Strong-Field Driven Charge and Spin Dynamics in Solids

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Zusammenfassung

Moderne Lasertechnologie ermöglicht es, optische Pulse zu erzeugen, die nur wenige Femtosekunden lang sind. Die Verwendung solcher ultrakurzer Laserpulse zur Steuerung von elektrischen Strömen könnte die Geschwindigkeit der Signalverarbeitung um mindestens drei Größenordnungen im Vergleich zur gegenwärtigen Spitzentechnologie erhöhen. Zu diesem Zweck müssen die mikroskopischen Grundlagen der Licht-Materie-Wechselwirkung erforscht werden. Dazu bietet sich die Anwendung der Attosekunden-Messtechnik an, die den Zugang zu Elektronenbewegungen auf deren natürlichen Zeitskala ermöglicht. Die vorliegende Arbeit behandelt die Entwicklung und Anwendung der Attosekundenmethodik, um die Wechselwirkung zwischen einem ultrakurzen optischen Laserimpuls und Elektronen im Inneren eines Festkörpers zu untersuchen.

Im Rahmen der Arbeit, die in dieser Dissertation präsentiert wird, werden drei spektroskopische Attosekunden-Messmethoden verwendet, um die kohärente Kontrolle der elektronischen und magnetischen Eigenschaften von Festkörpern unterschiedlicher Art zu studieren. Besonderes Augenmerk wird auf Dynamiken von optisch-angeregten Ladungsträgern in Silizium (Si) und Nickel (Ni) gelegt. Silizium ist ein Halbleiter mit indirekter Bandlücke: Es besitzt eine energetisch-verbotene Zone zwischen Valenz- und Leitungsband (Bandlücke), in der sich das Fermi-Niveau befindet. Im Gegensatz dazu ist Nickel ein Metall. Daher überlappen sich das Valenz- und das Leitungsband und das Fermi-Niveau befindet sich oberhalb der Leitungsbandkante. Die Untersuchung der Wechselwirkung zwischen ultrakurzen Laserpulsen und Festkörpern mit unterschiedlicher Bandstruktur könnte die Frage beantworten, ob es jenseits der alltäglichen linearen Wechselwirkung eine universelle Antwort von Festkörpern auf optische Anregung durch ultra-starke elektrische Felder gibt.

Durch Anwendung von Transienter Attosekunden-Absorptionsspektroskopie (TA) wird hier zum ersten Mal gezeigt, dass die elektronische Antwort von beiden Materialien auf einer Zeitdauer manipuliert werden kann, die kleiner als ein halber Zyklus des anregenden Laserpulses ist. Dennoch zeigen die experimentellen Ergebnisse einen wichtigen Unterschied in der Antwort der zwei betrachteten Materialien. Während die Ladungsträgerantwort von Silizium meistens durch die induzierte Polarisation gegeben ist, wird die Ladungsträgerantwort von Nickel stark durch die Anwesenheit von Elektronenströmen beeinflusst. Dies ist auf die optisch induzierte Beschleunigung der freien Elektronen zurückzuführen, die sich im Leitungsband eines metallischen Materials befinden.

Polarisations-Sampling Spektroskopie (PS) wird für die zeitaufgelöste Untersuchung der in den beiden Festkörpern auftretenden Nichtlinearitäten eingesetzt. Wenn sich der optische Puls im Medium ausbreitet, ändert er dessen elektronische Eigenschaften, d. h. das Material wird polarisiert. Die induzierte Polarisation gibt Aufschluss über die reversible und irreversible Energiemenge, die vom Puls auf das Material übertragen wird. Für zukünftige optoelektronische Anwendungen ist die dissipierte Energie ein wichtiger Faktor, der untersucht und idealerweise unterdrückt werden muss.

