\( \approx 50 \text{fs} \)). Therefore, the FEL pulses look like a “continuous” excitation to the

\textsuperscript{15}Greatly indebted to G. Salvatella for coding the simulations.
\textsuperscript{16}http://tesla.desy.de/~lfroehli/astra/
\textsuperscript{17}Many thanks to Christoph Wetli for performing these experiments.
electron gas. And the resulting electron cascade should look similar whether it was generated by a continuous electron beam or an ultrashort VUV pulse.

Particle tracking is computationally a heavy task. Therefore, Astra can not track each emitted electron. We tracked a constant number of $10^5$ particles to get the simulation result within less than half a day of computation time on a regular desktop computer. The simulation tracks particles, randomly drawn at an energy $E$ from the measured distributions $P(E)$ and $Y(E)$. The particles are simulated to be released spatially as a gaussian distribution of $\sigma_{x,y} = 50 \mu m$ and temporally as an exponential decreasing function with a decay constant of 100 fs. The acceleration of the particles by the voltage of the first lens element is taken into account.

The varying total charge $Q$ released per FEL pulse is modeled by attributing to each particle the charge $Q/10^5$. It is assumed that the total charge emitted scales linearly with the FEL intensity $Q \propto I_{FEL}$. The proportionality constant is the only free parameter in the simulation and has been determined by fitting the simulation result to the measured data.

The simulation traced each particle which can reach the entrance of the first electrostatic lens element. Then, the simulation provides two new distributions, the polarization $\tilde{P}(E, I_{FEL})$ and the yield $\tilde{Y}(E, I_{FEL})$ at the first lens element, in dependence of the FEL intensity. From these distributions, the average spin polarization to be measured in the Mott detector is calculated as the weighted average

$$\hat{P}(I_{FEL}) = \int_0^{E_b} \tilde{P}(E, I_{FEL}) \frac{\tilde{Y}(E, I_{FEL})}{\tilde{Y}_0} dE,$$

where the integration bound $E_b = 30 eV$ is given by the measurement interval and $\tilde{Y}_0 = \int_0^{E_b} \tilde{Y}(E, I_{FEL}) dE$.

The simulated relative change of $\hat{P}(I_{FEL})$ is overlaid as black line in Figure 2.8 (a) and fits the measured decrease of the polarization well.

The simulation elucidates that the physical cause of the observed spin polarization reduction can be explained by the loss of the low energetic ($< 2.5 eV$), but highly spin polarized electrons – compare Figure 2.8 (c) and (d) – where the blue area and the arrow indicate the loss of particles for an increasing FEL flux. At the beginning of the photoemission process, the fast electrons leave the sample first, followed by the slower, less energetic ones. Above the threshold FEL intensity of $10 \mu J/cm^2$, the space charge generated by the fast electrons is getting large enough to push the slower electrons back to the sample. Thus, they can not reach the detector anymore and account for the reduced spin polarization.

The simulated intensity normalized yield $\hat{Y}$ is plotted as the black line in Figure 2.8 (b) and exhibits a nearly identical asymptotic behavior as the fit to the data for
high FEL pulse intensities. Please note: as the transmission through the electro-optical lens system is not known, the simulated $\hat{Y}$ has been scaled to match with the asymptotic behavior of the measurements. However, there is a considerable difference for values below $10^2 \mu J/cm^2$ where the simulated $\hat{Y}$ is constant.

The reason for this deviation might be given by the fact that the simulation tracks only the electrons reaching the first lens element, 40 mm away from the sample. From the first lens element to the Mott detector, there is still about 1 m of lens system not taken into account by the simulation. The electron cloud is still expanding transversally, as the gathered transversal momentum from space charge repulsion is conserved. Therefore, even more electrons are lost during their flight through the lens system towards the Mott detector which would change the constant behavior also into a decreasing function.

In summary, we can conclude that the observed reduction of the polarization, in the FEL intensity resolved measurement, can be explained by space charge effects alone and not by a FEL induced demagnetization. This finding helps to design novel spin resolved photoemission experiments with FEL sources.
2.4.2 Time resolved reflectivity experiments

To start the time resolved measurements, we performed an experiment to check the time synchronization between the infrared pump laser and the FEL. It allowed us to distinguish, for the time resolved demagnetization experiments, whether the measured demagnetization time is dominated by an inherent demagnetization process, or by the time resolution of the experiment.

We employed a technique called “x-ray correlation” introduced by C. Gahl et al. [89]. During this experiment the infrared laser and the FEL swapped their role. The FEL was used to induce (pump) a reflectivity change in silicon nitride, and the IR pulse was used to measure (probe) the induced reflectivity change, see Figure 2.9 (a). The reflected IR signal was picked up by a fast photodiode and the electric signal was sampled by a fast analog digital converter\textsuperscript{18}. The FEL ran at 182 eV photon energy, with a repetition rate of 100 kHz, providing 30 pulses per macro-bunch. The monochromator was used in 0\textsuperscript{th} order to deliver FEL pulses with a large enough intensity ($\sim 10 \mu J/pulse$) to induce the reflectivity change. The probing IR laser provided bursts of 200 kHz repetition rate, each containing 60 pulses. Hence, we measured 30 pulses which were pumped and probed ($R(\Delta t)$) and 30 which were only probed ($R_0(\Delta t)$), used as a reference. The time induced reflectivity is calculated as

$$\frac{\Delta R}{R} = \frac{R(\Delta t)}{R_0(\Delta t)} - 1.$$  \hspace{1cm} (2.8)

Figure 2.9 (b) shows the normalized reflectivity change for two different scans. The red curve depicts the reflectivity change for a short measurement (delay stage velocity 0.1 ps/s, 1 min total measurement time) where each delay data point was measured only once. We observe a fast reflectivity change. The signal decays in about 100 fs. The blue curve, however, shows the same experiment for a longer integration time of 30 min, where the delay stage scanned each delay value 40 times. In contrast to the fast measurement, the signal is now smeared out by about 600 fs. The reason for picking up so much time jitter was a dysfunctional beam arrival monitor software which did not save synchronized arrival times. Therefore – unfortunately – the pulse-to-pulse time jitter could not be corrected during our first beam time.

2.4.3 Time- and spin-resolved experiments

We performed two type of time- and spin resolved measurements at FLASH: The first experiment made use of the the 20° deflector (see Figure 2.1 (b)). In this configuration, we had a broad energy acceptance of $E < 100\text{eV}$, collecting most of the

\textsuperscript{18}Acqiris converter running at 1 GHz sampling rate.
secondary electrons. However, as mentioned above, the time resolution was impaired by a broken beam arrival monitor.

In a second experiment series, we used an energy analyzer to try to access the time dependent demagnetization of valance band and the cascade electrons independently. The intensity of the FEL probe beam was for both experiments in the range of $5 \cdot 500 \mu J/cm^2$, indicated by the red arrow in Figure 2.8 and given by the inherent intensity fluctuations of the FEL.

We know from the intensity resolved measurements that this FEL flux interval results in space charge effects. Still, we do not expect the time resolved measurement to be altered by space charge. More than $10^4$ FEL pulses contribute to a single time resolved data point which effectively averages out any space charge contribution.

A prerequisite for a time dependent measurement on the cascade electrons is that the cascade needs to form much quicker than the demagnetization signal. Otherwise, the measurement would be smeared out by the lifetime of the cascade. It is known from theory and experiments [90] that the lifetime of an electron state in iron above the work function is in the sub-femtosecond regime. Thus, the cascade is expected to form very quickly $< 10 fs$ and the time resolution should not be impaired by the cascade decay time.

In the following, the two experiments series are discussed independently:

**Broad energy acceptance**  This experiment was performed in the same beam time as the reflectivity measurements, compare section 2.4.2. Thus, the FEL’s pulse-to-pulse time jitter could not be removed due to the malfunctioning BAM. Still, the slow timing drifts could be corrected with the streak camera.

The FEL provided 30 pulses per macro-bunch with a pulse repetition rate of 100 kHz.
The IR laser ran also at 100 kHz, but time delayed, such that the first 15 pulses were only probed (serving as a reference) and the last 15 pulses of the FEL macro-bunch were pumped and probed. For the time resolved spin analysis only data points are used where the pump and the probe were simultaneously on and \( P(t) = P_y(t) \). The sample (15 ML thick Fe films on W(110)) was grounded and the first lens element was on \( V_0 = 890 \text{ V} \). The delay stage was continuously scanning with a velocity of 0.2 ps/s.

Figure 2.10 (a) shows the time resolved quenching of the polarization upon heating with the IR pulse of 13 mJ/cm\(^2\) intensity. The relative polarization change is calculated as

\[
\frac{\Delta P(t)}{P_0} = \frac{P(t)}{P_0} - 1,
\]

here \( P_0 \) is the average polarization before time zero.

The demagnetization curve was fitted by applying the standard double exponential fit function convoluted with a gaussian \( G(t, \sigma) \) as:

\[
\frac{\Delta P}{P} = A(1 - e^{-t/\tau})e^{-t/\rho} \Theta(t) \otimes G(t, \sigma).
\]

Here, \( \tau \) is the demagnetization time constant, \( \rho \) the remagnetization time constant, \( \Theta(t) \) the Heaviside step function, and \( \sigma = \text{FWHM}/(2\sqrt{2\ln(2)}) \). The temporal broadening is estimated based on the reflectivity measurements to be FWHM = 0.6 ps. Applying this fit\(^{19}\) routine to the graph shown in Figure 2.10 (a) resulted in \( \tau = 620 \pm 10 \text{ fs} \), \( \rho = 43 \pm 0.5 \text{ ps} \), and \( A = -25.5 \pm 0.1 \% \). The demagnetization-time constant \( \tau \) describes the time it takes to reduce the magnetization to 1/e of its minimal value. Note that this demagnetization time is only an upper bound for the effective demagnetization time due to the above described problems with the beam arrival monitor. The recovery time constant \( \rho \) describes similarly the time it takes to recover to 1/e of the unperturbed magnetization.

We need to discuss, if the pump pulse can alter the electron yield. In two photon-photon emission experiments, the maximum of the electron yield is a measure for the precise temporal overlap \([91]\) of the pump and the probe beam. In our case, however, where the IR pulses alone produces a negligible amount of secondary electrons, such an effect would indicate a strong non-linearity in the photoemission process caused by the hot electron gas. Such an effect, together with space charge, might alter the measurement of the time resolved spin polarization since the cascade formation would be different at temporal overlap. Figure 2.10 (b)

\(^{19}\)The fitting routine used the robust, non linear, least absolute residual method, and as weights the amount of data per time bin.
shows the measured time dependent relative electron yield

\[ \frac{\Delta Y(t)}{Y(t)} = \frac{Y(t)}{Y_0(t)} - 1, \]

where \( Y_0(t) \) is the yield generated by only probe pulses, and \( Y(t) \) is the electron yield for pump and probe pulses. Here, the electron yield is again defined as the sum of the four Mott channels for both magnetization directions. We observe that the yield does not change around time zero. This implies that the cascade formation and therewith the spin polarization is not impaired by the pump pulses. The step observed at about 7 ps and the slight variation of the relative yield are a cause of the varying amount of data per time bin as indicated by the diameter of the data points.

**Energy analyzer** We were granted a second beam time at FLASH to perform time- and spin resolved experiments with an electron energy analyzer. The intention was to use an electron spectrometer to select the directly emitted electrons from the valance band (see Figure 2.7) and measure their demagnetization behavior. The FEL photon energy was lowered from 182 eV to 40 eV in this experiment, as the photo absorption cross section for these lower energetic photons in the valence band is enhanced by a factor of 4.5 [92]. This should result in a higher electron yield and a reduced integration time. Furthermore, a lower photon energy produces a weaker cascade reducing space charge effects.

Let us estimate how much integration time we need to measure the directly emitted electrons at 182 eV. The demagnetization curve presented in Figure 2.10 (a) was measured with the cascade electrons with a good signal to noise ratio. The acquisition took three hours. We would like to reach the same statistics also with electrons originating from the valance band. The electron yield of these electrons is about a factor of 100 lower than the directly emitted electrons. It is obvious that an integration time of 300 hours is unfeasible. To increase the signal, we increased the repetition rate of the FEL to 300 pulses per macro-bunch. Every second FEL pulse was pumped by the IR laser. This change enhanced the counting rate by a factor of 10. Resulting in a potential integration time of about 30 hours. This number seems feasible, as the signal to noise ratio scales with the square root of the amount of data collected. Hence, even collecting data during only one FEL shift of 8 hours, the signal to noise ratio would be affected only by a factor of two.

Despite this estimation, we were unable to perform the time- and spin resolved experiment on the directly emitted electrons from the valance band. It was very difficult to find the temporal overlap with the small yield of valance band electrons. Furthermore, the transmission through the energy analyzer was lower than
Figure 2.11: Ultrafast demagnetization observed with the cascade electrons. The diameter of the points is proportional to the amount of data per time bin. (a) Ultrafast polarization signal with the IR pump pulse on ($P_{IR\&FEL}$) and the reference signal ($P_{FEL}$) measured without pump pulses. The data was averaged in 200 fs broad time bins but not filtered. The ultrafast response of the polarization is clearly visible at time zero. (b) Relative change of the polarization. The same data as in (a) is binned to 25 fs intervals and filtered by a Savitzky-Golay filter of degree 3 and window size 11. The dashed lines represent the one $\sigma$ error bars of the fit (see text). Image adopted and reprinted with permission from [93]. Copyright 2014, American Institute of Physics.
expected. We ended up with a maximum counting rate of 3 electrons per FEL pulse and detector channel at about 300 $\mu l/cm^2$ FEL flux. In the previously described experiment in section 2.4.3, we had at maximum one thousand electrons per FEL pulse and detector at the same flux. Therefore, the statistics were too low to perform the experiment with the valance band electrons in conjunction with a Mott detector.

However, we were able to measure with these settings the ultrafast demagnetization of the cascade electrons, but this time with the help of a working beam arrival monitor. The energy analyzer was tuned to a kinetic energy of 100 eV\textsuperscript{20} and the sample was biased with -98 V. This gave an energy acceptance of $\Delta E = \pm 2.4$ eV at the peak of the cascade. The examined Fe on W(110) film was 8 ML thick. The IR pump fluence was set to 12 mJ/cm\textsuperscript{2}. Figure 2.11 (a) shows the time resolved polarization data binned in 200 fs intervals. The step-like demagnetization is easily recognizable as the deviation of $P$ from the $P_0$ curve. Here, $P$ is the polarization with the pump pulse on and $P_0$ is the polarization without the pump laser. Figure 2.11 (b) shows the relative demagnetization change only around the magnetization drop calculated as

$$\frac{\Delta P}{P} = \frac{P(t)}{P_0(t)} - 1.$$  (2.12)

The same raw data as shown in Figure 2.11 (a) was binned here in 25 fs intervals and smoothed with a Savitzky-Golay filter of degree 3 and window size 11. The filter was chosen as an increase in bin size automatically broadens the time resolved peak, in the worst case to twice the bin size. The Savitzky-Golay filter\textsuperscript{94} circumvents this problem. It passes higher frequency components maintaining the position and shape of the filtered curve in a much better extent than by simply increasing the bin size. The fit\textsuperscript{21} was performed on the raw data with equation 2.10. The broadening through the pump and probe pulse length was captured by calculating the FWHM for $G(t)$ by geometrically adding the pulse length of the pump- and the probe beam, reading FWHM = $\sqrt{120 \text{fs}^2 + 50 \text{fs}^2} \approx 130$ fs. The fit gave a demagnetization constant of $\tau = 45 \pm 50$ fs, a recovery time constant of $\rho = 5 \pm 3$ ps, and an amplitude of $A = -22 \pm 3\%$. Note that the oscillations observed in the demagnetization curve (Figure 2.11 (b)) are caused by noise spikes in the measured signal. To conclude this section, the measured demagnetization time shows that an iron thin film can indeed be quenched on a time constant of less than 100 fs.

\textsuperscript{20}The pass energy was set to 200 eV and the lens mode to ”Medium area 3.5 keV”.

\textsuperscript{21}The fitting routine used the robust, non linear, least absolute residual method, and as weights the amount of data per time bin.
Concluding discussion  The photo electrons generated by FEL pulses of 40 eV can excite electrons from everywhere within the whole valence band (∼10 eV). Therefore, they allow the measurement of a magnetic average over the total valence band. With this method, we observed an ultrafast reduction of the spin polarization of the cascade electrons and concluded that the magnetization of the whole valence band can be reduced on 100 fs timescale. This observation renders a demagnetization process unlikely where spin angular momentum is “hidden” deeper in the band structure [46] where it would not be accessible by other optical methods. In addition, the measured demagnetization timescale is fully compatible with magneto optical measurements performed by Carpene et al. [86].

The measurement of the directly emitted valence band electrons is a very demanding experiment which could not be achieved with our setup due to the limited electron yield. Measuring the spin polarization of the cascade electrons, however, has the advantage over the directly emitted electrons that the cascade provides an inherent electron gain during its formation. In addition, the spin polarization of the cascade electrons is also enhanced due to the spin filter effect but still reflects the magnetization of a sample.

It is important to discuss whether the IR pump pulse can impair the spin filter effect which would directly affect the measured ultrafast spin polarization drop. Based on particle conservation, for each absorbed photon an electron will be excited leaving behind an empty state. The total number of empty states – responsible for the spin-filter effect – is not changed, but they appear at a different binding energy. Therefore, the cascade forming process is most likely not altered by the pump pulse. In addition, the secondary electron cascade shows the highest spin polarization for the first 10 eV [96]. These electrons have surpassed the work function barrier of 5.1 eV for Fe(110) [98, p.40] and have thus a kinetic energy of 5-15 eV within the iron film. This energy scale is much larger than the maximal width of the pump induced electron redistribution of ±1.55 eV around the Fermi level. Providing further evidence that the formation of the secondary electron cascade is not impaired by the action of the pump laser. This argumentation is consistent with the observation that no correlation of the electron yield with the pump-probe delay time has been observed (Figure 2.10 (b)).

We have seen in this chapter that space charge effects are present and can influence the measured spin polarization. Nevertheless, the time resolved measurements are not affected as space charge effects can be averaged out efficiently, as noted earlier at least 10⁴ FEL pulses contribute to one time bin.

²²As discussed in Refs. [95, 96], the spin filter effect is caused by the imbalance of available empty states for the majority and minority electrons (predominantly d-states). Thus, a lower density of final states will result in a smaller scattering probability, as can be readily seen from Fermi’s Golden Rule. Hence, the majority electrons have a longer lifetime [90] which results in a higher escape probability [97].
2. TIME AND SPIN RESOLVED PHOTOEMISSION
IMAGING SPIN FILTER DETECTOR

The low figure of merit of Mott spin-polarimeters makes it very demanding to measure the time resolved polarization of directly photo emitted electrons from the valence band. This obstacle can only be overcome by a more efficient spin-polarimeter, in our case an imaging SPLEED detector. In this chapter, the working principle, and the performance of such a detector are studied and compared to the Mott detector. In addition, a special delay line detector with extended multi hit capability has been successfully employed for photoemission experiment at the free electron laser in Hamburg. Both, the static spin asymmetry of the cascade, and the valence band, could be measured by ultrashort VUV pulses.