Die Analyse von Silizium zeigt, dass die Zwei-Photonen-Absorption und der Kerr-Effekt die zwei dominierenden nichtlinearen Effekte dritter Ordnung sind, die durch den optischen Puls induziert werden. Es wird beobachtet, dass sich diese beiden nichtlinearen Effekte, die den Brechungsindex von Silizium in entgegengesetzte Richtungen ändern, gegenseitig annähernd ausgleichen. Die nichtlineare Polarisation zeigt jedoch eine schwächere Intensitätsskalierung auf, als für eine Nichtlinearität dritter Ordnung erwartet wird. Dieses Verhalten zeigt, dass Nichtlinearitäten höherer Ordnung in ähnlicher Größenordnung wie Nichtlinearitäten niedrigster Ordnung (dritter Ordnung) einsetzen, was auf Tunneln durch die direkte Bandlücke (3.4 eV) von Silizium als Hauptanregungskanal für Elektronen schließen lässt. Die auf Silizium übertragene Energiemenge enthält eine reversible und eine irreversible Komponente, entsprechend der linear und nichtlinear übertragenen Energie. Durch den Vergleich zwischen der hier beobachteten nichtlinearen Eigenschaften von Silizium mit den Nichtlinearitäten von Quarzglas untersucht von Sommer et al. [1] ist bewiesen worden, dass die beiden Bandlücke-Materialien unterschiedlich auf die Anregung eines starken Feldes reagieren. Zusammenfassend beweist das PS Experiment, dass sich Silizium durch die optische Anregung von Elektronen mit starken optischen Feldern über die direkte Bandlücke von einem linearen Absorber in einen nichtlinearen Multi-Photonen Absorber umwandelt.

Das PS-Experiment in Nickel zeigt faszinierende Ergebnisse. Die primäre Nichtlinearität, die durch den optischen Puls verursacht wird, ist sättigbare Absorption die sich in unserem Experiment als Zunahme der Transmission bei steigender Intensität bemerkbar macht. Der Effekt kann als ein De-Metallisierungsprozess interpretiert werden, der durch Pauli-Blockierung der Elektronen im Leitungsband induziert wird. Der gemessene Phasenschub überschreitet den Wert $\pi/5$. Die entsprechende räumliche Verzögerung ist **10** mal die Dicke der Schicht. Folglich verhält sich die dünne metallische Schicht wie ein ultraschneller, schaltbarer Amplituden- und Phasenmodulator für ultrakurze optische Pulse.

Zum Schluss wird die ultraschnelle Magnetisierungsdynamik in Nickel erforscht. Als neuartige Messtechnik wird Attosekunden-Zirkulardichroismus angewendet, um gleichzeitig die Ladungs- und Spindynamik zu verfolgen. Die Technik kombiniert die Attosekunden-Zeitauflösung, die durch einen TA-basierten Aufbau gegeben ist, mit der Spin-Sensitivität, die aus dem magnetisch-zirkularen Dichroismus des magnetischen Materials folgt. Durch Verfolgung der elektronischen Antwort ist es möglich, die Ankunftszeit des Anregungspulses zu bestimmen. Die Ergebnisse zeigen den allerersten Prozess der Demagnetisierung auf einer Sub-Femtosekunden-Zeitskala. Das Experiment wurde sowohl mit einer Ni Schicht als auch mit einem Nickel/Platin- (Ni/Pt) Multilagen-System durchgeführt. Die Verringerung des magnetischen Moments in Nickel während der Wechselwirkung des Materials mit dem ultrakurzen Lichtimpuls wird nur in dem Ni/Pt-Multilagen-System beobachtet. Daraus folgt, dass der optisch-induzierte Spin-Transfer (OISTR) die primäre Ursache der ultraschnellen Demagnetisierung ist. OISTR ist die Migration Spin-gerichteter Elektronen von der Nickel- zur Platinschicht, die eine makroskopische Reduktion des magnetischen Moments von Ni verursacht. Dieser Grenzflächeneffekt wird in der Arbeit, von der in dieser Dissertation berichtet wird, zum ersten Mal experimentell bewiesen.

Abstract

Modern laser technology enables the generation of optical pulses which are only a few femtoseconds long. The use of such ultrashort laser pulses to produce electron currents could increase the speed of information processing by at least three orders of magnitude. For this purpose, the fundamentals of light-matter interaction need to be investigated. The application of attosecond metrology provides access to the electronic motion on its natural time scale. Therefore, it can be used to study the interaction between an ultrashort optical laser pulse and electrons inside a solid.

In the work of this thesis, three attosecond spectroscopic techniques are applied to study the coherent control of the electronic and magnetic properties of solids of different natures. Particular emphasis is given to the optically driven charge dynamics in silicon (Si) and nickel (Ni). Silicon is an indirect band-gap semiconductor: it has an energetically forbidden region between the valence and the conduction band (band-gap) where the Fermi level is located. In contrast, nickel is a metal: the valence and the conduction band overlap and the Fermi level resides above the conduction band edge. Studying the interaction between ultrashort optical pulses and solids with different electronic band structures could determine whether there is a universal response of solids to optical excitation.

By applying attosecond Transient Absorption (TA) spectroscopy, it is shown, for the first time, how the electronic response of both materials can be manipulated faster than a half cycle of the exciting laser pulse. However, the experimental results show an important dissimilarity in the response of the two materials. While silicon's carrier response is given only by the transient population transfer of electrons from the valence to the conduction band, nickel's carrier response is strongly influenced by the presence of electron currents. This is due to the optically-induced acceleration of the free electrons residing in the conduction band of a metallic material.

Polarisation Sampling (PS) spectroscopy is applied for the time-resolved study of the nonlinearities occurring in the two solids. When the optical pulse propagates through the medium, it changes its electronic properties, i.e. the material gets polarised. The induced polarisation provides information about the reversible and irreversible amount of energy transferred from the pulse to the material. For future optoelectronic applications, the dissipated energy is an important factor which should be investigated, and ideally suppressed.

The study of silicon reveals two-photon absorption and the Kerr effect as the two main third-order nonlinear effects induced by the optical pulse. These two nonlinear effects, which change the refractive index of silicon in opposite directions, are observed to balance each other out. However, the nonlinear polarisation exhibits a weaker intensity scaling than what is expected for a third-order nonlinearity. This behaviour indicates that higher-order nonlinearities are setting in with similar magnitude to the lowest order (thirdorder) nonlinearities, suggesting tunneling through the direct band gap (3.4 eV) of silicon as the main excitation channel for electrons. The amount of energy transferred to Si contains a reversible and an irreversible component, corresponding to the linear and nonlinear transferred energy. By comparing silicon's nonlinear features observed in the present experiment with the nonlinearities of fused silica studied by Sommer *et al.* [1], it is demonstrated that the two band gap materials react to strong-field excitation in a different manner. In conclusion, the PS experiment proves silicon's strong-field driven transition from being a linear absorber to being a nonlinear, direct band-gap absorber.

The PS experiment on nickel shows intriguing results. The main nonlinearity induced by the optical pulse is saturable absorption, which manifests as an increase in nickel's transmission with increasing intensity. This effect can be interpreted as a de-metallisation process induced by Pauli blocking within the conduction band. Ni's transition from a conducting to a semi-conducting material is reflected in the increase in the phase velocity of the transmitted pulse with respect to the incident pulse. The measured phase shift is larger than $\pi/5$. The corresponding spatial delay is **10** times the layer thickness. As a result, the thin metallic film acts as an ultrafast switchable amplitude and phase modulator for ultrashort optical pulses.

Finally, the ultrafast magnetisation dynamics of nickel are investigated. A novel technique called "atto-MCD" is applied to simultaneously track the charge and spin dynamics. The technique combines the attosecond time-resolution given by a transient absorption-based setup with the spin sensitivity given by the magnetic circular dichroism of a magnetic material. The results demonstrate the first measured process of demagnetisation on a sub-femtosecond time scale. The experiment is performed on a nickel film as well as on a stack of Nickel/Platinum (Ni/Pt) multilayers. The reduction of Ni's magnetic moment, while still interacting with the pulse, is observed only in the Ni/Pt multilayer system, indicating that Optically-Induced Spin Transfer (OISTR) is the main channel of ultrafast demagnetisation. OISTR consists in the migration of spin-oriented electrons from the nickel to the platinum layer, causing the macroscopic reduction of Ni's magnetic moment. This interface effect is first experimentally proven in the work reported in this thesis.

List of Publications and Conference

Contributions

I. List of Publications

• J. A. Gessner, Strong-field Band-structure Metamorphosis, in preparation.

The author designed and performed the experiment, analysed the data, discussed the results with the collaborators, prepared the figures and contributed to the manuscript.

M. Ossiander, K. Golyari, K. Scharl, L. Lehnert, F. Siegrist, J. P. Bürger, D. Zimin, J.A. Gessner, M. Weidman, I. Floss, V. Smejkal, C. Lemell, F. Libisch, N. Karpowicz, J. Burgdörfer, F. Krausz, M. Schultze, *Exploring the speed limit of optoelectronics*, submitted to Nature Communications (under review).

The author contributed to the benchmarking of the Linear Petahertz Photo-Conductive Sampling (LPPS) technique in gas.