Parts of this chapter have been published in Ultramicroscopy 130, 63 (2013).
We have seen in the previous chapter that the figure of merit (FoM = $S^2 I / I_0$) of the Mott detector together with space charge effects hindered us from measuring the time dependent demagnetization of the valence band. In principle, one could increase the repetition rate of the experiment to acquire more electrons per time. Practically, however, such a measure does not work because a higher repetition rate in a pump-probe experiment inevitably leads to excessive dc heating of the sample.

Only one step can be taken: to make use of a spin detector with a higher detection efficiency, in particular, increasing the Sherman function affects the FoM and herewith the measurement time quadratically.

Despite the Mott detector, other detection schemes have been developed for spin analysis, such as exchange scattering on magnetic thin films or spin polarized low energetic (<100 eV) electron diffraction (SPLEED). The former method has a relatively high FoM of $10^{-3}$, see Ref. [99] and references therein. Nevertheless, the preparation of the analyzer magnetic thin film is an experiment in the experiment, making this technique unsuitable for measurements at a source like FLASH. Therefore, we have chosen the SPLEED type detector as no deposition of thin films is involved. SPLEED detectors making use of the (2,0) reflex on a W(100) surface have been successfully employed and are described in literature [100, 101]. Instead of the widely employed tungsten, we will make use of an iridium analyzer crystal. Iridium has the advantage over tungsten to maintain longer a clean surface. In our experiments, working hours of up to 10h at $2 \cdot 10^{-10}$ mbar without crystal preparation could be achieved. Furthermore, theoretical calculations predict iridium to have a high figure of merit [102].

### 3.1 The Physics of a SPLEED Detector

In the used SPLEED detector design, low energy electrons (<100eV) are scattered on an iridium (100) crystal surface, and the specular reflected beam is analyzed [102]. This configuration is special since the scattering angle is independent of the kinetic energy of the electrons. Spin dependent scattering effects on non magnetic materials are caused by the spin orbit (LS) coupling. In a central potential $\Phi(r)$ the LS coupling potential reads:

$$V_{SO} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{d\Phi}{dr} \vec{S} \vec{L},$$

(3.1)

where, $m$ is the electron mass, $c$ the speed of light, and $\vec{S}$ and $\vec{L}$ are the spin- and momentum operators, respectively. We see that $V_{SO}$ depends on the relative direction of the spin- and the angular momentum which enables the spin selective scattering intensity $I_{\uparrow, \downarrow}$ in a SPLEED detector. Because in a Coulomb field
The spin orbit potential scales like $V_{SO} \propto Z$, the effect is the most pronounced for high-Z materials like iridium or tungsten. The above explanation considers only scattering from a single atom. In this view, we are in the limits of the first Born approximation. However, in a realistic metallic crystal electrons form Bloch states and multiple scattering needs to be considered [103, p. 24]. It is hence expected that when the incident electrons do not match an empty crystal state (in energy, direction, and angular momentum), their reflectivity will be higher, as pointed out by Kirschner [103, p. 31]. This effect implies that typically highest reflectivity does not match highest spin selectivity, and that scattering intensity and spin selectivity crucially depend on the relative orientation between the iridium crystal, the spin polarization, and the incident direction of the electrons. We will observe these effects in the performed experiments.

The low energetic electrons (< 100 eV) penetrate the crystal only a few monolayers [104] wherefore the crystal's surface has a large effect on the spin analysis capability. Furthermore, clean iridium produces a 5x1 reconstruction at the (100) surface [105] which is expected to modify the spin analysis compared to the unreconstructed surface [102]. Collaborators performed SPLEED calculations for the iridium unreconstructed (100) surface, see Fig. 2 in Ref. [102]. Two working points could be identified: One at about 9 eV and a second, broader one, at 40 eV kinetic energy. We investigated mainly the 9 eV working point due to its larger FoM [102].

The spin selective scattering process can be described by a Sherman function when the spin polarization $P(E, \alpha)$ of the incident electrons is known:

$$S(E, \Theta, \varphi) = \frac{1}{P(E, \alpha)} \frac{I_1(E, \Theta, \varphi) - I_1(E, \Theta, \varphi)}{I_1(E, \Theta, \varphi) + I_1(E, \Theta, \varphi)}.$$  

(3.2)

Here, $E$ is the kinetic energy of the electrons impinging on the Ir crystal, $\Theta$ is the polar-, $\varphi$ the azimuthal scattering angle, and $\alpha$ is the angle between the sample surface normal and the emission direction, see Figure 3.1. The scattered intensities $I_1(E, \Theta, \varphi)$ need to be measured for an up- (↑) or down (↓) magnetized sample. Therefore, it is necessary in a SPLEED experiment that the magnetization of the sample can be switched.

### 3.2 Imaging SPLEED Detector

The FoM of a single channel SPLEED detector can be boosted several orders of magnitude by using the specular beam of the scattered electrons as shown by Kolbe et al. [106]. The momentum conservation along the surface of the analyzer crystal makes it possible to use the analyzer crystal as an “electron mirror”. Placing this spin selective “mirror” at the exit of an electron energy analyzer [106] allows for simultaneous recording of the energy, the angle, and the spin of the electrons,
Figure 3.1: Schematic view of the imaging SPLEED detector along the energy selective plane. (Note: The scattering plane is for convenience rotated by $90^\circ$ in respect to the energy selective plane.) A stripe mask can be placed at the energy analyzer’s entrance to pattern the exit field image for testing the angular resolution of the detector. The polar scattering angle $\Theta$ is fixed at $45^\circ$ and the azimuthal angle $\varphi$ can be varied by a precision rotation feedthrough. $\varphi = 0^\circ$ is defined as a Ir $<100>$ direction pointing along the y-direction. Two detectors are installed: A delay-line detector on a shifter and a multichannel plate (MCP) intensified phosphorous screen with a CCD camera. **Image inset:** Shows the cascade edge for three different kinetic energies. An energy sweep is performed by varying the sample’s bias voltage. The picture’s design is according to figure 3 in Ref. [102].
3.2. Imaging SPLEED Detector

see Figure 3.1. It is this parallel detection scheme which scales up the FoM. In a spin- and angle resolved photoemission (SR-AREPS) experiment with a single channel energy analyzer, such as a Mott detector, there needs to be an aperture at the exit of the hemispherical energy analyzer defining the energy and angular window to be measured. All the other electrons which can not pass this window are lost. In contrary, the imaging SPLEED (in the following imaging SPLEED will be used synonymously to SPLEED) allows for the parallel detection of the full energy- and angle-space present at the exit of the hemispherical energy analyzer. Hence, the FoM of the 2 dimensional detector scales with the number of channels \( N \) which can be simultaneously measured, \( \text{FoM}_{2D} = N \cdot \text{FoM} \). The possible number of channels is determined by the energy and angular acceptance of the instrument and the energy smearing of the photoemission lines. A conservative estimation\(^1\) of a room temperature SR-APRES experiment gives \( N = 80 \times 20 = 1600 \) which is a FoM increase of more than three orders of magnitude over a single channel analyzer! Furthermore, the energy- and angular resolution can even be selected after the experiment. The recorded images can be binned to the desired energy- and angular resolution.

To test and optimize the imaging capability of the SPLEED, we used a slit aperture at the analyzer’s entrance, blocking certain emission angles and imprinting here-with a stripe pattern. This aperture has a pitch of 1 mm between the slits and is mounted directly at the entry of the energy analyzer, 40 mm in front of the sample. Typical ARPES images with the slit aperture are shown in the inset in Figure 3.1. The images have a field of view of \( \pm 3.5^\circ \) by \( \pm 2 \text{ eV} \).

3.2.1 The Setup

Chamber The preparation-, the measurement chamber, and the hemispherical energy analyzer (Phoibos 150) are used as shown in Figure 2.1 (c). The measurement chamber has been improved by a mu-metal lining installation. The Mott detector depicted in Figure 2.1 (c) is replaced by the mu-metal shielded SPLEED chamber\(^2\). The SPLEED is pumped by a titanium sublimation pump, a cooling trap, and turbo pump reaching \( 2 \cdot 10^{-10} \text{ mbar} \) during measurements. Oxygen for crystal preparation is provided by a 0.5 mm thick silver tube, diffusing oxygen from air into the vacuum chamber while heated.

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\(^1\) A 50 meV resolution in a 4 eV broad exit image has been assumed, yielding 80 energy channels. At least 20 different angles can be separated in the image (see inset in Figure 3.1). Giving \( N = 80 \times 20 \).

\(^2\) The chamber was designed and assembled by Prof. Schönense’s group in Mainz. In a fruitful collaboration with him and his group, the detector was commissioned and improved in our lab at the ETH in Zurich and at the PSI in Villigen. I would like to thank particularly Dima Kutnyakho, Pavel Lushchcyk, M. Kolbe, and Prof. G. Schönense for their big help and expertise.
**Electrostatic lens system**  Figure 3.2 shows a drawing of the lens system together with simulated electron trajectories for a typical lens mode where the electrons impinge mostly parallel onto the analyzer crystal. Lens groups are highlighted by the same color. The SPLEED process is very sensitive to the incidence direction of the electrons onto the analyzer crystal.

There is a 30 mm by 35 mm wide aperture (long opening along dispersive direction) at the entrance of the SPLEED detector to select the electrons with minimal angular deviation. However, the Phoibos’ exit field is 20 mm (angular direction) by 70 mm (dispersive direction) resulting in an effective aperture of 20 mm by 35 mm. Due to angular sensitivity, lens modes with a focus point on the crystal yielded generally much worse FoM’s over modes with parallel incidence. The electrons in the Phoibos fly only an arc of 175°. To perturb the trajectory of the electrons as little as possible, the first flange of the SPLEED chamber is tilted by 5° to capture the electrons at the exit field of the Phoibos as directly as possible.

The first lens group is a quadrupole deflector followed by a transfer lens system. The next section is the valve group, between “Valve-Lens 2” and “Valve-Lens 3” a plate valve is installed. It can be closed during analyzer crystal preparation. The smaller diameter of these lenses suppresses field deviations introduced by the valve. Experiments and simulations showed that the electron beam has to pass the valve group in a narrow beam to provide the best imaging quality. Therefore, “Channel 4&5” are generally on a high potential, typically at a voltage of about 1-2 kV. Before the electrons can reach the analyzer crystal, there is a further quadrupole deflector and a cone lens. We used predominantly the 9 eV working point of the iridium crystal which leaves the electrons most sensitive to field deviations around the crystal. It was an important step in getting good images and spin resolution to realize that the “Cone”, the crystal, and “Deflector 4” need to be at the same potential to form a homogeneous potential landscape around the crystal. The crystal itself can have a slightly different potential (a few 100 meV off) to find an optimal working point. Over time (in the order of hours), the working point moves slowly, caused by the small change of the work function due to adsorbates. This can be easily compensated by re-tuning the crystal potential.

After the electrons have scattered on the analyzing crystal, they are brought to the imaging system by the transfer lens group formed by “Lens 3-5”. The electrons are projected either on a delay line detector (see section 3.3.1), mounted on a linear possitioner, or on a multichannel plate intensified phosphorous screen recorded with CCD camera. The size of the image on the detector is adjusted by tuning the voltage on “Lens 5”.

An important factor to find good lens modes efficiently is the usage of digitally controlled deflector voltages. Each of the four deflector channels is connected to an in-house developed floating digital-to-analog converter allowing to reproducibly
save and restore deflection and stigmatic settings by a computer. Small angle deviations and good image- and spin resolution are reached by tuning the Phoibos to a path energy of 80 eV and a kinetic energy of 63 eV. This setting is used in all the SPLEED measurements giving a 9.3 eV wide energy window at the 35 mm broad exit aperture. Typically, only half of that energy window is projected onto the iridium crystal due to its limited size. Good working conditions could be found for all the angular-dispersion modes of the hemispherical analyzer. To perform an energy sweep, the voltages of the lens system and the Phoibos are kept constant, only the bias voltage \( V_{\text{bias}} \) of the sample is changed. This was necessary as a short to ground of a deflector plate in “Deflector 2” hindered us from sweeping the kinetic energy of the analyzer and accordingly the lens elements of the SPLEED. Note that changing \( V_{\text{bias}} \) also changes the angular acceptance. In the following discussion, the angular acceptance \( \Delta \alpha \) is always stated for \( V_{\text{bias}} = 0 \) V.

We used either the HeII line at 40.08 eV of a VUV helium source, or the secondary electron cascade generated from electron bombardment (4 keV kinetic energy) to emit electrons from a 15 ML Fe on W(110) film (see section 2.1.1 for sample preparation). The photons are sent onto the Fe film under 45° to the surface normal along the [11\( \sqrt{2} \)] direction of the tungsten crystal. The crystal is oriented as shown in Figure 2.2.

### 3.2.2 Analyzer Crystal Preparation

A clean analyzer crystal surface is needed due to its large influence on the SPLEED process as discussed above. The recipe for cleaning is mainly given by Musket et al. [105]. The crystal was heated 10 - 20 times, depending on the contamination level, to 1100 K in a \( \text{O}_2 \) atmosphere of \( 8 \cdot 10^{-8} \) mbar. Each cycle took about 1 min. The surface is cleaned from remaining oxygen, CO, and \( \text{CO}_2 \) by a short (20 s) high temperature flash to 1600 K at \( 3 \cdot 10^{-10} \) mbar. This procedure leads to a clean 5x1 reconstructed Ir(100) surface [105]. However, graphene layers can form on platinum metal surfaces such as Ir(100) [107, p. 209]. These graphene layers are chemically inert and can not be removed by the above cleaning procedure. They need to be removed by argon sputtering. Until realizing this issue, most of our experiments were done with graphene contamination. However, the graphene layer did neither change the imaging resolution nor introduce image distortions but affected the analyzing power by at least

\[ \Delta \alpha' = \arctan \left( \arctan \frac{\Delta \alpha}{2} + \frac{V_{\text{bias}} q}{E_{\text{kin}}} \right) \]  

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\(^3\) Special thanks to Sven Mähl from SPECS, providing the simulation files of the Phoibos and helping us to find the best lens modes.

\(^4\) The angular acceptance at any non zero bias voltage \( \Delta \alpha' \) is given by:

\[ \Delta \alpha' = \arctan \left( \arctan \frac{2 \Delta \alpha}{V_{\text{bias}} q / E_{\text{kin}}} \right) \]  

depending on \( V_{\text{bias}} \) for a given kinetic electron energy \( E_{\text{kin}} \).
FIGURE 3.2: SPLEED electro-optical lens system overlaid by traces of simulated electron trajectories for a typical lens mode. Simulation: The red, green, and blue lines represent electrons with 80 eV kinetic energy released at different positions at the input aperture. Each line bunch consists of 5 trajectories emitted at $-1^\circ$, $-0.5^\circ$, $0^\circ$, $0.5^\circ$, and $1^\circ$ measured versus the aperture plane normal. The black lines emerging after the iridium crystal are secondary electrons of 5 eV kinetic energy.
3.2. Imaging SPLEED Detector

3.2.3 Sherman Factor Determination

The Sherman factor of an imaging SPLEED type detector needs to be defined for each pixel on the detector as \( S_{i,j} \) \[106\]. The electron trajectories within the SPLEED do not change while sweeping \( V_{bias} \). Thus, one Sherman image for the cameras’ field of view provides sufficient information to calculate the polarization. Illuminating the analyzer crystal with a constant polarization \( P(E, \alpha) \approx P_0 \) within the analyzers acceptance window reduces equation 3.2 to

\[
S_{i,j} = \frac{1}{P_0} A_{i,j} = \frac{1}{P_0} \frac{I_{i,j}^\uparrow - I_{i,j}^\downarrow}{I_{i,j}^\uparrow + I_{i,j}^\downarrow},
\]

where for each pixel \((i,j)\), \( A_{i,j} \) is the asymmetry and \( I_{i,j}^\uparrow, I_{i,j}^\downarrow \) are the intensities for either an up- or down magnetized sample. Experimentally, a constant polarization distribution \( P(E, \alpha) \approx P_0 \) is found in a good approximation in the secondary electron emission from Fe on W(110) at about \( E_{kin} = 30 \) eV (compare Figure 2.8 (c)). Also its angular distribution at this energy is relatively flat as measurements by Kirschener et al. \[108\] have shown.

The so-acquired Sherman map \((S_{i,j})\) measured with a clean iridium surface reaches values as high as 0.8 (see Figure 3.3 (a)). Demonstrating that the SPLEED has a very high spin selectivity. The corresponding intensity distribution (a measure for the electron reflection effectivness on the Ir crystal) is shown in Figure 3.3 (b). We observe that high intensity typically anticorrelates with a large Sherman function, as it is expected from the discussion in section 3.1.

3.2.4 Image Processing

The electron intensity image at the exit plane of the SPLEED has a limited field of view along the dispersive direction of a few electron volts (see inset in Figure 3.1). Generally, one is interested in the measurement of spectra exceeding the energy width of the field of view of the detector. For that reason, a set of overlapping images is taken at different kinetic energies covering the energy spread of the spectrum. The pixel values of the recorded images corresponding to the same energy and angular value are collected to form a new image covering the measured spectral width. This new image is called “panorama”. Figure 3.4 depicts the procedure. Three panoramas can be constructed; two containing the electron intensity distribution for either an up- or down magnetized sample, and a third one holding the corresponding spin polarization. Each of these panoramas have a second “page”, attributed to the error of each value. In the following, the filling of the panoramas
3. IMAGING SPIN FILTER DETECTOR

Figure 3.3: (a) Sherman map and (b) normalized sum of the intensities $I_{i,j}^\uparrow + I_{i,j}^\downarrow$. The line pattern is caused by the stripe mask in front of the analyzer. The images were recorded at $E_{\text{kin}} = 30\,\text{eV}$ in “WideAngleMode” and $P_0 = 12\%$.

Figure 3.4: Image processing: The panoramas of the intensities and the polarization are constructed by summing the measured intensity- and polarization distribution to the panoramas. The error panoramas are depicted in the background. The algorithm is suitable to construct the panoramas on the fly during the measurement. For the sake of clarity no pixel grid on the detector images is shown.
3.2. IMAGING SPLEED DETECTOR

is sketched:

**Step 1:** The process starts with a set of pixel images of the electron intensity distribution $I_{E_{kin};i,j}^{↑,↓}$ recorded at the exit field of the SPLEED detector. The pictures are acquired for up ($\uparrow$) and down ($\downarrow$) magnetization. The spectrum is covered by taking overlapping images at various center energies $E_{kin}$. The intensity error for each pixel is estimated based on counting statistics as

$$I_{err;E_{kin};i,j}^{↑,↓} := \sqrt{I_{E_{kin};i,j}^{↑,↓}}.$$  \hspace{1cm} (3.5)

The polarization of each pixel is calculated based on equation 3.4 with known Sherman coefficients $S_{i,j}$ as:

$$P_{E_{kin};i,j} = \frac{1}{S_{i,j}} \frac{I_{E_{kin};i,j}^{↑} - I_{E_{kin};i,j}^{↓}}{I_{E_{kin};i,j}^{↑} + I_{E_{kin};i,j}^{↓}}.$$  \hspace{1cm} (3.6)

The error $P_{err;E_{kin};i,j}$ is calculated through regular error propagation of equation 3.6. Regions with sufficient counting statistics are selected by a boolean window function $W_{i,j} = \{0, 1\}$.

**Step 2:** This set of intensity- and polarization images is added to panoramas. The energy- and angular pixel indexes in the panoramas are denoted $u$ and $v$, respectively. Each pixel has an energy and angular spread of $\Delta E$ and $\Delta \alpha$. The intensity panoramas are denoted $\Upsilon_{E_{kin};i,j}^{↑,↓}$ and $\Upsilon_{E_{kin};i,j}^{↑,↓;err}$ for their construction, the summation goes over the set of images $I_{E_{kin};i,j}^{↑,↓}$ such that the energy $E_i$ and the angular value $\alpha_j$ fall in the selected pixel $\Upsilon_{E_{kin};i,j}^{↑,↓}$ as

$$\Upsilon_{E_{kin};i,j}^{↑,↓} = \sum_{E_{kin} : (E_u < E_i < E_u + \Delta E) \cap (\alpha_v < \alpha_j < \alpha_v + \Delta \alpha)} W_{i,j} I_{E_{kin};i,j}^{↑,↓}.$$  \hspace{1cm} (3.7)

Here, $E_u$ is the energy of a pixel with index $u$ and $\alpha_v$ is the angle of a pixel with index $v$. The corresponding error intensity panorama is constructed accordingly:

$$\Upsilon_{E_{kin};i,j}^{↑,↓;err} = \sqrt{\sum_{E_{kin} : (E_u < E_i < E_u + \Delta E) \cap (\alpha_v < \alpha_j < \alpha_v + \Delta \alpha)} (W_{i,j} I_{E_{kin};i,j}^{↑,↓;err})^2}.$$  \hspace{1cm} (3.8)

The construction of the intensity panoramas described by equations 3.7 and 3.8 is depicted by a + sign in Figure 3.4. Note that the panorama can have a different energy and angular resolution as the original picture set. Hence, care needs to be taken to circumvent aliasing effects.

The construction of the polarization panoramas $\Pi_{u,v}$ and $\Pi_{E_{kin};i,j}^{↑,↓;err}$ works along the
same idea. Still, the asymmetry term in equation 3.6 can introduce significant noise to the polarization value by near zero deviations. However, such artifacts can be efficiently suppressed by weighting each pixel $P_{i,j}$ quadratically with its error. Thus a pixel with large error will have a smaller weight than a pixel with a small error:

$$P_{E_{kin};i,j} \rightarrow P_{E_{kin};i,j} := \frac{P_{E_{kin};i,j}}{P_{err;E_{kin};i,j}} W_{i,j}. \quad (3.9)$$

The corresponding weights are defined as

$$a_{E_{kin};i,j} := \frac{1}{P_{2err;E_{kin};i,j}} W_{i,j}. \quad (3.10)$$

The values $p_{i,j}$ and $a_{i,j}$ are added to the polarization panoramas $\Pi_{u,v}$ and $\Pi_{err;u,v}$. The error panorama can be understood as tracking the sum of the weights

$$\Pi_{err;u,v} = \left( \sum_{E_{kin};(E_u<E_i<E_u+\Delta E)\cap(\alpha_v<\alpha_j<\alpha_v+\Delta \alpha)} a_{E_{kin};i,j} \right)^{-1}. \quad (3.11)$$

And, finally, the polarization is the sum of each weighted polarization value divided through the sum of the weights:

$$\Pi_{u,v} = \left( \sum_{E_{kin};(E_u<E_i<E_u+\Delta E)\cap(\alpha_v<\alpha_j<\alpha_v+\Delta \alpha)} P_{E_{kin};i,j} \right) \frac{1}{\Pi_{err;u,v}}. \quad (3.12)$$

The process described by equations 3.12 and 3.11 of weighting and adding data to polarization panoramas is depicted in Figure 3.4 with a $\oplus$ sign.

**Spectra** Angle integrated intensity- ($I_u$) and polarization ($P_u$) spectra (see Figure 3.5 (b)) can be obtained by summing the panoramas $\Upsilon_{u,v}$ and $\Pi_{u,v}$ over the angle index $v$:

$$I_u = \frac{1}{V} \sum_{v=1}^{V} \Upsilon_{u,v}, \text{ and} \quad \Pi_{u,v} \quad (3.13)$$

$$P_u = \frac{1}{V} \sum_{v=1}^{V} \Pi_{u,v}, \quad (3.14)$$

where $V$ is the angular pixel resolution.
3.2. IMAGING SPLEED DETECTOR

Figure 3.5: Angle integrated intensity- and polarization distribution of the occupied surface states in Fe(110): (a) Measured with a Mott detector. The number of counts is the sum over all four Mott counters for both polarization directions. (b) Measured with the SPLEED detector. The difference in the shape of the intensity distribution is caused by enhanced oxygen contamination as discussed in the text.

3.2.5 EFFICIENCY COMPARISON BETWEEN THE SPLEED AND THE MOTT DETECTOR

To show the improvement off the detection efficiency off the SPLEED detector over the Mott detector, the intensity- and polarization distribution of the photo emitted electrons from a 15 ML Fe film on W(110) are measured with both detectors. Photo electrons are produced by the HeII line from a VUV source. The integration time was set in both cases to 3 h and the same photon flux was used. Details of the experiments are described in appendix B. The main difference between the two measurements is the larger angular acceptance for the Mott measurement caused by the larger path energy. All the other parameters were kept alike. Still, the SPLEED detector outperforms the Mott detector; Figure 3.5 shows the angular integrated intensity- and polarization distribution for Fe(110) measured with the Mott detector (a) and in (b) with the SPLEED detector\(^5\). The energy resolution of

\(^5\)The peak at about -6 eV in Figure 3.5 (a) is caused by oxygen [109]. Oxygen is also the cause for the difference in the intensity distribution shapes between the Mott and the SPLEED measurement, compare Figure 3.5 (b). A larger oxygen coverage produces a shoulder at about -2.5 eV binding energy and shifts the -6 eV peak to higher binding energies as measurements by E. Vescovo et al. [109] showed. This is exactly what we observe in Figure 3.5 (b). However, the oxygen does not alter the conclusion that the SPLEED performs better than the Mott. The opposite is the case: it is known from measurements by Vescovo et al. [110] that oxygen coverages quenches the spin polarization.
both detectors is similar as can be seen from the steepness of the intensity decay at the Fermi level.

The performance of the two detectors can be compared by the noise in the polarization signal $\Delta P$ at a binding energy of $-7$ eV. It is $\Delta P_{\text{Mott}} \approx 8\%$ and $\Delta P_{\text{SPLEED}} \approx 4\%$. Thus the noise level is about a factor of two better for the SPLEED detector, even though the Mott measurement has a larger angular acceptance. This shows that the SPLEED detector has indeed a better detection efficiency. Actually, the SPLEED would perform even better: The experiment was performed with a graphene contaminated iridium crystal. The maximal achieved Sherman function was only about 0.2-0.25, compare appendix B, whereas a clean crystal can produce a Sherman function $> 0.8$ as shown in Figure 3.3. Therefore, for a clean iridium crystal we could expect at least a $2 \cdot (0.8/0.25)^2 \approx 20$ times\footnote{The factor of two accounts for the already twice better noise performance of the SPLEED compared to the Mott.} better measurement performance than with the Mott detector!

### 3.2.6 Azimuthal Orientation and Balancing

This section does not provide an in-depth study of the azimuthal dependence of the asymmetry (azimuthal angle $\phi$ in Figure 3.1). It is rather intended to give an idea of the influence the azimuthal angle has on the asymmetry/Sherman map.

A 15 ML Fe film on W(110) served as the magnetic sample. Secondary electrons were generated by bombarding the sample with 4 keV electrons. Figure 3.6 shows the asymmetry maps for four different azimuthal angles $\phi = -20^\circ, -15^\circ, -10^\circ, -5^\circ$ (the azimuthal orientation is defined in Figure 3.1). These images were recorded with the bias voltage tuned to collect the iron’s secondary electrons at 30 eV kinetic energy. At $\phi = -20^\circ$ there are only positive asymmetry values. By turning the crystal from $\phi = -20^\circ$ towards $\phi = -5^\circ$, a negative asymmetry feature arises in the upper left corner which is getting more and more pronounced. Furthermore, the positive feature in the right middle, at $\phi = -20^\circ$, completely vanishes during the turn.

A bipolar asymmetry as in $\phi = -5^\circ$ can prove itself useful for measurements at fluctuating sources, for example at FLASH. The region with positive and negative asymmetry mimics the opposite counters in a Mott detector and provides a way to apply a balancing technique to reduce noise in pump and probe experiments, see appendix B.2.2 on that matter.

### 3.2.7 Oxygen Covered Surface

An oxygen covered iridium surface was achieved by performing the cleaning procedure (see section 3.2.2) without the final high temperature flash\footnote{Note that the surface will also be contaminated with CO and CO$_2$ molecules.}. The azimuthal
3.2. Imaging SPEEED Detector

Figure 3.6: Asymmetry and intensity maps for four different azimuthal crystal orientations. The 30 eV kinetic energy electrons in “Wide Angular Dispersion” mode were acquired with the stripe aperture in.

Figure 3.7: (a) The oxygen covered iridium crystal shows a Sherman map with a antisymmetric polarization feature. The upper part of the map has a negative- while lower part shows a positive Sherman function. (b) Intensity distribution (normalized sum of images for magnetization up/down). The pictures were recorded at 30 eV kinetic energy in the “Wide Angular Dispersion” mode with the stripe aperture in. The angular resolution is distorted and therefore no axis is given. Note, however, that the angular spread between adjacent lines is 1.43° (for $V_{bias} = 0$ V).
angle optimized for best image quality is found at $\varphi = 17^\circ$. Otherwise the experiment was performed as described in section 3.2.6. The so-treated crystal shows a Sherman map as depicted in Figure 3.7 (a). There is a clear bipolar feature in the Sherman function and the region of high Sherman values is about 2.5 eV wide, nearly double as wide as for the uncontaminated surface, compare Figure 3.3. The stripe pattern in Figure 3.7 (b) looks distorted. The reason might be a trapping of charge in the oxide layer promoted by inhomogeneities in the iridium surface structure.

3.3 FLASH

FLASH (the free electron laser at DESY in Hamburg) is a pulsed source and it would be desirable to record SPLEED images for each FEL pulse for a shot-by-shot correlation with machine parameters. Up to know, there are no commercial CCD cameras available running at a frame rate of 1 MHz, the FEL pulse repetition frequency. Furthermore, the best linearity and dynamic range is achieved by individually counting every electron reaching the exit of the SPLEED detector. These requirements can be met by a so called delay line detector [111].

3.3.1 DELAY LINE DETECTOR

A delay line detector (DLD) is an imaging electron detector with high spacial ($\approx 50 \mu$m) and temporal resolution ($\approx 100$ ps) [111]. The position and time information are recorded electrically. Therefore, no “slow” optical image detectors are involved. A DLD is capable of handling up to 4 million electrons per second in random detection regimes [111]. Each electron is registered digitally as a single event. Thus, a DLD provides excellent linearity surpassing any optical – electron to light conversion.
3.3. FLASH

– detection method. The capability of recoding not only the spacial position of an electron impact, but also its time, is employed in energy resolved time of flight microscopy [111].

The working principle of regular DLD is depicted in Figure 3.8 (a). A stack of multi channel plates (MCP) amplifies the charge of a single electron [111] by a factor of $10^7$. Beneath the MCP stack are two electrically insulated wire meanders for the determination of the x- and y electron impact position. The secondary electron shower from the MCPs induces an image charge in the wires [111] and generates thus voltage pulses traveling along the wires in either direction. The arrival time of the voltage pulses at the wire ends can be measured by so-called time to digital converters with picosecond precision [111] and are denoted $t_{x1,y1}$ and $t_{x2,y2}$. The time difference of the arrival times for either x- or y- coordinates is $\Delta t_{x,y} = t_{x1,y1} - t_{x2,y2}$. These time differences are each a linear function of the impact position. Thus, the electron position is uniquely determined by an arrival time measurement, see Figure 3.8.

This meander wire design has about 15 ns dead-time [111] for each registered electron. However, in an ultrafast photoemission experiments, photo electrons will arrive in a time window shorter than this dead-time. Thus, a novel DLD layout has been built in a collaboration with the company “Surface Concept” and Prof. Schönhense’s group from Mainz. Figure 3.9 shows the layout and the working principle of this custom designed DLD detector. The detector consist of 16 columns with 9 pixels each, every pixel is a metallic pad registering the electron shower from the MCP stack. The specialty of this DLD is that every row has its own time to digital converter electronics – making it in principle possible to capture 16x9=144 simultaneously arriving electrons. Figure 3.9 (b) shows one pixel row of the delay line. The pixels are interconnected with a reference- and a delay line. Let’s suppose that two electrons hit pad 5 and 9. The charge induced by the electron shower produces a short voltage pulse in each pad. This pulse travels subsequently along the reference and the delay lines. As the electric signal travels nearly with the speed of light, the partial signals traveling along the reference line overlap and produce only one spike at $t_0$. This spike triggers the time capture electronics which measures the time differences to the following pulses arriving over the delay line. As a result, the time to digital detector will output $5\tau$ and $9\tau$ with $\tau$ the delay interval between each pixel. Hence, the positions of the electrons are uniquely determined by the time in multiples of $\tau$.

The detector is oriented with the energy dispersive direction mapped onto the 16 channels (see Figure 3.9). Otherwise, different long flight times, of electrons with

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8Special thanks to Andreas Oelsener and the people from Surface Concept for the tremendous work done during the development commissioning of the DLD.
different kinetic energies, could interfere with the position determination.

### 3.3.2 Measuring the Asymmetry

We used this custom made DLD to measure the magnetic asymmetry of the photo emitted electrons excited by FLASH. The FEL produced 100 fs long pulses (also called “microbunches”) at 40 eV photon energy with $< 1 \text{nJ}$ per pulse. Each FEL macrobunch\(^9\) is filled with 221 microbunches with a repetition rate of 1 MHz. Let’s first observe the electron count capability of the DLD. Figure 3.10 (a) shows one prototypic macrobunch. We see clearly that there are electrons from microbunch id 1 to 221. Before and after the microbunches, no electrons are counted even tough the DLD is active, showing that the DLD produces basically no dark counts. As an example of the multi hit capability, the 15 detected electrons of microbunch 43 are highlighted as white pixels in Figure 3.10 (a) on the right.

The intensity- distributions for the cascade- and valence electrons\(^10\) are depicted in Figure 3.10 (b). These pictures are acquired based on the summation of all microbunch images. Before each macrobunch, the magnetization of the Fe film was switched in a random manner. Therefore, we can calculated the polarization asymmetry by summing over all images corresponding to one magnetization direction (Figure 3.10 (b)). This shows that it is possible with a SPLEED detector to measure the spin polarization of the secondary- and directly emitted electrons generated by ultrashort VUV pulses.

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\(^9\)A burst of microbunches. The macrobunches have a repetition rate of 10 Hz.

\(^10\)The spectrometer is used in the “Wide Angle mode”, slit 5, $V_{bias}$ is set to -60 V to measure the cascade and to -25 V to sample the valence band, all the other parameters are used as described for the other SPLEED measurements.
Figure 3.10: (a) Count histogram around one FEL microbunch. There are only electrons detected in the DLD when the FEL was active (1 to 221). Before and after these indexes no electrons are recorded. For a selected microbunch, the picture on the right shows in white the pixels where an electron was detected. A pad can only count one electron at once. (b) Total counts and asymmetries images measured for either electrons emerging from the cascade or from the valance band (in both cases about 100 million electrons are analyzed). The asterisk marked row has a lower detection efficiency wherefore it appears dimmer. Both the cascade and the valence band show a clear magnetization asymmetry.
We have seen in chapter 1 that the present bulk theories have difficulties to explain ultrafast demagnetization. During the analysis of various physical properties of magnetic materials in search for a correlation with the ultrafast demagnetization time, astonishingly, I have discovered two correlations: First, the demagnetization time correlates with the bulk resistivity and, second, also with the film thickness. These observations lead to the hypothesis that ultrafast demagnetization is based on transport and that demagnetization itself is an interface effect – namely by either acting as an effective spin-flip center, or that spin polarized currents deplete the magnetic thin film from majority spins, pass the interface, into the substrate.
In this chapter, first the hypothesis that the interface plays a major role in the ultrafast demagnetization is formulated. Then, the statements are evaluated by experimental and theoretical arguments.

4.1 Hypothesis

The interfaces – namely the surface and the contact plane between the thin film and the host material – act as efficient spin-flip centers. Hence, these are the locations where the actual ultrafast loss of spin angular momentum occurs.

For the validation of this hypothesis, we have to understand why the interfaces have the capability to efficiently flip the electron spin: the physical origin lies in the reduced symmetry of the interfaces compared to the bulk. This leads to an enhanced spin-orbit coupling due to the reduced quenching of the orbital angular momentum [112]; manifested in magnetic surface anisotropies [113, p.31]. Furthermore, the electron-phonon coupling is strengthened at metal surfaces [114], which likely opens another pathway for the transfer of angular momentum to the lattice.

Measurements performed by Erekhinsky et al. [115] on non local spin valves support strongly the above statements. They observed a three order of magnitude enhanced spin-flip probability on the surface as compared to the bulk.

Based on these experimental findings, the above stated hypothesis is plausible. Its further validity can be tested by its implications: If ultrafast demagnetization is caused on an interface – then the ultrafast demagnetization

- of the surface is faster than the bulk’s.
- time has to increase for thicker films, a fingerprint for interface effects.
- is caused by spin transport.
- exists also on insulators, such as MgO and SiO$_2$.
- has to depend on the resistivity of the material.