F. Siegrist, J. A. Gessner, M. Ossiander, C. Denker, Y.-P. Chang, M. Schröder, J. Walowski, U. Mertens, A. Guggenmos, Y. Cui, U. Kleineberg, J.K. Dewhurst, M. Münzenberg, S. Sharma and M. Schultze, *Light-Field Coherent Control of Magnetism*, Nature, 571, 240, (2019)

Together with F. Siegrist, the author performed the experiment, analysed the data and contributed to the manuscript.

T. P. Butler, D. Gerz, C. Hofer, J. Xu, C. Gaida, T. Heuermann, M. Gebhardt, L. Vamos, W. Schweinberger, J. A. Gessner, T. Siefke, M. Heusinger, U. Zeitner, A. Apolonski, N. Karpowicz, J. Limpert, F. Krausz, and I. Pupeza, "Watt-scale

50-MHz source of single-cycle waveform-stable pulses in the molecular fingerprint region," Opt. Lett. 44, 1730-1733 (2019)

The author built the FROG setup and performed the FROG measurements for the characterisation of the mentioned laser system.

II. List of Conference Contributions

- J. Gessner, F. Siegrist, M. Ossiander, C. Denker, Y. Chang, M. C. Schröder, A. Guggenmos, Y. Cui, J. Walowski, U. Martens, J. K. Dewhurst, U. Kleineberg, M. Münzenberg, S. Sharma, and M. Schultze, *Petahertz Magnetization Dynamics*, Conference on Lasers and Electro-Optics Europe (CLEO), <u>highlighted talk</u> (2019)
- F. Siegrist, J. A Gessner, M. Ossiander, C. Denker, Y. Chang, M. C. Schröder, A. Guggenmos, Y. Cui, J. Walowski, U. Martens, J. K. Dewhurst, U. Kleineberg, M. Münzenberg, S. Sharma, and M. Schultze, *Light-Wave Driven Magnetization Dynamics*, Conference on Attosecond Science and Technology, (2019)
- J. A. Gessner, F. Siegrist, M. Ossiander, C. Denker, Y. Chang, M. C. Schröder, A. Guggenmos, Y. Cui, J. Walowski, U. Martens, J. K. Dewhurst, U. Kleineberg, M. Münzenberg, S. Sharma, and M. Schultze, *Attosecond Spintronics*, American Physics Society (APS) March Meeting, <u>invited talk</u> (2020)
- J. A. Gessner, F. Siegrist, M. Ossiander, C. Denker, Y. Chang, M. C. Schröder, A. Guggenmos, Y. Cui, J. Walowski, U. Martens, J. K. Dewhurst, U. Kleineberg, M. Münzenberg, S. Sharma, and M. Schultze, *Ultrafast Charge and Spin Dynamics in Ferromagnets*, Conference on Lasers and Electro-Optics USA (CLEO), <u>highlighted talk</u> (2020)

III. List of Prices and Awards

 Tingye Li Innovation Prize, Conference on Lasers and Electro-Optics Europe (CLEO) (2020)

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Chapter 1

Introduction

In the past century, the development of faster and more efficient electronic devices has given access to the processing and transfer of information on Gigahertz clock rates [2]. However, modern electronics is based on classical charge transport, which is intrinsically an incoherent process. This constitutes the fundamental limit to go beyond GHz frequencies. In fact, in the absence of coherence, heat generation and power dissipation occur, limiting the progressive miniaturization of electronic devices [3,4]. Since **1975**, the progress of technology has followed Moore's law by being able to double the number of transistors on a microprocessor chip every ~ two years [5]. This has generally coincided with a doubling of the chip performance as well. Nevertheless, Moore's prediction is expected to slow down in the coming years, as the limitation in downsizing inevitably leads to a limitation in integration on a chip [6].

New fabrication techniques as ultraviolet (UV) lithography have enabled the realisation of few nanometre sized transistors [7,8]. The actual record of **1** nm long physical gate is reached by a device consisting in a MoS_2 bilayer as a channel material and a carbon nanotube gate electrode [9].

The implementation of such lithographic techniques has the disadvantage of being expensive, which restricts the production of nanometre transistors and their on-chip integration. Furthermore, the downsizing of electronic devices is not only limited by energy losses, heating and costs, but also by a more fundamental physical limit: the interatomic distance. When the size of the circuit approaches a few nanometres, quantum-mechanical effects set in. More precisely, in a system constituting of only a few atoms, electrons are able to tunnel through energetically forbidden regions. Clearly, such devices are unpredictable and unreliable [6,10].