4.2 Interface versus Bulk Demagnetization

If interfaces play a crucial rule during the ultrafast demagnetization process, the surface must demagnetize faster than the bulk. The lantanides are good candidate to verify this proposition since they show a typical bulk demagnetization time of about $\tau \approx 1\text{ ps}$ which can be accurately resolved. Figure 4.1 (a) shows the demagnetization of a bulk Gd sample measured with XMCD$^2$. Due to the long absorption

---

1The plural indicates that the surface and the interface between the thin film and the host material are addressed.

2X-ray magnetic circular dichroism.
4.2. INTERFACE VERSUS BULK DEMAGNETIZATION

length of the x-rays, the magnetic state along the whole Gd film thickness of 10 nm [116] is probed. In contrast to this bulk measurement, Figure 4.1 (b) shows the change of second harmonic generation of Gd which is a surface sensitive probe for the magnetization [117]. A drastic difference is observed [118]: The bulk has a demagnetization time of $\tau = 760 \pm 250$ fs [116] whereas the surface's lies below 50 fs [117]!

Two indistinguishable processes may lead to the faster demagnetization of the surface: The first process might be a depleting of the majority electrons on the Gd surface through (super-) diffusion [30], and thus, no actual demagnetization is necessary. This process has already been suggested by Sultan et al. [118] to be responsible for the enhanced surface demagnetization rate in Gd. Or, the surface itself acts as an efficient spin-flip center, flipping the spin of the majority electrons directly at the surface. Such an effect would raise the question: Why the surface is not always demagnetized (also in thermal equilibrium)? The solution might be given by the principle of detailed balance, which states

$$\frac{N^\uparrow}{\tau_{\uparrow\uparrow}} = \frac{N^\downarrow}{\tau_{\downarrow\downarrow}},$$

(4.1)

where $N^\sigma$ is the number of electrons of a spin species $\sigma = \uparrow, \downarrow$ and $\tau_{\sigma\sigma^*}$ is the scattering rate from $\sigma$ to $\sigma^*$. Hence, in thermal equilibrium the spin-flips from majority to minority electrons, or vice versa, cancel each other, and the surface can maintain a static magnetization. Because this principle is only valid in thermal equilibrium, once the sample has been heated, the scattering rates $\tau_{\sigma\sigma^*}$ change, leading to demagnetization.

Regardless which process is responsible for the difference, it shows already that the interface has a special role in the demagnetization process.
4. Ultrafast Demagnetization; An Interface- and Transport Effect

4.3 Thickness Dependence of the Demagnetization Time

In surface physics, surface contributions on an observable are experimentally accessible by thickness dependent measurements [112, 115] as the surface influence scales inversely with film thickness. The demagnetization time versus film thickness for transition ferromagnets and alloys thereof is plotted in Figure 4.2. The data points are compiled from literature and tabulated in appendix A. An universal increase of the demagnetization time on film thickness is observed for the transition ferromagnets – a fingerprint for an interface effect.

Let us examine this further: The total spin-flip rate \( r \) per volume, responsible for the ultrafast demagnetization, can be decomposed into an interface \( r_I \) and a bulk contribution \( r_V \) as

\[
r = r_V + \frac{r_I}{d},
\]

(4.2)

where \( d \) is the film thickness. The spin-flip rate is proportional to the inverse of the demagnetization time yielding in

\[
\tau \propto \frac{1}{r} = \frac{1}{r_V + \frac{r_I}{d}}.
\]

(4.3)
The observed demagnetization time increase is best described by equation 4.3 when the bulk scattering rate is zero ($r_V = 0$), see dashed line in Figure 4.2. Thus equation 4.2 reduces to a simple linear expression

$$\tau \propto \frac{d}{r_I}.$$  (4.4)

This equation implies that the ultrafast demagnetization is dominated by the interface.

#### 4.4 Spin Transport

We have seen in the previous section 4.3 that spin-flips causing the demagnetization are very likely to happen at an interface. However, for this mechanisms to work, the electrons need to be transported towards an interface. Figure 4.3 depicts such a model process: The pump pulse drives the electrons towards the bulk of the material. The spins get either flipped at the interface or get transported further into the substrate where they are out of reach of the measurement technique. Note that the employed measurement techniques have only a limited probing depth\(^3\). Therefore, in the limit of a thick ferromagnet (thicker than the probing depth), demagnetization can also be induced without the need of spin-flips, only by transporting majority electrons deeper into the material [34] and minority ones towards the surface (see Figure 4.3).

\(^3\)For example, second-harmonic generation can only observe the first atomic layers, the magneto-optical Kerr effect is limited to the penetration depth of the used light; about 20 nm for the transition ferromagnets, spin resolved photoemission is limited by the mean free path of the excited electrons, and XMCD is an element specific measurement technique with a propping depth of \(\sim 100\) nm.
This implies that strong spin currents are involved depleting the ferromagnet of its angular momentum. Experimentally, such a transport effect has been observed first by Malinowsky et al. in 2008 [29] and later on by several other authors [31, 32]. In 2010, Battiato et al. [34] constructed a super diffusive model explaining ultrafast demagnetization also as a transport effect. Recent experiments employing the inverse Spin-Hall effect could even measure the order of magnitude of the spin currents [33] to be in the $10^{13}$A/m$^2$ range.

### 4.5 Demagnetization on Insulators

Considering the fact that insulators do not conduct current, it is difficult to understand how only spin transport could lead to an efficient ultrafast demagnetization. However, we know from experiments (see table A.1 in appendix A) that demagnetization works equally well with thin magnetic layers on insulators as on metallic substrates.

This discrepancy can be resolved by considering the above discussed spin-flips at the ferromagnet/insulator interface. A laser induced spin current drives the majority electrons towards the interface and the minority electrons in the opposite direction (see Figure 4.3). This mechanism can also work efficiently even when the spin-flip probability for an majority electron, arriving at the interface, is not 100 %. The spin current simply pushes the majority electrons steadily towards the interface, until they are flipped (Figure 4.3).

Neglecting both interface and bulk spin-flips, as this is done in the spin transport calculations of Battiato et al. [34], leads to unrealistic small demagnetization amplitudes on insulating substrates. They performed spin transport calculations for nickel and iron deposited on the insulator MgO. Their model predicts, in the case of a 10 nm thick iron film, a surface demagnetization of only 10 % at a pump flux as high as one photon absorbed per atom. This value corresponds to the tremendous pump flux$^4$ of $> 35$mJ/cm$^2$ at which the iron film would immediately evaporate. This gives further evidence that the transport alone can not account for ultrafast demagnetization.
4.6 Resistivity Dependence

Given that the demagnetization is promoted by a transport effect, we would expect the demagnetization time to depend on the electrical resistivity of the material: the higher the resistivity of the ferromagnet, the lower the electron mobility which consequently results in a longer demagnetization time.

Indeed, this behavior of the demagnetization time is found. Figure 4.4 shows the demagnetization time plotted versus the bulk resistivity at the measurement's base measurement temperature.

---

For a conservative estimation it is assumed that the whole impinging light flux \( (I) \) can be absorbed in the iron film. Then, in the first 2 monolayers the absorption probability of a photon is \( p = \frac{a}{\alpha} \), where \( \alpha = 17.3 \text{ nm} \) is the absorption length of iron at 1.55 eV, \( a = 287 \text{ pm} \) the lattice constant of iron. Thus, the minimal bound of the flux is \( I = \frac{N h \omega}{p A} = \frac{a}{2 \pi A} \frac{1.55 \text{ eV}}{0.017} \frac{\text{eV}}{\text{m}^2 \cdot \text{J}} \approx 35 \text{ mJ/cm}^2 \). Here, \( N = 1 \) is the number of absorbed photons per atom, and \( A = d^2/2 \) the cross section of an atom at the surface, the factor 2 estimates the BBC center atom also to be at the surface.

Polycrystalline bulk values are considered at the base measurement temperature, the values are tabulated in appendix A. The bulk resistivity is chosen instead of the lateral resistivity, as the heat gradient from the pump laser pulse is strongest into to the bulk. This is due to the fact that the laser’s absorption length of \( \approx 20 \text{ nm} \) is much smaller than the diameter of the laser spot (\( \approx 100 \mu\text{m} \)). Therefore, transport into the bulk dominates over any lateral transport. Moreover, the bulk resistivity is a well defined physical quantity, whereas the lateral resistivity of a thin films depends crucially on surface scattering and thus on surface quality.
base temperature. Remarkably, the correlation holds for a broad class of materials, the transition ferromagnets, the lanthanides, and even the half-metals and Heusler compounds. This finding has the potential to be used for the tailoring of the ultrafast response of magnetic media. Moreover, it provides further evidence that ultrafast demagnetization is a spin current induced interface effect.
The observation of a dependence of the demagnetization time on resistivity and on film thickness indicates that ultrafast demagnetization bases on strong spin currents depleting the ferromagnet of its spin angular momentum. In this chapter, an intuitive semi-classical thermodynamical model is introduced, explaining ultrafast demagnetization via a diffusive transport effect. The calculations rely only on three well known material specific parameters: the spin dependent density of states, the pump laser’s absorption length, and the macroscopic resistivity. The framework will also be applied to explain the observed shift in x-ray linear absorption spectroscopy measurements.
5.1 SPIN CALORITRONICS

Thermoelectric effects such as the Seebeck- [119] and the Peltier-effect [120] are known since the mid 19th century. The former one describes that a conductor subjected to a heat gradient can build up a voltage gradient along the heat flow; and the latter one describes the opposite situation, where a charge current causes a heat flow. Both effects find various commercial applications as thermometers, electric chillers, and power generators. Their physical origin lies in the different electronic structure above and below the Fermi level. Electric currents, in the presence of a heat gradient, can be described by the three terms of the linearized Boltzmann transport equation [121, p. 321]: they can be caused by an applied electric field, a gradient of the chemical potential, and different transport properties for electrons above and beneath the chemical potential (Seebeck/Peltier effect).

However, it took about 150 years that also their spin counter parts have been discovered: Namely the spin-Seebeck effect [122, 123] and the spin-Peltier effect [124, 125]. They are in analogy to the non spin dependent effects and describe that either a heat gradient along a magnetic material induces a spin current or a spin current induces a heat flow. Nowadays, there is a lot of interest in such spin dependent thermoelectric effects with possible applications in data processing and heat harvesting. The field is called: “Spin caloritronics” where the interplays between charge-, spin-, and heat-currents are studied.

The question arises, why it took so long to observe such spin caloritronic effects? The reason is that the technology to grow and contact high quality magnetic thin films was missing. Before this technology was available, spin dependent phenomena in thermoelectric effects could not have been observed because the spin-diffusion length\(^1\) is very short, typically around \(\approx 10\) nm [126] in ferromagnets, washing out most spin dependent caloritronic phenomena in macroscopic samples.

The very heart of spin caloritronics is spin dependent transport. For the following derivation see Ref. [127] and references therein. Spin transport can be modeled by the famous two-current conduction model. It was first suggested by Mott [128] in 1936 and it’s validity was confirmed for the first time experimentally by Campbell et al. [129] in 1966. Today, this concept is generally employed for the description of spin currents in spintronic devices, for a recent review see Ref. [130]. In the two-current model, each spin channel (majority- \(\uparrow\) and minority electrons \(\downarrow\)) carries current independently of the other one. Hence, each spin channel is described by its own conductivity \(\sigma_{\uparrow,\downarrow}\). The classical conduction is given as the sum of the two conductivities \(\sigma = \sigma_{\uparrow} + \sigma_{\downarrow}\). In analogy to the response caused by applying an electric potential along the sample – which would act on both spin channels equally – spin dependent chemical potentials \(\mu_{\uparrow,\downarrow}\) are introduced acting separately on each

\(^1\)Describing an average length an electron can move until its spin is flipped.
spin channel. Thus, we can define a chemical potential driving the charge current as $\mu_c = (\mu_\uparrow + \mu_\downarrow)/2$ and a spin voltage describing spin transport by $\mu_s = \mu_\uparrow - \mu_\downarrow$. The interplay between charge-, spin-, and heat-current densities ($\vec{j}_c$, $\vec{j}_s$, and $\vec{Q}$) can be expressed for a monodomain, isotropic, and metallic ferromagnet as a matrix equation [127]:

$$
\begin{bmatrix}
\vec{j}_c \\
\vec{j}_s \\
\vec{Q}
\end{bmatrix} = \sigma(E_F) \begin{pmatrix} 1 & P & ST \\
PT & 1 & P'ST \\
ST & P'ST & \kappa T/\sigma \end{pmatrix} \begin{pmatrix} \nabla \mu_c / q \\
\nabla \mu_s / 2q \\
-\nabla T / T \end{pmatrix},
$$

(5.1)

where $P = (\sigma_\uparrow - \sigma_\downarrow)/\sigma$ is the conductivity spin polarization and $P' = \partial \mu/\partial E |_{EF} / \partial \sigma / \partial E |_{EF}$, $\kappa$ the thermal conductivity, $q$ the elementary charge, and $S$ the Seebeck coefficient. In the forthcoming discussion, we are mainly interested in the spin current density:

$$
\vec{j}_s = \sigma(E_F) (P \nabla \mu_c / q + \nabla \mu_s / 2q - P'S \nabla T).
$$

(5.2)

The last term in equation 5.2 contains the derivative of $P$ which is a value attainable by first-principle calculations [131]. For the simplification of the analysis, we will focus on the following calculations only on the non Seebeck terms. Still, we will discover that their contribution is sufficient to explain ultrafast demagnetization. Nevertheless, to understand the scenario in more detail also the influence of the Seebeck term should be studied, but this is out of the scope of this thesis. Applying the described reduction, equation 5.2 simplifies to

$$
\vec{j}_s = \sigma(E_F) (P \nabla \mu_c / q + \nabla \mu_s / 2q - \nabla \mu_\uparrow / q + \nabla \mu_\downarrow / q). 
$$

(5.3)

The first term on the left side in equation 5.3 describes the spin current generated by an applied voltage and the second term the contribution from a spin voltage.

### 5.2 The Chemical Potential

The chemical potential $\mu$ is a thermodynamical quantity of an ensemble describing the amount of energy necessary for a particle to enter it. We are interested in metals where the thermalized electron gas obeys the Fermi-Dirac statistics, describing the occupation probability of states at an energy $E$ and temperature $T$ by

$$
f(E, \mu, T) = \frac{1}{1 + e^{(E-\mu)/k_B T}},
$$

(5.4)

where $k_B$ is the Boltzmann constant. Usually, the chemical potential is identified with the Fermi energy $\mu \approx E_F$. This approximation is only valid for low enough temperatures and holds strictly only at zero temperature. Let's examine this closer
since we will propose it to be a major driving mechanism for spin transport in ultrafast demagnetization.

We consider a metallic system with an electron density \( n \) which cannot exchange particles with its surrounding. Then, at zero temperature, only states up to the Fermi level are filled, and we can write

\[
\begin{align*}
    n &= \int_{-\infty}^{E_F} G(E) dE, \\
    \text{(5.5)}
\end{align*}
\]

with \( G(E) \) the density of the electronic states (DOS). When the system is heated to a temperature \( T \), the number of electrons cannot change, but electrons are thermally excited to higher energy states. This is taken into account by weighting the DOS by the Fermi-Dirac statistics

\[
\begin{align*}
    n &= \int_{-\infty}^{\infty} G(E) f(E, \mu, T) dE. \\
    \text{(5.6)}
\end{align*}
\]

The only unknown parameter in this equation is the chemical potential \( \mu(T) \) which is a temperature dependent value. It will adjust itself to keep the number of electrons within the system constant. The chemical potential can now be acquired by numerically solving equation 5.6 for a given \( n \).

To get a feeling how \( \mu(T) \) behaves when the temperature is changed, three prototypic DOSs are depicted in Figure 5.1: a constant, a decreasing, and an increasing DOS at the Fermi level. We see that the chemical potential does not depend on temperature for a constant DOS around the Fermi level, see Figure 5.1 (a). For a decreasing DOS the excited electrons cannot find enough empty states above the Fermi level to maintain particle conservation, hence, the chemical potential rises

---

**Figure 5.1**: The direction of the heat induced chemical shift depends on the shape of the DOS. (a) In the flat region the chemical potentials do not change their position. (b) When the DOS is decreasing around the Fermi level the chemical potentials rise; in similarity to a majority band. (c) An increasing DOS around the Fermi level reduces the chemical potential; in similarity to a minority band.
above the Fermi level to access more states, see 5.1 (b). This is a typical condition found for the *majority* band of transition ferromagnets. The opposite is true for a decreasing DOS around the Fermi level where the chemical potential descends to account for the lower amount of hole states beneath the Fermi level, see 5.1 (c). In analogy to *minority* states in transition ferromagnets.

In the two-current conduction model majority and minority electrons have their own chemical potentials. We assume that the electron-electron interaction will immediately equalize the temperature between the majority- and minority band. Thus, we can solve equation 5.6 for each spin direction with one common temperature. This has been done for Ni, Fe, and Co for a fixed electron gas temperature of 3600 K, and the results are shown together with their DOS in Figure 5.2. In addition, the temperature dependence of the chemical potentials for these materials is shown in Figure 5.3. We observe the intriguing fact that the majority chemical potential rises, whereas the minority chemical potential resides close to the Fermi level. Having realized this effect, we have the necessary tool at hand to analyze heat induced transport effects.
5.3 Ultrafast Temperature- and Chemical Gradients

In this section, we will first discuss the absorption of electromagnetic radiation in metals. From the derived intensity profile, the temperature gradient of the electron gas and the corresponding chemical gradient will be calculated. We will see that the chemical potentials at the surface can drive a spin current away from the surface, depleting for example a thin film of its magnetic moments. Calculations for the transition ferromagnets Fe, Ni, and Co reveal that the proposed mechanism can quantitatively explain the observed demagnetization-time and amplitude.

5.3.1 Laser Absorption

Electromagnetic waves, in our case from an IR laser (800 nm), can penetrate metals only to a certain depth. The distance from the surface where the initial intensity is attenuated to $1/e$ is called the extinction depth $\alpha$. The absorbed intensity profile of a laser beam within a metal can be described by combining the Fresnel equation and the Beer-Lambert law:

By continuity, the free space laser field intensity $I_0$ needs to be equal to the sum of the reflected ($I_R$) and the transmitted ($I_T$) intensity at the sample’s surface: $I_0(z = 0) = I_R(z = 0) + I_T(z = 0)$, with $z > 0$ towards the bulk of the sample. The branching ratios of how much energy is reflected $R_{s,p} := I_R(z = 0)/I_0(z = 0)$ and transmitted into the sample $T_{s,p} := I_T(z = 0)/I_0(z = 0)$ can be calculated for s- and p-polarized
5.3. Ultrafast Temperature- and Chemical Gradients

![Figure 5.4: Surface transmittance of 800 nm laser light. Shown for the transition ferromagnets in function of the incidence angle for s- and p-polarized light.]

light by the non-magnetic Fresnel formulas (see for example [134]):

\[
R_s = \left| \frac{n_1 \cos(\theta) - n_2 \cos(\beta)}{n_1 \cos(\theta) + n_2 \cos(\beta)} \right|^2, \tag{5.7}
\]

\[
R_p = \left| \frac{n_2 \cos(\theta) - n_1 \cos(\beta)}{n_2 \cos(\theta) + n_1 \cos(\beta)} \right|^2, \text{ with} \tag{5.8}
\]

\[
\frac{\sin(\theta)}{\sin(\beta)} = \frac{n_2}{n_1} \quad \text{and} \quad T_{s,p} = 1 - R_{s,p}. \quad \text{Here,} \quad \theta, \beta \quad \text{are the incidence and transmission angles measured relative to the surface normal. Furthermore,} \quad n_1 = 1 \quad \text{is the refraction index of free space and} \quad n_2 = n' + ik \quad \text{the complex refraction index of the magnetic material, see table 5.1. Albeit metals are generally thought to be highly reflective, we see from Figure 5.4 that for p-polarized light with an incidence angle of 45° to the surface normal, only about half of the beam’s initial energy is reflected. The other half enters the metal. This is the reason why an IR laser pulse can heat the electron gas of a transition ferromagnet efficiently [53]. The intensity} \quad I_T(z) \quad \text{transmitted through a thin film with thickness} \quad z \quad \text{is described by the Beer-Lambert law [135]:}
\]

\[
I_T(z) = I_T e^{-z/\alpha}, \tag{5.10}
\]

\hl{Due to the high frequency of optical waves, the magnetization can not follow the light’s magnetic field and the relative magnetic permeability reaches 1 and the non-magnetic Fresnel equations can be used as observed by Hagen et al. [133] in 1903.}

\hl{A pulse with} \quad I_T \quad \text{> 1 mJ/cm}^2 \quad \text{with a pulse length < 100fs}
where \(1/\alpha = \frac{4\pi fk}{c}\), \(k\) the extinction coefficient, \(c\) the speed of light, and \(f\) the frequency of the light wave. Please note that these coefficients depend crucially on the light's wavelength \([136]\). Table 5.1 lists extinction coefficients and extinction depths for a few selected ferromagnets at 800 nm wavelength, the standard pump wavelength. We are interested in the amount of absorbed energy per volume

<table>
<thead>
<tr>
<th>Element</th>
<th>(n')</th>
<th>(k)</th>
<th>(\alpha) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe[136]</td>
<td>3.03</td>
<td>3.69</td>
<td>17.3</td>
</tr>
<tr>
<td>Ni [136]</td>
<td>2.58</td>
<td>4.39</td>
<td>14.5</td>
</tr>
<tr>
<td>Co[136]</td>
<td>3.06</td>
<td>4.85</td>
<td>13.1</td>
</tr>
</tbody>
</table>

Table 5.1: Optical extinction depths \(\alpha\) and parameters of the complex refraction index \(n_2 = n' + ik\) for selected ferromagnets at 800 nm.

\(i_{\text{abs}}(z)\) and the total absorbed intensity \(I_{\text{abs}}(z)\) within the ferromagnet of thickness \(z\). These terms are derived with equation 5.10 and the fact that an infinitely thick film absorbs the whole intensity \(I_T\):

\[
i_{\text{abs}}(z) = \frac{I_T}{\alpha} e^{-z/\alpha},
\]

and

\[
I_{\text{abs}}(z) = \int_0^z i_{\text{abs}}(z') dz' = I_T(1 - e^{-z/\alpha}).
\]

Please note that equation 5.11 is only rigorously valid for semi infinite slabs. We make here the approximation that it can also be used for thin films, without solving Maxwell's equation.

In ultrafast demagnetization experiments, magnetic thin films have a thickness on the order of the absorption depth. It has been argued that in this case the thin films are homogeneously pumped \([46, 137]\). However, the exponential decrease of the deposited energy described by equation 5.12 implies that actually a temperature gradient is always present; even for films thinner than the absorption length.

### 5.3.2 Electron Gas Thermalization

In the following, the goal is to calculate the temperature gradient of the electron gas and the corresponding chemical potential gradient from the absorbed intensity profile and material properties, see equation 5.10. This can only be done, if the electron gas is already thermalized to a good extend. Otherwise, the electron system is not well described by a Fermi-Dirac distribution.

Let us first consider what happens when a metal is subjected to a pump laser of
5.3. Ultrastable Temperature- and Chemical Gradients

Figure 5.5: Photoemission yield in function of energy measured for different pump probe delays for Nickel: (a) 1 ps, (b) 0 ps, (c) 0.2 ps, (d) 0.4 ps, and (e) 0.8 ps. Already at 0 ps delay, the main part of the electrons can be well approximated by a straight line. Excerpt of Fig. 1 from Ref. [53] superimposed by red line. Reprinted with permission from Ref. [53]. Copyright (2003) by the American Physical Society.

The absorbed photons will excite electrons from an interval $\hbar \omega$ below the Fermi level to states above it. These excited electrons lose energy by scattering events. At the early stage of the relaxation process electron-electron collision dominate over electron-phonon scattering events [84] since the energy of the hot electrons is yet too large to couple efficiently to the phonons. While the hot electrons undergo inelastic scattering events the electron gas thermalizes towards a Fermi-Dirac distribution through which the electron gas temperature is defined. The time it takes for the electron gas to reach a Fermi-Dirac distribution has been discussed controversially in literature; two approaches are being used: First, the electron gas is found in a strong out-of-equilibrium condition during the first few 100 fs and thermalizes after $\approx 500$ fs [34, 138]. Second, the electron gas can always be approximated as being thermalized [28, 139].

Battiato, and Carva et al. [34, 138] argued for the first approach. Their conclusions are based on experiments performed on gold and silver [140–143]. These noble metals posses a constant and small density of states around the Fermi level [144, 145]. Yet, transition ferromagnets provide d-states with large densities of states in the proximity of the Fermi level [132]. Hence, by applying Fermi’s golden rule, one readily sees that experiments on noble metals can not directly be compared to transition ferromagnets as their larger DOS should promote a much faster electron relaxation rate. Thus, the second argumentation, of a nearly immediate thermalization, seems reasonable for these systems: Dürr showed in his review
[139] that for the electron gas of nickel a temperature can be attributed at all times.

At this point, the discussion can be clarified by examining the experiment which is able to measure the ultrafast laser heated electron gas temperature: The most direct way to acquire its temperature is to measure the energy-resolved photo electron yield \( n(E) \) in a pump-probe photoemission experiment and fitting the spectra with a Fermi-Dirac distribution [53, 137, 146]. Graphically, this can be done by plotting \( \log(n(E)) \) in function of \( E - E_F \). When the data points above the Fermi level follow a straight-line, the electron gas has thermalized. And the slope of the line is inverse-proportional to the electron temperature. An example of such an experiment performed on nickel by Rhie et al. [53] is shown in Figure 5.5. The tail of the electron yield follows nicely the overlaid red line, see Figure 5.5. Remarkably, even when both pump and probe beam arrive simultaneously on the sample (Figure 5.5, trace b) only high energetic electrons branch off from the red line. However, their contribution to the total energy in the system is small. Hence, we can assume a thermalized electron gas at all times to render thermodynamic calculations possible.

Despite the ease of this measurement principle, care needs to be taken by evaluating such spectra as the Fermi-Dirac distribution is not directly measured in these experiments. The electron yield \( n(E) \) is the product of the density of states \( G(E) \), the photoemission efficiency \( \epsilon(E) \), and the Fermi-Dirac distribution \( f(E) \):

\[
n(E) = \epsilon(E)G(E)f(E).
\]

The photoemission efficiency depends on the symmetry of the involved initial- and final states as well as the energy and polarization of the involved photons.

5.3.3 Surface Temperature and Chemical Potentials

Based on the discussion in section 5.3.2, we consider the electron gas as being thermalized at all times. The concept of chemical potentials is thus applied to ultrafast heated electron gases. For the forthcoming discussion, we assume sufficiently short laser pulses that during the laser pulse heat transport by hot electrons can be neglected.

**Surface temperature** It is well known that the heat capacity \( c_e \) of the electron gas scales with its temperature \( T_e \) like \( c_e \propto T_e \). This relation is approximately valid up to thousands of Kelvins as calculations from Lin et al. [147] indicate for nickel. If we can calculated the surface temperature \( T_S \) of the sample right after the arrival of the ultrafast pump laser pulse, we can make use of equation 5.11 and describe the temperature profile \( T(z) \) within the sample approximately by a modified Beer-Lambert law:

\[
T(z) = T_S e^{-z/2\alpha}.
\]
Figure 5.6: Calculated surface electron gas temperature $T_S$ in function of the transmitted intensity $I_T$ for Fe, Ni, and Co. Note, for zero $I_T$ the temperature remains at room temperature (RT).

Here, $\alpha$ is the optical penetration depth and the factor 2 accounts for the quadratic dependence of the electron gas’ heat density on temperature.

The surface temperature $T_S$ can be calculated by equating the absorbed laser energy density with the increase of the inner energy density $u(T_S) - u(T_0)$ within an infinitesimal slab at the surface

$$\left.\frac{dI_{\text{abs}}}{dz}\right|_{z=0} = \frac{I_T}{\alpha} = u(T_S) - u(T_0)$$

(5.14)

and

$$u(T_S) - u(T_0) = \frac{N}{V} \sum_{\sigma = \uparrow, \downarrow} \int_{-\infty}^{\infty} G_{\sigma}(E)E\left[f(T_S, E, \mu_{\sigma}(T_S)) - f(T_0, E, \mu_{\sigma}(T_0))\right] dE.$$  

(5.15)

Here, $T_0$ is the temperature before the pump beam has arrived and is assumed to be 298K, $N$ is the number of atoms per unit cell, and $V$ the volume of the unit cell. Equation 5.14 and 5.15 are numerically solved for a given $I_T$ by varying $T_S$. The temperature dependence of $\mu_{1,1}(T_S)$ is known from the numerical solution of equation 5.6 as explained in section 5.2. The results are shown for Fe, Co, and Ni in Figure 5.6. These curves have the same shape reflecting the square root dependence of the electron gas temperature on stored heat.
Figure 5.7: Sketch of the two current model. The laser heating of the ferromagnet will produce a spin voltage at the surface larger than that one at the interface \((U(0) - U(d) > 0)\), driving the majority electrons away from the surface. This difference will drive a spin current density of \(j_s = j_1 - j_1 = 2j_1\).

The voltage drop over each resistor is denoted by \(U_{\uparrow}\).

5.4 Spin currents and ultrafast demagnetization: The R-model

We are going to develop a semi-classical transport model. It is called the R-model since it makes use of the resistivity of the material. In chapter 4, the effect that the demagnetization time scales with the resistivity of the material was observed. Therefore, it seems reasonable to develop a diffusive model based on the resistivity of the material.

In the two current model we can depict our situation as shown in Figure 5.7. Each spin channel has its own resistance \((R_{\uparrow} = \rho_{\uparrow}d, R_{\downarrow} = \rho_{\downarrow}d, \text{ where } d \text{ is the film thickness})\). The chemical potentials at the surface generated by the pump pulse act as a spin battery of strength \(U(z = 0) = (\mu_{\uparrow}(0) - \mu_{\downarrow}(0))/q\), where \(q\) is the elementary charge. A similar battery is also present at the interface \(U(z = d) = (\mu_{\uparrow}(d) - \mu_{\downarrow}(d))/q\), however with a smaller voltage, \(U(0) > U(d)\), as the laser pulse can heat electrons within the slab only to a smaller temperature than at the surface. Note that the battery at the interface provides the spin-flips in case of an insulating substrate. The batteries will drive the same current density through both resistors\(^4\) in order to maintain charge neutrality:

\[
j_{\uparrow} = -j_{\downarrow} \approx \frac{U(0) - U(d)}{d(\rho_{\uparrow} + \rho_{\downarrow})}.
\]

Therefore, the total spin current density in units of coulombs/second/area reads

\[
j_s := j_1 - j_1 = 2j_1.
\]

\(^4\)Note, that we assume a constant potential gradient \(\frac{U(0) - U(d)}{d}\) over the film thickness. The voltages can drive a spin current as long as a temperature gradient is present between the surface and the interface.
Furthermore, depending on the relative size of the resistivities, we get different voltage drops across the resistors:

\[
U^\uparrow = \frac{(U(0) - U(d))\rho^\uparrow}{\rho^\uparrow + \rho^\downarrow}, \quad (5.18)
\]

\[
U^\downarrow = \frac{(U(0) - U(d))\rho^\downarrow}{\rho^\uparrow + \rho^\downarrow}. \quad (5.19)
\]

However, which resistance values has to be used for \(\rho^\uparrow, \rho^\downarrow\)? From measurements on transition ferromagnets [77, 148, 149] it is known that the majority channel conducts the electrons approximately a factor \(\approx 4\) better than the minority channel. This implies that by measuring the resistance \(\rho\) of a macroscopically large sample at room temperature, primarily the majority resistivity \(1/\rho = 1/\rho^\uparrow + 1/\rho^\downarrow \approx 1/\rho^\uparrow\) is measured.

Furthermore, we need to know how the room temperature resistivities scale for the laser heated case. Goodings [150] pointed out that presumably the resistivity in ferromagnets at higher temperatures is caused by electron-phonon and electron-magnon scattering. Electron scattering experiments performed by Wang et al. [151] showed that it takes about 2 ps to fully excite the phonon system. Hence, during the first 100 fs we can expect the electron-phonon scattering to still reside at its room temperature value. Furthermore, magnons need first to be created by spin-flip scattering to activate the electron-magnon scattering channel. Therefore, we use in a first approximation the initial temperature value of the majority/minority resistivity for the hot electron gas. As we do not precisely know the minority resistivity, we assume \(\rho^\downarrow = 4\rho^\uparrow\) [77, 148, 149] in the case of Fe, Ni, and Co. This assumption should at least allow to reveal qualitative trends, and order of magnitude estimations. Please note that very little is known about spin dependent resistivities for the ultrafast laser heated case and it would be very desirable to access such values by ab-initio calculations. Battiato et al. [34] assumed in their calculations an unpolarized current flowing back from the cold side to the hot side of the film to maintain charge neutrality. Therefore, they made the implicit assumption that both spin channels conduct equally well around the Fermi level. In our model, however, charge neutrality is automatically fulfilled and we can do the calculation for any choice of \(\rho^\uparrow\) and \(\rho^\downarrow\).

The idea of the R-model is to calculate the pump pulse induced spin current. This is done by applying Ohm’s law to the pump pulse induced chemical potential gradient \((U(0) - U(d))/d\).

The question remains up to which current densities Ohm’s law is valid. E. Guth et al. [152] performed calculations on that matter: they predict that currents of up to \(10^9 A/cm^2\) only cause a deviation from Ohm’s law by 1%. Our calculation will yield
current densities about the same order of magnitude which implies that Ohm’s law should still be applicable.

Our goal is to calculate the demagnetization time \( \tau \) and the demagnetization amplitude \( \Delta M(\tau)/M_0 \), where \( M_0 \) is the saturation magnetization.

A short IR pump laser pulse deposits its energy into the electronic system and, therefore, only electrons can transport heat during the first few 100 fs. Thus, we define the demagnetization time \( \tau \) as the transit time it takes for the hot electrons generated at the surface to travel through the film. After this, the temperature gradient at the surface, generating the chemical potentials, should have mostly vanished. This means, that we will not be able to exactly compare the fitted demagnetization times gathered by measurements with the above definition. However, if the model is valid, we expect the calculated values at least to to lie within an order of magnitude from the measured demagnetization times. The demagnetization time can be defined as

\[
\tau = \frac{1}{2} \left( \frac{d}{v_\uparrow} + \frac{d}{v_\downarrow} \right).
\]

The drift velocities can be gathered by expressing the spin current density in terms of a transport approach for the majority electrons \( j_\uparrow = n_\uparrow v_\uparrow q \) and equally for the minority holes \( j_\downarrow = h_\downarrow v_\downarrow q \). Our point of view lies at the surface of the ferromagnet, therefore, we describe the majority current in the electron- and the minority current in the hole picture. Here, \( n_\uparrow \) is the average free electron- and \( h_\downarrow \) the free hole density taken over the film thickness

\[
n_\uparrow = \frac{1}{d} \int_0^d \int_{\mu_\uparrow(z)}^{\infty} G_\uparrow(E) f(E, \mu_\uparrow(z), T(z)) dE dz,
\]

\[
h_\downarrow = \frac{1}{d} \int_0^d \int_{-\infty}^{\mu_\downarrow(z)} G_\downarrow(E) (1 - f(E, \mu_\downarrow(z), T(z))) dE dz.
\]

These integrals end each at \( \mu_{\uparrow,\downarrow}(z) \), since it is assumed that for the majority channel the electrons above the chemical potential can be mainly injected into the colder part of the film, and for the minority channel likewise the holes beneath the chemical potential. The numerical implementation reveals that even if the electrochemical potentials are set to the constant Fermi level, the numerical results for \( n_\uparrow \) and \( h_\downarrow \) change only marginally. The reason for this insensitivity are the broad Fermi functions at high temperature. Based on these values, we can already state the first
5.4. SPIN CURRENTS AND ULTRAFAST DEMAGNETIZATION: THE R-MODEL

Figure 5.8: Results of the R-model for Fe, Ni, and Co for 10 nm thick films and $\rho_\downarrow = 4 \rho_\uparrow$: (a) Free charge carriers (b) Spin current density (c) Demagnetization time (d) Surface demagnetization amplitude.

The main result of the calculations, namely the demagnetization time as:

$$\tau = \frac{1}{2} \left( \frac{dn_\uparrow q}{j_\uparrow} + \frac{dh_\downarrow q}{j_\downarrow} \right) = \frac{d^2 n_{\text{free}}(\rho_\uparrow + \rho_\downarrow)}{U(0) - U(d)},$$

(5.23)

where $n_{\text{free}} := (n_\uparrow + h_\downarrow)/2$ is defined as the mean free carrier density over the film thickness. Also the transport based relative change of the surface demagnetization, is readily calculated. Leading to the second main result:

$$\Delta M(\tau)/M_0 = -\frac{j_s \tau \mu_B}{d q}/M_0 = -2 n_{\text{free}} \mu_B / M_0.$$

(5.24)

Interestingly, equation 5.24 is independent of the resistivity and depends only on the mean free carrier density. Hence, the demagnetization amplitude is expected to be a robust value, depending only weakly on material parameters. Equations
5.23 and 5.24 can be solved when knowing the resistivity $\rho$, the extinction coefficient $\alpha$, the saturation magnetization $M_0$, and the density of states $G_{\uparrow,\downarrow}$, \textit{without any fit parameter}.

The calculations have been carried out for all transition ferromagnets$^5$ and the results are shown for 10 nm films of Fe, Ni, and Co in Figure 5.8.