One of the possible alternatives for pushing data processing to much higher speed is given by optical technology [11]. Conventional electronics is based on the manipulation of the charge of electrons by applying a voltage to the circuit. By comparison, optoelectronics is based on the control of the electrons' charge with light, which is an entirely coherent process. In the last **25** years, the progress in the field of laser physics has led to the generation of light pulses which last only a few femtoseconds. These ultra-short laser pulses can be used to control the flow of electrons in a circuit on the same time-scale as the pulse duration or even shorter.

The natural time scale of electronic motion is in the attosecond (10^{-18} s) regime. The birth of attosecond metrology in 2001 [12,13], enabled the real-time observation of the interaction between light pulses and electrons in atomic systems. These revolutionary measurement techniques have opened the door to the investigation of materials which can

be potentially used in future optoelectronic devices. Silicon photonics represents a captivating candidate, as it is possible to use the same underlying technology of electronic devices [14]. In conventional electronics, the electron flow between the valence and the conduction band is controlled by applying an external voltage. The speed of switching, however, is limited by the impedance of the electrodes and interconnecting structures. The optical control and switch of the conducting state of silicon (Si) has already been demonstrated in **1974** by D. H. Auston [15]. With the so-called "Auston switch" it has been demonstrated that the electronic signal can be optically manipulated on a picosecond time scale. Further experiments in the following years have improved the speed of the optical control in Si [16] and extended it to a wide range of semiconducting materials [17,18].

Additionally, insulators have gained attention for applications in optoelectronics. As insulators have a larger band-gap compared to semiconductors ($E_g > 4 \text{ eV}$), the required peak intensities for the laser pulses are one or two orders of magnitude higher. Recent developments in the field of laser technology have enabled the generation of short and intense pulses, making it possible to investigate wide-band gap materials. Studies on fused silica have shown that its electron dynamics can be manipulated with sub-femtosecond time resolution [19]. Furthermore, the change of the electron population distribution was found to reverse in less than **5** femtoseconds. These results represent a promising step towards future insulator-based optoelectronic devices.

Recently, thin metallic and semi-metallic nano-films have started to gain interest. Examples are graphene [20], titanium nitride [21], gold and silver [22]. The treatment of nanometre thick membranes allows to bypass the problem of low optical transmittance, which is typical of metallic bulk materials. In this manner, also the study of their optical properties has become less challenging.

Metallic structures are attractive not only in the field of optically driven electronics, but also in plasmonics and spintronics. The first is based on metal-dielectric interfaces on the nanometre scale for the optical manipulation of electrons [23]. It utilizes the coherent, optically-induced electron oscillations (the so-called *surface plasmon polaritons*, or SPPs) which travel along the interface between the dielectric and the metal.

Spintronics uses both the charge and spin properties of ferromagnetic materials for optical processing of signals. The introduction of an additional degree of freedom, compared to standard electronics, increases the efficiency of the storage and transfer of data. The pioneering experiment in the field of ultrafast demagnetisation was the one performed by Beaurepaire *et al.* in **1996** [24]. The authors measured, for the first time, the reduction of the magnetic moment inside a ferromagnet on a sub-picosecond time scale. The experiment was performed with a **60** fs long optical pulse by measuring the time-resolved magneto-optical Kerr effect (MOKE) inside nickel. Future works have shown further improvement in the speed of demagnetisation in ferromagnetic films [25,26], as well as in multilayers and alloys [27–29].

For the realisation of spintronic devices, it is crucial to not only change the state of magnetisation, but also to switch it back to its original state. The first successful attempt was accomplished in **2002** [30] by using a picosecond magnetic field pulse. However, the first all-optical switching was achieved six years later with the application of circularly polarised pulses [31]. Here, the direction of switching is given only by the helicity of the laser pulse. In the experiment, the change in the magnetic moment was observed with a polarising microscope. As a consequence, the time scale on which the magnetic state was changed could not be determined.

2

The advent of attosecond metrology enabled the observation of not only the time-resolved interaction of light with the charge of electrons, but also the interaction of light with the electronic spin. For instance, attosecond XMCD (X-Ray Magnetic Circular Dichroism) spectroscopy permits to time-track the change of magnetic moment, induced by an optical pulse, by probing the dynamics with circularly polarised XUV pulses.