Discussion

\textbf{Free charge carrier density} Figure 5.6 (a) shows the dependence of the free carrier density on pump flux. Intuitively, we would expect a linear increase of the charge carriers on laser flux as this is the case e.g. in photodiodes. The reason why we see for the transition ferromagnets a sub-linear dependence of $n_{free}$ for increasing pump power, is the large difference in carrier lifetime. In heavily doped silicon, for example, the charge carriers have recombination times in the nanosecond time scale [156], in contrast to transition ferromagnets where an excited carrier possesses a lifetime of only a few femtoseconds [90]. Therefore, the excited carriers thermalize quickly back into unoccupied states below the Fermi level, reducing the net free carrier density. Thus, the shape of the curves resemble a square root behavior on pump flux as the width of the Fermi distribution scales like $\sim 4k_BT_e \sim \sqrt{IT}$.

\textbf{The current density} The current densities show a common feature for Fe, Co, and Ni, see Figure 5.6 (b); They are nearly zero for a pump fluence below 0.2 mJ/cm$^2$. The reason for this threshold type of dependence is that the chemical potential starts to deviate from the Fermi level not before the temperature of the electron gas has reached $\approx 1000$ K, see Figure 5.3. This threshold effect might be one of the reasons why in photoemission experiments by Vaterlaus et al. [9], where slow laser pulses of 30 ps length were used, no demagnetization was observed.

At higher pump fluences ($>0.2$ mJ/cm$^2$) the spin current density increases. Iron shows the smallest spin current density of all the transition ferromagnets. The calculation show that the reason for this behavior is irons’ large resistivity, and its small chemical potential shift on temperature compared to all the transition ferromagnets. Experimentally, this is in line with the general observation that iron needs the highest pump flux to be demagnetized among the transition ferromagnets.

The R-model predicts in the case of iron and for a pump pulse energy of $IT =$

$^5$The bulk resistivity ($\rho \approx \rho_{\uparrow}, \rho_{\downarrow} = 4\rho_{\uparrow}$) for polycrystalline samples at 298 K are used for the calculations: $\rho_{Fe} = 9.87 \mu\Omega\text{cm}$ [153], $\rho_{Co} = 6.0 \mu\Omega\text{cm}$ [154], $\rho_{Ni} = 7.12 \mu\Omega\text{cm}$ [153]; The extinction coefficients shown in table 5.1; The saturation magnetizations in units of Bohr magnetons per atom taken from [155]: $M_0^{Fe} = 2.22$, $M_0^{Co} = 1.72$, and $M_0^{Ni} = 0.62$; The spin resolved density of states for Fe, Ni, and Co from [70].
1 mJ/cm² a spin current density of $\approx 7 \cdot 10^{12}$ A/m². Kampfrath et al. [33] measured a peak spin current density of $\approx 1 \cdot 10^{13}$ A/m² in close agreement with the R-model’s prediction.

**Demagnetization time**  The model predicts a divergence of the demagnetization time at small pump pulse energies. This behavior is on one side comprehensible as for zero pump flux $\tau \to \infty$ the sample should also not be demagnetized, see Figure 5.6 (c). However, such a pronounced dependence has not been observed experimentally [28, 157]. It is likely that the consideration of a spin current contribution from the spin-Seebeck effect, which is not incooperated in the R-model, might lift this divergence.

The high flux regime shows a weak change of the demagnetization time. This is in line to flux dependent experiments [28, 157] where only a moderate increase of the demagnetization time on pump flux has been observed. Note, we have not considered the temperature influence on the resistivity. Thus, the fact that the onset of magnon and phonon creation increases the resistivity of the material would result, after equation 5.23, in an increase of the demagnetization time, in line with experiments [28, 157].

Despite the simplistic nature of the R-model, the calculated ($\tau_{calc}$) demagnetization times at a flux of $I_T = 4$ mJ/cm² are in close agreement to experimental minimum demagnetization times ($\tau_{min}$), see table 5.2.

<table>
<thead>
<tr>
<th>Material</th>
<th>d</th>
<th>$\tau_{calc}$</th>
<th>$\tau_{min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>15 nm</td>
<td>550 fs</td>
<td>400 – 600 fs [28]</td>
</tr>
<tr>
<td>Ni</td>
<td>10 nm</td>
<td>550 fs</td>
<td>500 – 700 fs [27]</td>
</tr>
<tr>
<td>Fe</td>
<td>10 nm</td>
<td>400 fs</td>
<td>300 – 500 fs [27]</td>
</tr>
</tbody>
</table>

**Table 5.2:** Comparison of calculated ($\tau_{calc}$ for $I_T = 4$ mJ/cm²) and the time of the measured demagnetization minimum ($\tau_{min}$) as extracted from the cited papers.

**Demagnetization amplitude**  It has been shown experimentally by several authors [28, 157] that the demagnetization amplitude scales approximately linear with pump power. This experimental finding is only approximately reproduced by the R-model, see Figure 5.8 (d). Still, the calculated amount of demagnetization is in reasonable agreement to measurements, and the calculation predicts correctly, for a fixed pump flux, nickel to exhibit the largest demagnetize among the transition ferromagnets [28]. In the calculations, iron shows the smallest demagnetization as it has the largest saturation magnetization of all the transition ferromagnets.
5. MODELING ULTRAFAST DEMAGNETIZATION

5.4.1 IMPLICATIONS OF THE R-MODEL

The physical mechanisms of the R-model are similar to the super diffusional approach from Battiato et al. [30, 34]. In his model, the imbalance between the velocities and scattering times above the Fermi level, for the two spin channels, cause a spin current to flow. For example in nickel, the physical origin is the steeper DOS for the majority states, causing the group velocity of the majority electrons to be higher than for the minority ones. The very same reason also drives the spin current in the R-model. A steeper DOS generates an enhanced shift of the chemical potentials for the majority electrons. However, the R-model reviles the involved physical processes in a more direct way.

The R-model predicts, by solving equation 5.23 for various film thicknesses, an approximately linear dependence of the demagnetization time on film thickness (see Figure 5.9 (a)) which is in line with the experimental data presented in Figure 4.2. Please note that the slope of the demagnetization increase on film thickness is about a factor of four off compared to the measurements. However, as discussed earlier, we do not expect the demagnetization time calculated by the R-model to precisely correspond with the measurements as the definition of the demagneti-
zation time in the R-model corresponds rather to the minimum of the demagnetization (see table 5.2) as a $1/e$ decay. Furthermore, the model is intended to reveal trends and orders of magnitudes, which it clearly can deliver. The R-model not only explains the relation between the demagnetization time and film thickness, it also explains the observed increase of the demagnetization time on bulk resistivity, see Figure 5.9 (b). As the resistivity is getting larger also the spin transport is less efficient and the demagnetization time increases. Equation 5.23 predicts a linear dependence of $\tau$ on resistivity $\rho$. However, Figure 5.9 (b) shows a more quadratic dependence $\tau \propto \rho^2$. A reason might be the fact that for $\tau > 1$ ps the assumption of a cold lattice, and thus equal resistivity for the laser heated or cold sample is not valid anymore. Furthermore, in the R-model, the sum of the spin dependent resistivities ($\rho_\uparrow + \rho_\downarrow$) is the important transport parameter. Thus, especially in half-metals, the minority conductivity will dominate $\rho_\downarrow$ and thereby the demagnetization time ($\tau \approx \rho_\downarrow$). Therefore, we expect the demagnetization time to grow super-linear on the measured resistivity (mostly $\rho_\uparrow$) for half-metallic samples. Please note that this view is compatible with recent observations [158, 159]: a larger degree of half-metallicity correlates with a slower demagnetization. The authors of Refs. [158, 159] explain this effect as the reduced density of minority states (in the view of the R-model corresponding to a higher resistivity in the minority channel) which suppresses majority to minority scattering events. It is intriguing that the two views, one based on scattering and the other one based on transport, describe similarly the enhanced demagnetization time for a higher degree of half-metallicity even though the explanations are fundamentally different. As the demagnetization time in the R-model depends crucially on the temperature gradient ($(U(0) - U(d))/d$), we would expect a homogeneously (along the film depth) heated electron gas not to demagnetize through spin transport. A way to achieve homogeneous heating is by using pump laser pulses in the picosecond regime. The time is large enough that the electron gas can equalize temperature gradients. A photoemission experiment employing such laser pulses (30 ps) was performed by Vaterlaus et al. [9]. Indeed, no demagnetization has been observed during the pulse, even though the pulses were strong enough to melt the iron film. However, pulses in the nanosecond time scale could demagnetize the film. Thus, the R-model unifies not only concepts of spintronics with ultrafast demagnetization, but can also explain the observed demagnetization time gap in iron on the picosecond time scale. To round-up the discussion, it is remarkable that the R-model, despite its simplicity, can reproduce and explain, without any fit parameters, a rich variety of ultrafast demagnetization observations.
5.5 I MPLICATION ON X-RAY ABSORPTION SPECTROSCOPY

Having seen that the chemical potentials of the hot electrons can be different for the two spin species and it’s gradient can give rise to a spin current, we can apply the framework to other experiments. Ultrafast time resolved XMCD measurements performed by Stamm et al. [46] showed a shift of the Ni $L_3$ x-ray absorption edge by $\approx 130$ meV toward smaller binding energy upon pumping with an intense IR pulse. This effect was attributed to an increase of valance band electron localization.

In this interpretation, the effect of the heat induced redistribution of electrons above the chemical potential was not considered and an intuitive understanding of the effect is missing. Carva et al. explained the effect by a repopulation of occupied states below the Fermi level, giving access to lower energetic states [138]. In the following, the effect is discussed for a thermalized electron gas and quantitative temperatures are derived to explain the effect.

In the above described x-ray absorption spectroscopy (XAS) experiment a 15 nm thick nickel film was heated by a IR pump pulse of 8 mJ/cm$^2$. The x-rays followed the pump beam at a constant time delay of 200 fs ([46]). Experiments performed by Rhie et al. [53] showed that the electronic distribution of nickel after 200 fs can...
already be well described by a Fermi-Dirac distribution. In their experiments, infrared laser pulses of 13 mJ/cm² intensity have been used. The electronic temperature was measured to lie far above 1000 K at 200 fs pump-probe delay. In the XAS experiment approximately half the pump power was used and it seems reasonable to assume, as a lower temperature bound, a homogeneously hot electron gas of 1000 K along the 15 nm thick nickel film. The nickel film after 200 fs has been measured by XMCD to be already ≈ 60% demagnetized [46], hence the magnetic reduction can not be neglected and needs to be considered: In a band picture, demagnetizing a ferromagnet can be understood as shifting the density of states for the majority electrons \( G^\uparrow (E + \Delta E^\uparrow) \) above the Fermi level, by an amount \( \Delta E^\uparrow \), and simultaneously shifting the minority density of states \( G^\downarrow (E + \Delta E^\downarrow) \) below the Fermi level, by an amount \( \Delta E^\downarrow \). During this process, an amount of \( \Delta n \) electrons are flipped from up- to down states. For the above procedure, we need to assume that a demagnetization does not change the shape of the spin resolved DOS. For nickel this is a valid assumption as DOS calculations [160] indicate. Mathematically, the amount of electrons per volume to be flipped to account for demagnetization can be expressed as:

\[
\Delta n = m^0 D / 2, 
\]

where \( m^0 = n^0_\uparrow - n^0_\downarrow = \int_{-\infty}^{\infty} (G_\uparrow(E) - G_\downarrow(E)) dE \) is the saturation magnetization in units of one per atom and \( D \) is the amount of demagnetization, \( D = 0 \) fully magnetized, \( D = 1 \) fully demagnetized. Here, \( n^0_{\uparrow,\downarrow} \) are the number of majority- and minority electrons per atom at zero temperature, respectively. With these values, the energy shift \( \Delta E_\sigma \) of the DOS \( G_\sigma (E + \Delta E_\sigma) \) for \( \sigma = \uparrow, \downarrow \) can be calculated to account for the demagnetization of \( D = 60 \% \) by numerically solving the equations:

\[
0 = n^0_\uparrow - \Delta n - \int_{-\infty}^{E_f} G_\uparrow(E + \Delta E^\uparrow) dE, 
\]

\[
0 = n^0_\downarrow + \Delta n - \int_{-\infty}^{E_f} G_\downarrow(E + \Delta E^\downarrow) dE. 
\]

The last step is to calculate the chemical potentials \( \mu_\sigma (T = 1000 \text{ K}) \) by numerically solving

\[
n^0_\uparrow - \Delta n = \int_{-\infty}^{\infty} G_\uparrow(E + \Delta E^\uparrow) f(E, \mu^\uparrow (T)) dE, 
\]

\[
n^0_\downarrow + \Delta n = \int_{-\infty}^{\infty} G_\downarrow(E + \Delta E^\downarrow) f(E, \mu^\downarrow (T)) dE. 
\]
After these calculations, we are ready to plot the occupation of the spin dependent DOS \( <n_\sigma(E)> = G_\sigma(E)f(E,\mu_\sigma(T),T) \) together with the chemical potentials, see Figure 5.10 (a). The chemical potentials are very close to the Fermi level and, hence, do not play a role for the discussion. The thermal energy within the electron system excites electrons to states above the Fermi level. This opens hole pockets below the Fermi level (red shaded areas in Figure 5.10) where x-rays can efficiently inject electrons. The effect is shown in more details in Figure 5.10 (b). Here, the sum for spin up- and down hole states \( n_h = n^1_h + n^\downarrow_h \) is plotted because XAS measurements were performed with linearly polarized x-rays [46] which do not distinguish between the minority- or majority band. A good measure to describe the shift is the center of mass of the heat induced hole states. Its absolute value is \( \approx 77 \text{meV} \) close to the observed shift of \( \approx 130 \text{meV} \) [46]. As discussed above, the calculated value lies below the observed value as the temperature of the electron gas is likely to be underestimated. A temperature of 1700 K of the electron gas would account for the observed \( \approx 130 \text{meV} \) shift. In addition, the above derivation is strengthened by the experimental finding that the XAS shifts approximately linearly towards lower binding energies when the nickel film is pumped harder [47].

Kachel et al. [47] argued that the \( L_3 \) satellite peak, shifts less than the \( L_3 \) peak, in favor of the localization explanation. However, in their calculations, laser induced repopulation was not considered. Still, it alone can already explain the XAS shift of the \( L_3 \) edge by a physically intuitive temperature effect.
In this chapter, we want to gather further experimental evidence for the presented theory in chapter 5 (R-model) and the underlying demagnetization mechanisms. For that purpose, pulse length dependent as well as double-pump experiments are carried out. The results of both experiments are in qualitative and quantitative agreement with the R-model. Furthermore, the experiments provide evidence that spin-flips based on the Elliott-Yafet process seem to have a minor influence for the ultrafast demagnetization.
JHON Kerr published in 1877 [35] and 1878 [36] two papers in which he described his observations that linear polarized light, reflected on a magnetized iron core, changes the polarization (rotation as well as ellipticity) depending on the magnetization direction. Today, such effects are summarized under the term magneto-optical Kerr effects (MOKE). MOKE is relatively easy to implement [161] and provides in first order a linear proportionality between the change of the polarization and the magnetization of the sample. Due to these amenities, MOKE became a standard technique in the quantitative study of equilibrium surface magnetization [161] and technologically relevant for magneto-optical data storage [162]. It was therefore evident to extend this technique also for the use in ultrafast pump-probe measurements [10].

In this chapter, time resolved MOKE measurements are discussed. All of them are in line with the R-model. The model implies that a longer pump pulse should result in a less efficient demagnetization, as the electronic system is given time to equilibrate its temperature. Pump length dependent experiments were carried out to study this effect. Moreover, the R-model predicts that the demagnetization time scales linearly with the sample’s resistivity. Thus, the demagnetization dynamics of a hot sample should be slower than for a cold sample. This effect is examined with a double pump pulse experiment where the demagnetization dynamics is measured for two shortly (picoseconds) delayed pump pulses.

### 6.1 Does MOKE Measure the True Magnetization?

Weather or not time resolved MOKE (TR-MOKE) measurements reflect the true magnetization of a sample during the first picosecond has been discussed controversially. Oppeneer et al. [41] showed theoretically and Koopmans et al. [40] experimentally that state-blocking effects affect the TR-MOKE signals. Koopmans et al. showed this behavior through an inequality between the change of the pump induced ellipticity and rotation. Hence, they concluded that TR-MOKE on the first 0.5 ps [40] can not faithfully represent the magnetization of a hot electron gas. However, Zhang et al. [42] claimed, based on ab-inito calculations, that TRMOKE can indeed be used on a sub-100 fs scale, given that the probe’s photon energy lies below 2 eV. The confusion was enhanced by experiments of several authors [11, 39, 163–165] claiming that the difference between the pump induced ellipticity and rotation is only marginal. In particular, Bigot et al. [11] showed that in nickel the TR-MOKE change in ellipticity reacts only a few 10 fs faster than its rotation change.

At least experimentally, it seems that both are right; they only compare different MOKE quantities: Koopmans et al. [40] compared the pump induced change of el-
lenticity/rotation for one magnetization direction only. The other authors [11, 39, 163–165] analyzed the difference of the ellipticity/rotation change for an up- and down magnetized sample. Comin et al. [164] compared both methods in their paper. And conclusively, by taking the difference signal, optical bleaching artifacts can be suppressed. Hence, at least from an experimentalists point of view, the discussion seems to be less controversial as it might look. Moreover, our own time resolved photoemission experiments on iron films (see section 2.4.3) where we retrieve a demagnetization time of $\tau = 45 \pm 50$ fs is fully compatible with TR-MOKE measurements of Carpene et al. [86] ($\tau \approx 60$ fs). For the above reasons, it seems that TR-MOKE can indeed be used on a sub 100 fs time-scale to measure the ultrafast magnetization response.

6.2 The Kerr setup

We employed the transversal Kerr effect and analyzed the change of the polarization rotation. We focus on the rotation change as its reaction to the pump pulse is slower than the change of the ellipticity [11]. The slower signal is presumably less affected by an immediate electron redistribution and represents therefore better the actual pump induced magnetization dynamics. A dichromatic pump-probe scheme is employed to suppress optical bleaching [40, 41] artifacts. The pump pulses have a wavelength of 800 nm and the probe pulses are frequency doubled to 400 nm. In the employed transversal Kerr geometry, the probe beam is sent onto the sample under an angle of 45 degree to the surface normal. The polarization of the light is parallel to the scattering plane and parallel to the sample's magnetization. The polarization change of the specular reflected beam is in first order proportional to the magnetization component along the initial magnetic polarization of the sample.

Figure 6.1 shows the experimental setup: a Ti:Sapphire amplified laser system provides intense (1 mJ/pulse) and short ($\approx 20$ fs FWHM of a Lorentzian pulse profile) pulses at a wavelength of 800 nm. The laser system is composed of an oscillator (Vitara) and an amplifier (Evolution) from Coherent Inc.. The amplifier is a combination of a regenerative- and a single pass amplifier. The repetition rate of the amplifier is 10 kHz and delivers an average power of 10 W for the pump- and 2 W for the probe beam. A specialty of the system are the two pulse compressors (CP 1,2) which allow for an individual pulse length compression of the pump- and the probe beams. The pulse length can be varied from 20 fs up to several picoseconds by adjusting these pulse compressors. In the following, the optical paths of the pump- and the probe beams are explained:

The pump beams’s power is adjusted by a $\lambda/2$-plate and a Brewster polarizer. The s-polarized component of the beam is deflected into a beam block. The beam is
Figure 6.1: Time resolved MOKE setup: The sample is heated by an intense infrared laser pulse. The induced magnetization change is measured stroboscopically by a blue probe pulse. The gray shaded box named “double pulse” is only in use for the double pulse experiment to produce two equally intense, but delayed pump pulses. Here, the following abbreviations have been used: CP 1/2 are the two pulse compressors, BBO is the frequency doubling Beta-Bariumborat crystal, WP is a Wollastone prism, HM hot mirrors (high pass filters), H the magnetic field to switch the sample, pol represents polarizers, and p,s p-or s-polarized light.

subsequently sent into a delay line\(^1\) with a repeatability of \(<2\text{ fs}\). For the double pulse experiments, explained later in the text, the optical components in the gray shaded box, named “double pulse”, are built into the optical path and generate two pump pulses who’s delay is changed by DL 2. Two achromatic lenses (foci are \(f_1 = 150\text{ mm}\) and \(f_2 = -75\text{ mm}\)) focus the beam onto the sample. The pump beam is chopped at a fixed frequency of \(83\text{ Hz}\).

The probe path has also its own pulse compressor module CP 2. The polarization is turned by a \(\lambda/2\)-plate to s-polarization, minimizing dispersion by passing the two following Brewster polarizers in reflection. The beam is turned back to p-polarization by a further \(\lambda/2\)-plate. The laser beam is narrowed by two achromatic lenses (foci are \(f_1 = 150\text{ mm}\) and \(f_2 = -75\text{ mm}\)) and frequency doubled to 400nm in a Beta-Bariumborat (BBO) crystal\(^2\). The remaining 800 nm light is filtered off by three dichroic mirrors (optimized for p-polarized light, reflecting 400 nm and transmitting 800 nm light). The last dichroic mirror is used to collinearly direct the probe- together with the pump beam onto the sample. After reflection on the sample, the pump beam is blocked by an aperture\(^3\). Spurious elliptic contribution in

\(^1\)M-521.DD from PI with 204 mm travel length.
\(^2\)Femtolasers FO 030, 5x5mm in size and 20\(\mu\)m thick.
\(^3\)Angle divergence of the pump and the probe beam is less than \(<1^\circ\) to minimize time broadening from the pulses’ phase fronts.
the probe beam is compensated by a λ/4-plate. The probe beam is further filtered by two high pass filters (HM), effectively blocking any 800 nm stray light contribution. The weak TR-MOKE signal is measured by a balanced detector formed by a Wollaston prism (WP) and two photo diodes. The two diodes are electrically connected in an antiparallel fashion. The λ/2-plate is adjusted (balanced) such that both of them get an equal amount of light. Thus, there is only an electrical signal present if one diode measures more than the other one. The influence of intensity variations, either from the fluctuations of the laser power, or from pump induced reflectivity changes, are thereby largely reduced. The electrical current signal from the diodes is measured with a lock-in amplifier, referenced at the pump’s chopping frequency. Due to the small Kerr rotation (< 1°) the difference of the measured photo current \( \Delta I(t) = I^\uparrow(t) - I^\downarrow(t) \) for an up/down magnetically saturated film is directly proportional to the change of the rotation \( \Delta \Theta(t) \). Here, \( t \) is the time delay between the pump and the probe pulse. In first order, the magnetization change is determined as to the change of the photocurrent \( \Delta M(t) \propto \Delta I(t) \). The relative change of the magnetization \( \Delta M(t)/M \) is calculated by measuring the static value \( M \propto \Delta \Theta = \Theta^\uparrow - \Theta^\downarrow \) by blocking the pump beam.

For beam diagnostics, a CCD beam profiler measuring the spacial overlap of the beams and their spot sizes, and an autocorrelator to determine the pulse length was used. The probe pulses are always adjusted to be as short as possible (20 fs FWHM Lorentzian shape) by adjusting CP 2. As the autocorrelation signal provides only limited information about the actual temporal pump pulse intensity distribution \( I_{pump}(t) \), its effective shape was measured by the use of a standard cross-correlation technique, for details see appendix C.

6.2.1 Sample

We used a titanium capped nickel film as the magnetic sample. The stack was grown by e-beam evaporation\(^4\) on a glass substrate. Onto that substrate the following layers were deposited: 5 nm Cr/50 nm Cu/20 nm Ni/3 nm Ti. To minimize spurious TR-MOKE contribution from spin polarized electrons within the cap layer, the low Z-material titanium (see section 3.1) has been chosen due to its small spin lattice coupling [37]. Chromium is used as a seed layer and the relatively thick copper layer is intended to promote a flat film growth. The surface is indeed flat as seen on scanning electron microscopy images, compare appendix C. The hysteresis loop (see appendix C) implies that the film forms magnetic domains. The coercive field is \( H_C \approx 6.3 \text{ mT} \). Therefore, during the TR-MOKE measurements, the sample is held at magnetic saturation by a field of \( H = \pm 15 \text{ mT} \).

\(^4\)Many thanks to the people from the evaporation service of the ETH Zurich.
6.3 Pump power and its influence on the remagnetization

The glass substrate of the magnetic sample does not conduct heat well. At first, a pump power dependent experiment was conducted to find a pump flux region where the magnetization dynamics is not dominated by dc heating.

6.3.1 Method

The used pump and probe pulses are both 20 fs long (FWHM Lorentzian) and their power level deviates less than 1% during the measurements. The pump beam is focused\(^5\) to 3 mm in width and 1.7 mm in height and the probe pulse to 0.35 mm in width and 0.32 mm in height\(^6\), to measure a homogeneously pumped film.

6.3.2 Results and Discussion

Figure 6.2 shows demagnetization curves for pump powers spanning from 0.38 mJ/cm\(^2\) to 5.3 mJ/cm\(^2\). As expected, a higher pump intensity results in a stronger demagnetization, and the remagnetization time depends strongly on the pump power. A dc heating influence is observed for a pump power of 5.3 mJ/cm\(^2\). At that power level, the sample’s saturation magnetization\(^7\) is reduced by \(\approx 5\%\) compared to a non-pumped sample.

Looking closer at the recovery dynamics, one reviles a faster- followed by a slower remagnetization (see e.g. the 2.3 mJ/cm\(^2\) trace, the turn over happens at about 4 ps, marked by an arrow). The two processes can be distinguished by the shape of the remagnetization curve: The first, faster recovery period is well fitted by an exponential function\(^8\) (see solid black line in Figure 6.2). This implies that the underlying mechanism can be described by a rate equation. On the other hand, the slow remagnetization tail seems well approximated (dashed black line in Figure 6.2) by a

---

\(^5\)“Width” is along the optical table’s surface, “height” is perpendicular to it.

\(^6\)Beam diameter is defined as the FWHM of a Gaussian fit and measured with a beam profiler.

\(^7\)Magnetization measured 1 ps before the pump beam arrives.

\(^8\)The usual double exponential fit function: \(\Delta M/M = A(1 - e^{-t/\tau})e^{-t/\rho} \Theta(t) \otimes G(t, \sigma)\), where \(G\) is a Lorentzian with 20 fs FWHM.
6.3. Pump power and its influence on the remagnetization

Figure 6.2: Pump power dependent measurements: A pump power of >3.8 mJ/cm² leaves the sample so hot that it cannot fully remagnetize between two pump pulses. The shape of the remagnetization reveals two processes: At first, the magnetization recovery is well described by an exponential process, and for longer times by a diffusional term. This indicates a transition from a rate model governed process to heat diffusion. As an example the 2.3 mJ/cm² curve is fitted, see text for details. The red pulse at time zero shows a 20 fs FWHM Lorentzian, representing the pump pulse length.
heat diffusional term as proposed by Koopmans et al. [40] of the form\(^9\),

\[
\frac{\Delta M}{M} \propto \frac{1}{\sqrt{t + t_d}},
\]

where \(t_d\) depends on the heat diffusion constant and the initial heat profile. This indicates that the tail of the remagnetization process is dominated by heat diffusion.

In addition to the the fact that such a clearly observable turn over exists, it is intriguing that the temporal position of the transition point shifts to longer times for higher pump intensity. It is not clear what causes this effect which clearly demands for further investigation of the remagnetization dynamics.

For the following experiments, intended to test the validity of the R-model, a pump flux of about 1.5 mJ/cm\(^2\) has been chosen. Therefore, we can probe the sample in the limit of a small perturbation and we do not expect a dc heating influence.

6.4 Pump pulse’s length influence on the demagnetization

The R-model presented in chapter 5 predicts indirectly that a longer pump pulse has to result in a smaller demagnetization, given that the pulse energy is kept constant. The reason is that for longer pump pulses, the electrons have time to equalize their temperature. Therewith, the chemical potential difference is smaller, and the depleting spin current is reduced. To test this prediction, a pump pulse length dependent demagnetization experiment was carried out.

6.4.1 Method

The pump pulse length is adjusted by pulse compressor CP 1. The pulse energy was 88 \(\mu\)J resulting in a pump energy density of 1.53 mJ/cm\(^2\). The probe pulse’s length was compressed to 20 fs FWHM (Lorentzian).

The length of the pump pulse was measured with an autocorrelator\(^10\). The stated FWHM values in this section represent values for Gaussian fits of the measured autocorrelation signal if not explicitly noted otherwise. Please note, the autocorrelation signal does not reflect the actual pulse shape. Its effective temporal profile has

\(^9\) The exact solution of the 1 dimensional heat diffusion equation \(\frac{\partial q(x, t)}{\partial t} = D \nabla^2 q(x, t)\) with heat density \(q(x, t)\), a constant diffusion coefficient \(D\), and an initial Gaussian heat distribution \(q(x, t=0) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}(x/\sigma)^2}\) is \(q(x, t) = \frac{1}{\sqrt{2\pi} \sigma \sqrt{t + \sigma^2 / D}} e^{-\frac{x^2}{2(t + \sigma^2 / D)}}\). Hence, at the center of the pump pulse \((x=0)\) the temporal evolution of the heat density is \(q(x = 0, t) \propto \frac{1}{\sqrt{t + \sigma^2 / D}} = \frac{1}{\sqrt{t + t_d}}\).

\(^10\) PulseCheck from Photonic Solutions.
6.4. Pump pulse’s length influence on the demagnetization

Figure 6.3: Pump pulse dependent measurements: (a) As the pump pulse’s length increases, the demagnetization amplitude is reduced. The inset shows the negative minimum of the magnetization curves and the time at which the minimum occurs in dependence of the pump pulse length. The dashed line is a linear fit to the data. (b) The 7 ps long pump pulse shows a clear slow down of the demagnetization at 2 ps.

to be determined in a separate cross-correlation experiment between the pump and the probe pulse. Such measurements have been carried out; cross-correlation traces and the corresponding autocorrelation traces are presented in appendix C.

6.4.2 Results and Discussion

Figure 6.3 (a) shows the demagnetization curves\(^{11}\) for pump pulses spanning from 40 fs to 7 ps FWHM. Two effects are directly observable:

1) As predicted, the demagnetization amplitude is reduced for longer pump pulses. The demagnetization amplitude is most sensitive for pump pulses below 1 ps length. Then, between 1 ps and 3 ps, there is a turn over to a weaker influence of the pump pulse’s length on the demagnetization amplitude, see inset in Figure 6.3 (a). Crudely speaking, it seems as if the 40 fs trace is the mother curve, all other traces follow its shape for time delays larger then their respective magnetization minimum. In addition, the time of the magnetization minimum scales linearly with the pump length as shown by the square points in the inset in Figure 6.3 (a). Consequently, the temporal position of the demagnetization curve’s minimum scales

\(^{11}\)For a good comparison, time zero is defined as the first data point which shows demagnetization. This is a well defined quantity even for long pulses, since the actual pump pulse shape starts with a steep power increase; compare appendix C and Figure 6.3 (b)
with the pump pulse length.

2) For delays larger than 15 ps the magnetization time traces become indistinguishable irrespective of the pump pulse duration. This implies that the recovery of the magnetization is fully governed by the temperature of the sample at this time which is equal for all pulses, irrespective of their length, since a constant pulse energy was used.

In the framework of Elliott-Yafet scattering, the transition rate \( W_{\vec{k}↑;\vec{k}'↓} \) from a spin up state (↑) with wave vector \( \vec{k} \) to a spin down state (↓) with wave vector \( \vec{k}' \) is given by [166]

\[
W_{\vec{k}↑;\vec{k}'↓} \propto \frac{1}{\omega_{\vec{q}}} \left( n_{\vec{q}} \delta(\epsilon_{\vec{k}↑} - \epsilon_{\vec{k}'↓} + h\omega_{\vec{q}}) + (n_{\vec{q}} + 1) \delta(\epsilon_{\vec{k}'↓} - \epsilon_{\vec{k}↑} - h\omega_{\vec{q}}) \right). \tag{6.2}
\]

The first \( \delta \)-term describes the transition rate caused by phonon absorption, and the second \( \delta \)-term transitions caused by phonon emission. Here, \( \omega_{\vec{q}} \) is the frequency of the phonon, \( n_{\vec{q}} \) is the number of phonons with wave vector \( \vec{q} \) in thermal equilibrium [166]. Equation 6.2 states that the transition rate increase with the number of phonons \( W_{\vec{k}↑;\vec{k}'↓} \propto n_{\vec{q}} \). We know from experiments by Wang et al. [151] that it takes about 2 ps for the lattice to reach its maximum temperature. Therefore, we would in principle expect the demagnetization rate \( W_{\vec{k}↑;\vec{k}'↓} \) to be smaller before this moment (< 2 ps) and larger afterwards (> 2 ps) when it is cooling down slowly (on a ps time scale). However, experimentally exactly the opposite is observed, see Figure 6.3 (b). We notice that the rate of demagnetization is bigger for delay times smaller than 2 ps than for delay times exceeding 2 ps. The two red lines are a guide to the eye and indicate the two regimes. Interestingly, the change of the slope happens at 2 ps, the time it takes the lattice to be thermalized [151]. Because there is no correlation between the peak of the pump pulse intensity \( I(t) \) at 1 ps and an extremum of the demagnetization signal, a pump pulse induced change of the slope seems very unlikely. However, the pump pulse is still heating the sample at the time the slope change happens. Therefore, the number of phonons is still increasing which should result in an enhanced spin-flip rate \( W_{\vec{k}↑;\vec{k}'↓} \) and an even stronger demagnetization. Hence, the observed slow down of the demagnetization is incompatible with an Elliott-Yafet type process.

However, the slope change is in favor of the R-model: When the lattice is thermalized at about 2 ps, also the resistivity \( \rho \) should have reached a maximum as electron-phonon scattering has maximized. The R-model predicts \( \tau \propto \rho \), based on this relation, the slow down in the demagnetization can be interpreted as the effect of an increased electrical resistivity and the therewith reduced spin depleting efficiency.

We can conclude this section by stating that the presented results from the pump
6.5. **DOUBLE PULSE EXPERIMENT**

In this section, we want to further test the validity of the R-model by pumping the sample with two delayed, but equally powerful, laser pulses. The first laser pulse heats the sample up. Then, a second delayed pulse pumps the already excited sample (see Figure 6.4).

We foresee the demagnetization dynamics induced by the first pulse to be faster than the dynamics induced by the second pump pulse analogously to the slow down effect observed in section 6.4. For the second pump pulse, the lattice is already hot, wherefore the resistivity should have increased and the demagnetization time prolonged. Furthermore, we expect both laser pulses to induce a similar amount of demagnetization. In the R-model the total amount of the demagnetization is independent of the resistivity (equation 5.24) and depends only on the amount of laser generated free charge carriers – which should be identical for the two pump pulses.

6.5.1 **METHOD**

The experiment is performed as shown in Figure 6.1 with the second delay stage (DL2) built in. The double pump pulses are generated by a 50% beam splitter pair and temporally delayed by DL2. The splitter pair guarantees the two pump pulses to carry equal energy as both pulses have identical optical paths. Power
measurements indeed show that the pulse energies of the two pump pulses deviate less than 2% from each other. The two pump pulses are delayed respectively to the probe pulse with delay stage DL1. A pump intensity of 2.5 mJ/cm² per pulse has been used. The size of the overlapping pump beams is 1.53 mm in width and 0.29 mm in height (Gaussian FWHM size), smaller than during the other experiments. Therefore, the average pump power is 340 mW, more than four times smaller than during the measurement of the 5.3 mJ/cm² trace in Figure 6.2 which showed dc heating. Hence, even with a higher pump density the smaller spot size allows for a more effective cooling, and we don’t observe dc heating effects. The probe pulse has a width of 0.56 mm and a height of 0.24 mm (Gaussian FWHM size).