Regarding the electronic properties of a material, attosecond Transient Absorption (TA) spectroscopy can be applied for studying the change of electronic population distribution in the valence and the conduction band of a solid. One more aspect which plays a crucial role when a light pulse propagates through a medium, is the optically-induced linear and nonlinear modification of the material. In particular, the induced polarisation is responsible for the energy losses inside the solid, which are of fundamental importance in the field of signal processing. Polarisation Sampling (PS) spectroscopy allows to track the intraband carrier dynamics and derive the amount of energy deposited inside the material.

This thesis aims to study the fundamental processes of light-matter interaction on a subfemtosecond time scale. The above-described attosecond measurement techniques (TA and PS), are applied to scrutinize the charge dynamics in nickel (Ni) and silicon (Si). Four main questions are addressed in the study of their electronic properties: a) Do semiconductors and metals respond the same way to the excitation of a strong and ultrashort laser pulse? b) If not, what makes them behave differently? c) How fast can electrons be controlled in the two materials? d) What is the amount of energy transferred from the exciting pulse to the electronic system?

In addition to the charge dynamics, the magnetic properties of nickel are tracked with a novel measurement technique based on XMCD. Combining the time resolution given by attosecond spectroscopy with the generation of circularly polarised XUV pulses for tracking the magnetic moment, the optically-induced demagnetisation in Ni is studied on a sub-femtosecond time scale.

Descriptive Outline and Summary of the Most Important Results

The thesis is divided in eight chapters. The **second chapter** gives a theoretical background for understanding the main physical processes behind the work of this thesis. Starting from the nonlinear wave equation, the first part is dedicated to the description of third-order nonlinear effects such as two-photon absorption, the Kerr effect and saturable absorption. In the second part, the fundamentals of ferromagnetism and magnetic circular dichroism are given.

Before introducing the time-resolved experiments, the nonlinearities in silicon and nickel are examined in a time-integrated manner. The results are presented in **chapter 3**. Si is investigated by applying the z-scan technique: with a powermeter, the change in transmitted power is measured as a function of the position of the sample along the beam propagation axis, i.e. as a function of the incident intensity. As nickel exhibits a small change in transmission along z, the signal is detected with a photodiode and a boxcar averager. While silicon exhibits a lower transmission for high intensities, nickel shows the opposite behaviour. These phenomena and their origin are further investigated in a time-resolved way.

The **forth chapter** is dedicated to the description of the three attosecond measurements techniques applied in the work of this thesis. In all the experiments, the same Ti:Sa-based laser system is used (see Appendix A). First, the setup and the working principle of transient absorption spectroscopy is described. This is presented together with an

overview about streaking spectroscopy, as the technique is utilized for detecting the electric field of the pulse. After, the setup and the working principle of polarisation sampling are reported. The field-resolved detection technique used in this experiment is Linear Petahertz Photo-conductive Sampling (LPPS). Finally, the novel technique of atto-MCD is presented. For the realisation of circularly polarised XUV pulses, an XUV phase retarder is used. Its characterisation is also presented in this part of the thesis.

Both the optically-induced interband and the intraband charge dynamics in silicon are analysed in **chapter 5**. The first part is dedicated to the study of the interband dynamics. The results first demonstrate how the electronic motion in silicon can be manipulated within less than a half cycle of the laser pulse. This can be observed in the TA signal, which oscillates with twice the frequency of the laser pulse. Furthermore, by combining TA with attosecond streaking, the modulated carrier response is measured in synchrony with the waveform of the laser pulse, revealing the absolute timing (i.e. the phase) between the exciting electric field and the observed oscillations. The comparison shows perfect synchrony with the extrema of the electric field, which allows to recognise the induced polarisation as the main responsible for silicon's oscillating electronic response. In the second part, the intraband carrier motion in Si is studied with polarisation sampling. The measured transmitted electric fields at high and low intensity indicate for a balanced action of two-photon absorption and the Kerr effect. Moreover, the linear and the nonlinear components of the induced polarisation are retrieved from the measured fields and allow to determine the amount of energy deposited into the sample. The results exhibit a reversible linear component and an irreversible nonlinear component of the deposited energy. Finally, the study of the intensity dependence of the nonlinear polarisation demonstrates a strong influence of higher order nonlinearities, suggesting tunnelling through the direct band gap of Si as the possible main channel of electron excitation. As a result, silicon turns into a nonlinear direct band-gap absorber when interacting with a strong and ultrashort optical pulse.

The charge dynamics of nickel are studied in **chapter 6**. This chapter is structured as chapter 5. In the first part, the presented TA results exhibit the same oscillating behaviour of the XUV transmission change as in silicon. Differently, the parallel detection of the pulse waveform with streaking shows the oscillations to be in synchrony with the vector potential of the pulse. Therefore, the results prove that in a metallic system, the modulated electronic response is dominated by the electron currents within the conduction band.

The intraband dynamics of nickel is presented in the second part. Here, two main effects related to the amplitude and the phase of the transmitted pulse are observed. The detected transmitted fields show an intensity-dependent amplitude. In other words, for relatively low intensities, saturable absorption is the main effect governing nickel's nonlinear response. The observed increase in transmittance with increasing intensity can be understood as the optically driven de-metallisation of Ni and results in a negative nonlinear transfer of energy. The deposition of the total energy, as well as its linear and nonlinear component, is irreversible. The transition from a conducting to a semiconducting behaviour is observed as well in the increase of the phase velocity of the transmitted field with respect to the incident electric field. At high intensities, the saturation of absorption is reversed: Ni starts absorbing more again. On the other hand, the phase shift of the field after propagating through Ni continues to increase, reaching a maximum corresponding to **10** times the layer thickness. In conclusion, the findings reported in this chapter demonstrate the band-structure metamorphosis of a thin nickel film when interacting with a strong optical field. The observed effect implicates that the metallic film can be used for controlling the amplitude and phase of an ultrashort optical pulse.

Chapter 7 is dedicated to the spin dynamics in nickel. The presented results have been published in [32,33]. The novel technique of atto-MCD is applied to track the optically-induced change in magnetic moment in Ni on a sub-femtosecond time scale. At the same time, the technique allows to measure the electronic response of Ni, giving time-zero for the arrival of the laser pulse. The experiment is performed on a thin nickel film as well as on a Nickel/Platinum (Ni/Pt) multilayer system. The instantaneous reduction of the magnetic moment is observed only in the Ni/Pt sample, revealing the Optically-Induced Spin Transfer (OISTR) from the Ni to the Pt layer as the channel of ultrafast demagnetisation.

At the end of chapter 3, 5, 6 and 7, a section is dedicated to the main findings and possible future experiments related to the work reported here. The last chapter (**chapter 8**) summarizes all the important results presented in this thesis.

Chapter 2

Theoretical Description of Light-Matter

Interaction

The present chapter is divided into two main sections with the aim of providing robust theoretical fundaments for the experimental work performed in this thesis. The purpose is to study the dynamics of light-matter interaction, where both the electronic and the magnetic properties of a material can be modified by a strong laser pulse. The first part describes the formalism of charge dynamics based on the Maxwell equation and the work of Brabec and Krausz. This will be used to illustrate different nonlinear effects that can be induced in a medium by a strong pulse. After, the linear absorption of XUV radiation is presented. This plays a crucial role in detecting both charge and spin dynamics. The second part regards the description of magnetism. Here, the general concept of ferromagnetism is presented, as well as the principle of magnetic circular dichroism that is extended to sub-femtosecond time resolution in the cause of this work.

2.1 Strong-Field Induced Charge Dynamics

When a light pulse interacts with matter, its electric field changes the electronic properties of the material by creating oscillating dipoles which emit radiation. The created dipole moment per unit volume is defined as the polarisation of the medium $P(\vec{r}, t)$ induced by the light field $E(\vec{r}, t)$. The coupling between $E(\vec{r}, t)$ with $P(\vec{r}, t)$ is described by the Maxwell equations [34,35] which can be rewritten as the nonlinear wave equation [36]:

$$-\nabla^2 E(\vec{r},t) + \frac{1}{c^2} \frac{\partial^2 E(\vec{r},t)}{\partial t^2} = -\frac{1}{\varepsilon_0 c^2} \frac{\partial^2 P(\vec{r},t)}{\partial t^2}$$
(2.1)

Where c is the speed of light and ε_0 is the permittivity in vacuum. In the derivation of Eq.(2.1), it is assumed that there are no free charges ($\rho = 0$) and free currents (J = 0) [36]. If the electric field is weak, the induced polarisation depends linearly on $E(\vec{r}, t)$:

$$P(\vec{r},t) = P_L(\vec{r},t) = \varepsilon_0 \int d\vec{r} \chi^{(1)}(\vec{r},t) E(\vec{r},t)$$
(2.2)

Where $\chi^{(1)}(\vec{r}, t)$ is the first order susceptibility of the medium. $\chi^{(n)}(\vec{r}, t)$ are tensors of rank n + 1. To simplify the following theoretical model, it will be treated as a scalar and the material response will be assumed instantaneous.