6.5.2 RESULTS AND DISCUSSION
Figure 6.3 (a) shows the demagnetization change induced by the double pump pulse delays spanning from 0.5 ps to 4 ps. The two demagnetization steps are fitted by the standard fit function: \( \Delta M/M = A(1 - e^{-t/\tau_1})e^{-t/\rho} G(t,\sigma) \), where \( G(t,\sigma) \) describes a 20 fs Lorentzian. The resulting demagnetization constants \( \tau_1 \) for the first, and \( \tau_2 \) for the second pulse are shown in Figure 6.3 (b). Clearly, a longer demagnetization is observed for the second pump pulse. This is exactly the
result predicted by the R-model. Like in the pulse length dependent measurements, the observed prolonged demagnetization time is also incompatible with an Elliott-Yafet type interaction. In this model, the hot lattice for the second pulse should promote a higher spin-flip rate and a faster demagnetization. We can quantify the influence of the two effects: Equation 6.2 implies that phonons with the lowest energy (smallest \( \omega_\mathbf{q} \)) have the largest influence on the demagnetization. Hence, we can calculate the ratio between the scattering rates of a hot and a cold sample by approximating \( n_{-\mathbf{q}} + 1 \approx n_{\mathbf{q}} \) which holds in the limit of \( \omega_\mathbf{q} \to 0 \) as

\[
r(T_{\text{hot}}, T_{\text{cold}}) := \lim_{\omega_\mathbf{q} \to 0} \frac{W_{\mathbf{k}_1;\mathbf{k}_1'}(\omega_\mathbf{q}, T_{\text{hot}})}{W_{\mathbf{k}_1;\mathbf{k}_1'}(\omega_\mathbf{q}, T_{\text{cold}})} = \frac{n_{\mathbf{q}}(\omega_\mathbf{q}, T_{\text{hot}})}{n_{\mathbf{q}}(\omega_\mathbf{q}, T_{\text{cold}})} = \frac{g(\omega_\mathbf{q}, T_{\text{hot}})}{g(\omega_\mathbf{q}, T_{\text{cold}})} = \frac{T_{\text{hot}}}{T_{\text{cold}}}. \tag{6.4}
\]

Here, \( g(T, \omega_\mathbf{q}) = \frac{1}{e^{\hbar \mathbf{q}/k_B T} - 1} \) is the Bose-Einstein statistics. The used pump flux of 2.5 mJ/cm\(^2\) enhances the lattice temperature about 100 K\(^2\). The ratio of the rates in equation 6.4 has to be inversely proportional to the ratio of the demagnetization times

\[
r(T_{\text{hot}}, T_{\text{cold}}) = \frac{1/\tau_2}{1/\tau_1} = \frac{\tau_1(T_{\text{cold}})}{\tau_2(T_{\text{hot}})}. \tag{6.5}
\]

The numerical evaluation of equation 6.5 with \( T_{\text{cold}} = 300 \text{ K} \) and \( T_{\text{hot}} = 400 \text{ K} \) yields \( r(T_{\text{hot}}, T_{\text{cold}}) \approx 1.4 \). Therefore, based on an Elliott-Yafet interaction, we expect the second pulse (\( \tau_2 \)) to demagnetize about 40% faster than the first pulse. Experimentally, exactly the opposite is observed. The measurement for the 2 ps delayed pump-pump pulses gives a ratio\(^\text{13} \) of \( \tau_1/\tau_2 = 0.68 \pm 0.07 \), so a roughly 30% slower demagnetization for the second pulse. This discrepancy shows that an Elliott-Yafet type interaction is unlikely to be the main demagnetization promoter in our system.

The R-model predicts that the demagnetization time scales as \( \tau \propto \rho \). Using again the above temperature values, a ratio of \( \tau_1/\tau_2 = \rho(T_{\text{cold}})/\rho(T_{\text{hot}}) = 0.60 \) is estimated\(^\text{14} \); close to the measured ratio and herewith in line with the prediction of

\[\text{12}\] A p-polarized pulse impinging under 45° onto the sample has a transmission of about 40% into the film, see Figure 5.4. From an initial 2.5 mJ/cm\(^2\) strong pulse at best \( I = 1 \text{ mJ/cm}^2 = 2.5 \text{ mJ/cm}^2 \cdot 0.4 \) can be absorbed in a film thickness of \( d = 20 \text{ nm} \). This results in a temperature change of \( \Delta T = c_{\text{Ni}}d/\rho_{\text{Ni}} = 145 \text{ K} \) in the laser heated region, where \( c_{\text{Ni}} = 3.44 \text{ MJ/Km}^3 \). The temperature change is over-estimation as not the whole pump energy is absorbed and heat diffusion is neglected, therefore we use for the calculation the rounded value of \( \Delta T = 100 \text{ K} \), as we are only interest in a rough estimate.

\[\text{13}\] Note that the \( \pm \) spans a 95% confidence interval.

\[\text{14}\] Resistivity values are taken from Ref. [167] an interpolated to the given temperatures: \( \rho(T = 300 \text{ K}) = 7.12 \mu\Omega\text{cm} \) and \( \rho(T = 400 \text{ K}) = 11.8 \mu\Omega\text{cm} \). Note that in the R-model \( \tau \propto \rho_{\parallel} + \rho_{\perp} \). Since we used
the R-model.
We observed already in section 6.4 a slow down of the demagnetization in the pump length dependent measurements at a pump-probe delay of 2 ps. This effect was also interpreted as a sign of the resistivity increase. Hence, we would in principle also expect $\tau_2$ to depend on the pump-pump delay. Whether there exists such a relation for $\tau_2$ at short pump-pump delays remains speculative because the error bars in Figure 6.3 (b) are too large.

On the bases of the R-model, we expect the demagnetization amplitudes of the first pulse ($A_1$) to be close to the demagnetization amplitude of the second pulse ($A_2$) as they are predicted to be independent of the samples’ resistivities. Therefore, the ratios of the demagnetization amplitudes $A_1/A_2$ are expected to be close to unity. The computed ratios are presented in Figure 6.3 (c). The average over all four measured pulse-pulse delays is $\hat{A}_1/\hat{A}_2 = 0.92 \pm 0.06$. This value is slightly below one, indicating that the second pulse demagnetizes a bit more than the first one. However, taking also the 2% uncertainty of the pump power between the double pulses, and small alignment deviations of the three laser beams into account, the observed amplitude ratio is again in good agreement with the R-model.

\[ \rho_1 = 4\rho_1, \text{ where } \rho_1 \approx \rho \text{ we get } \tau_1/\tau_2 = \rho(T_{\text{cold}})/\rho(T_{\text{hot}}) \text{ and the factor 4 does not influence the result.} \]
DATA COMPILATION

Only literature data was considered where the demagnetization time was already fitted. Uncertainties in the demagnetization times were only taken in account if explicitly stated in the original papers, otherwise no error has been assumed. Table A.1 summarizes the used data points. It has been observed that the pump intensity can have an influence [157] on the demagnetization time. We took all trustable data for different quenching levels, avoiding an arbitrary selection. In case a paper presented several demagnetization times for different quenching levels, the points were averaged $\tau = \sum_{i=1}^{N} \tau_i / N$ and the error was calculated as: $\Delta \tau = \sqrt{\sum_{i=1}^{N} (\Delta \tau_i)^2 / N}$. Semiconducting half-metals have been excluded due to unpredictably large influence of the heat on the free carrier density and hence on resistivity. If data points had either the same thickness or the same resistivity value, they have been arithmetically averaged to form one data point.
### Table A.1: Compilation of literature data.

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<th>Sample</th>
<th>d (nm)</th>
<th>( r ) (fs)</th>
<th>( T ) (K)</th>
<th>( \rho ) (( \mu \Omega \text{cm} ))</th>
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</tr>
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<td>140</td>
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<td>140</td>
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<td>6.81</td>
<td>No</td>
</tr>
<tr>
<td>Fe(<em>{80})Ni(</em>{20})</td>
<td>10</td>
<td>89 ± 8</td>
<td>293</td>
<td>14 ± 1</td>
<td>No</td>
</tr>
<tr>
<td>Fe(<em>{80})Ni(</em>{20})</td>
<td>12</td>
<td>176 ± 12</td>
<td>298</td>
<td>14 ± 1</td>
<td>No</td>
</tr>
<tr>
<td>CrO(_2)</td>
<td>-</td>
<td>84000</td>
<td>298</td>
<td>250 ± 5</td>
<td>-</td>
</tr>
<tr>
<td>La(<em>{0.66})Sr(</em>{0.33})MnO(_3)</td>
<td>55</td>
<td>525000 ± 125000</td>
<td>298</td>
<td>1000</td>
<td>Yes</td>
</tr>
<tr>
<td>Sr(_2)FeMoO(_6)</td>
<td>bulk</td>
<td>95000 ± 850000</td>
<td>300</td>
<td>350 ± 20</td>
<td>Yes</td>
</tr>
<tr>
<td>SrRuO(_3)</td>
<td>600</td>
<td>90000 ± 600000</td>
<td>140</td>
<td>135 ± 10</td>
<td>No</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>15</td>
<td>&gt; 10(^6)</td>
<td>298</td>
<td>5000 ± 500</td>
<td>Yes</td>
</tr>
<tr>
<td>CoMnSb</td>
<td>100</td>
<td>18000</td>
<td>298</td>
<td>170 ± 10</td>
<td>No</td>
</tr>
<tr>
<td>Co(_2)MnSi</td>
<td>15</td>
<td>297</td>
<td>298</td>
<td>19 ± 1</td>
<td>No</td>
</tr>
</tbody>
</table>
B

ADDITIONAL INFORMATION ON THE SPLEED MEASUREMENTS

B.1 SPLEED-MOTT COMPARISON

B.1.1 SHERMAN FUNCTION
The Sherman function was acquired and the image was processed as described in chapter 3. The sample's bias voltage was tuned to select the secondary electrons of 20 eV kinetic energy in the flat P(E) region. The secondary electrons were generated by a 4 keV electron beam from a 15 ML Fe on W(110) film.

The raw camera images for an up and down magnetized sample were binned to 10 angular- and 100 energy intervals. One angular bin corresponds to one degree of angular acceptance. Figure B.1 (a) shows the intensity distribution and (b) the acquired Sherman map. This Sherman map is used to process the data presented in Figure 3.5. For the analysis, the window function \( W_{i,j} \) was chosen only for angular values with significant Sherman values, depicted as highlighted areas in Figure B.1.

B.1.2 SETTINGS
To compare the performance of the Mott with the SPLEED detector, the same spectrum of a 15 ML Fe on W(110) was measured with both detector types. The He VUV lamp was operated at the HeII line at 40.08 eV with the same photon intensity for both measurements. Table B.1 summarizes the measurements settings: The only

\[ V_{bias} = 0 \text{V}. \]
difference affecting the comparison of the two analyzers is the larger analyzer energy ($E_{kin}$) of the hemispherical energy analyzer during the Mott measurement causing a larger electron acceptance. Nevertheless, the SPLEED outperforms the Mott detector.

### B.2 Noise performance and balancing

#### B.2.1 Noise performance

In a Mott detector, the polarization of the incoming electrons is determined by equation 2.3. The relative change of the polarization $\Delta P/P$ in a pump probe experiment can then be determined by two different approaches:

**Method 1:** The pump and the probe pulses are always on. This means that the sample is always pumped yielding the time dependent polarization $P_{\text{pump}}(t)$, here $t$ denotes the time delay between the pump- and probe pulses. The relative polarization change is then given by

$$\frac{\Delta P}{P} = \frac{P_{\text{pump}}(t)}{P_0} - 1,$$

where $P_0$ is the polarization of the un-pumped sample.

**Method 2:** The pump pulses are only enabled for half of all the probe pulses. Therefore, we can determine a polarization for a pumped sample $P_{\text{pump}}$ and for a un-pumped sample $P_{\text{unp}}$. The relative change of the polarization is then given as

$$\frac{\Delta P}{P} = \frac{P_{\text{pump}}(t)}{P_{\text{unp}}(t)} - 1.$$
Table B.1: Overview of the measurements parameters for the Mott and the SPLEED comparison. The main difference of the two measurements is the larger analyzer energy ($E_{kin}$) during the Mott measurement. This results in a larger angular acceptance due to the larger sample bias $V_{bias}$, highlighted in bold. All the other relevant parameters are the same.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mott</th>
<th>SPLEED</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{path}$ (eV)</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Energy resolution (eV)</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>$E_{analyzer}$ (V)</td>
<td>100</td>
<td>63</td>
</tr>
<tr>
<td>$V_{bias}$ (V)</td>
<td>-80 to -60</td>
<td>-40 to -20</td>
</tr>
<tr>
<td>Step size of $V_{bias}$ (V)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Angular accept. ($V_{bias} = 0$V)</td>
<td>$\pm 2.2^\circ$</td>
<td>$\pm 3^\circ$</td>
</tr>
<tr>
<td>Angular accept. ($V_{bias} \neq 0$V)</td>
<td>$\pm 51$ to $\pm 63^\circ$</td>
<td>$\pm 35$ to $\pm 55^\circ$</td>
</tr>
<tr>
<td>Exit slit (mm)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Input slit (mm)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Int. time (h)</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Iris</td>
<td>fully open</td>
<td>fully open</td>
</tr>
</tbody>
</table>

Based on experience, Method 1 provides typically a better signal to noise ratio, since the signal is only divided through a constant, and not through an other noisy function. However, Method 2 might help to suppress drifts.

### B.2.2 Balancing

The importance of a balanced spin detector\(^2\) for time- and spin resolved photoemission is demonstrated in this section. We will see that without a balancing method no time resolved polarization spectra can be measured with a fluctuating photon source (such as an FEL). This effect is illustrated based on time- and spin resolved data acquired with the Mott detector at FLASH. The data used in this evaluation has also been used to generate Figure 2.9.

We limit our analysis to Method 1 (see section B.2.1) meaning that we treat only data where both the probe and the pump beam were on. As a reference trace, the

\(^2\)For example in a Mott detector, the two opposite electron detectors are balanced: for a given sample magnetization direction one detector counts more electrons than the other one. If the magnetization is reversed, the opposite is true.
fully balanced time resolved polarization change is defined as

$$\Delta P(C_1, C_3) := P\left(C_1^\uparrow(t), C_3^\downarrow(t)\right) - P\left(C_1^\downarrow(t), C_3^\uparrow(t)\right),$$  \hspace{1cm} (B.3)\]

where the function $P(C_1, C_2)$ is described by equation 2.3 and $C_{1,3}\uparrow, \downarrow(t)$ are the opposing electron detector signals in the Mott detector for either magnetization up ($\uparrow$) or down ($\downarrow$) at time delay $t$. Figure B.2 shows $\Delta P(C_1, C_3)$ in blue and we see a clear demagnetization curve.

We are interested in the question if it is also possible to retrieve time resolved spectra from a non-balanced detector. An example is a SPLEED with a constant Sherman map. This can be simulated by Mott data if we only consider the data of one electron detector (let’s assume $C_1(t)$). We would expect that by calculating $C_1^\uparrow(t) - C_1^\downarrow(t)$ a demagnetization signal should be visible. Far wrong, the green dots in Figure B.2 show that no demagnetization signal is recognizable. Hence, a reference signal is absolutely necessary. This implies that a SPLEED can only be used at a noisy source (FEL) if there are regions of high and low Sherman values in the Sherman map of the SPLEED. Fortunately, the Sherman map is generally not constant. It possesses regions of high and low Sherman values as can be seen for example in Figure B.1 (b). The easiest solution is to use the part where the Sherman function is almost zero as a reference ($I_0(t)$) and the part where it is larger as the signal ($C_1(t)$). This idea is tested on Mott data by defining $(C_2^\uparrow + C_4^\downarrow)/2 =: I_0$ which provides a magnetization state independent intensity measure\(^3\). We assume the signal channel to be $C_1(t)$. Thus we can calculate the polarization change $\Delta P(C_1, I_0) = P(C_1^\uparrow, I_0) - P(C_1^\downarrow, I_0)$ shown as the red curve in Figure B.2. We observe that this method delivers again the polarization signal! Of course, the noise level is worse than in the fully balanced case ($\Delta P(C_1, C_3)$) since the information of one detector is missing.

We can conclude that a time dependent polarization signal can only be retrieved (measured with a noisy source, such as a FEL) if a balancing signal is provided.

\(^3\text{Note the detector 2 and 4 measure the magnetization perpendicular to the easy direction.}\)
B.2. Noise performance and balancing

Figure B.2: The Mott data has been used to simulated different methods to retrieve the time dependent magnetic signal. Obviously, it is not possible to retrieve a signal by only one Mott detector channel (green curve). Two channels, providing balancing, are needed (blue and red curve) to retrieve the signal.
ADDITIONAL INFORMATION ON
THE MOKE MEASUREMENTS

C.1 PULSE LENGTH MEASUREMENT

Autocorrelation is a standard technique to measure a laser pulse’s length. However, with an autocorrelation measurement the pulse length can only be acquired by prior knowledge of the pulse shape. It’s shape is usually guessed by choosing from a set of standard fit functions (Gaussian, Lorentzian, Sech²) the one which fits the autocorrelation signal best. When the actual temporal pulse power $I(t)$ is of interest, the autocorrelation technique is insufficient to reconstruct $I(t)$, e.g. the autocorrelation is always symmetric.

Here, we are interested to measure $I(t)$ of the “pump” pulse. We do that by an optical cross-correlation technique (see Fig. (a)). A short (20 fs FWHM Lorentzian) sampling pulse is temporally and spatially overlapped with the “pump” pulse within a BBO crystal. Both are p-polarized, 800 nm beams. Their relative angle is $\delta = 5^\circ$, resulting in a time resolution of 50 fs given by the arrival time of the phase fronts. After the crystal, always two divergent beams at 400 nm emerge, the frequency doubled “pump”- and sampling beams. If the sampling- and the “pump” beam overlap also temporally, a third 400 nm beam emerges (cross-correlation signal) in the middle of the two other beams. This is due to the fact that frequency mixing conserves the photon momentum. The intensity of this third beam is proportional to the intensity of the “pump” beam at the time of the overlap. The whole trace $I(t)$ is then acquired by changing the delay $t$ between the “pump” and the sampling beam by a delay line. The cross-correlation signal is measured by a photodiode.
and any spurious 800 nm contribution is suppressed by a narrow bandwidth filter (path band 400 ± 20 nm). The photodiode’s current signal is conditioned with two lock-in amplifiers connected in series\(^1\).

Figure C.1 (b) shows the autocorrelation of differently long “pump” pulses. The legend denotes the FWHM determined by a Gaussian fit to the autocorrelation signals. Figure C.1 (c) depicts the cross-correlation for the same pulses, representing the actual \(I(t)\). From a glance, it is obvious that the autocorrelation signals do not represent the actual \(I(t)\) measured by the cross-correlation. The sampled pulses are not symmetric in time: they start with a steep increase, followed by a maximum in intensity, at their intermediate part they are flat, and slowly decreasing towards the end.

### C.2 SAMPLE CHARACTERIZATION

For the time resolved MOKE measurements, we used a e-beam grown sample (glass substrate/5 nm Cr/50 nm Cu/20 nm Ni/3 nm Ti). Figure C.2 (a) shows a hysteresis loop as measured by a continuous 650 nm laser beam in the longitudinal MOKE configuration. The hysteresis loop indicates the formation of magnetic domains.

---

\(^1\)The first lock-in is referenced at 10 kHz, the repetition rate of the laser, with a filter bandwidth of 1 ms. The second lock-in amplifier referenced at the chopping frequency of 83 Hz, filter bandwidth set to 100 ms.
The nickel film has a coercive field of $H_C \approx 6.3 \text{ mT}$. The flat tails for field strength above the coercive field ($|H| > H_C$) show magnetic saturation of the nickel film. Figure C.2 (b) depicts scanning electron microscopy images of the sample. The inhomogeneities at the bottom of the image are exceptions. Normally, the film appears structureless. The inset in Figure C.2 (b) shows the enlargement of a small particle residing on the film. The edges of the particle indicate the resolution of the SEM image to be $\sim 20 \text{ nm}$. The film on the side of the particle appears structureless, indicative for a good growth quality. The examined film was two month old and stored at ambient air.
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