If the electric field is strong, nonlinear effects take place inside the material and also higher order terms must also be considered in the polarisation:

$$P(\vec{r},t) = \varepsilon_0 \int d\vec{r} (\chi^{(1)} E(\vec{r},t) + \chi^{(2)} E^2(\vec{r},t) + \chi^{(3)} E^3(\vec{r},t) + \mathcal{O}(E^4(\vec{r},t')))$$
(2.3)

$$P(\vec{r},t) = P^{L}(\vec{r},t) + P^{NL}(\vec{r},t)$$
(2.4)

 $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order susceptibility, respectively. It shall be noticed that nonlinear phenomena are a property of the medium through which light propagates and not of light itself, therefore they can't be observed in vacuum if not at extremely high intensities.

Even orders of nonlinear interaction with a strong field can't be observed in centrosymmetric media because of inversion symmetry ($\chi^{(0)} = 0$, for *l* even). Since both materials subject to our study (silicon and nickel) are centrosymmetric, second-order effects won't be discussed. In this case, third-order nonlinearities are the dominant response to strong fields. They can take place in both centrosymmetric and noncentrosymmetric media.

The following part is dedicated to the derivation of a generalized nonlinear Schrödinger equation. It was first obtained by Brabec and Krausz [36,37] and can be used to describe many nonlinear effects.

As a first step, the displacement field $D(\vec{r}, t) = \varepsilon_0 E(\vec{r}, t) + P(\vec{r}, t)$ is introduced, which similarly to the polarisation can be decomposed in its linear and nonlinear part:

$$D(\vec{r},t) = D^{L}(\vec{r},t) + P^{NL}(\vec{r},t)$$
(2.5)

Considering Eq.(2.5) and the relation between first order susceptibility and permittivity $\chi^{(1)} = \varepsilon^{(1)} - \mathbf{1}$, the linear component of the displacement field becomes $D^{L}(\vec{r}, t) = \varepsilon_{0}\varepsilon^{(1)}E(\vec{r}, t)$.

Equation (2.1) can now be rewritten as follows:

$$-\nabla^2 E(\vec{r}, t) + \frac{\varepsilon^{(1)}}{\varepsilon_0 c^2} \frac{\partial^2 E(\vec{r}, t)}{\partial t^2} = -\frac{1}{\varepsilon_0 c^2} \frac{\partial^2 P^{\text{NL}}(\vec{r}, t)}{\partial t^2}$$
(2.6)

By Fourier-transforming $E(\vec{r}, t)$ and $P^{\text{NL}}(\vec{r}, t)$

$$E(\vec{r},t) = \frac{1}{2\pi} \int \tilde{E}(\vec{r},\omega) \exp(i\omega t) d\omega$$
(2.7)

$$P^{\rm NL}(\vec{r},t) = \frac{1}{2\pi} \int \tilde{P}^{\rm NL}(\vec{r},\omega) \exp(i\omega t) d\omega$$
(2.8)

We get Eq.(2.6) in the frequency domain:

$$\nabla^{2} \tilde{E}(\vec{r},\omega) + \frac{\varepsilon^{(1)}\omega^{2}}{c^{2}}\tilde{E}(\vec{r},\omega) = -\frac{\omega^{2}}{\varepsilon_{0}c^{2}}\tilde{P}^{\mathrm{NL}}(\vec{r},\omega)$$
(2.9)

Eq.(2.9) can be solved with the slowly-evolving wave approximation, where the amplitude of the propagating electric field $E(\vec{r}, t)$ and of the induced polarisation $P^{\text{NL}}(\vec{r}, t)$ are assumed to not change significantly within one wavelength:

$$E(\vec{r},t) = A(\vec{r},t) \exp(-i(k_0 z - \omega_0 t)) + c.c.$$
(2.10)

With its amplitude:

$$A(\vec{r},t) = \frac{1}{2\pi} \int \tilde{A}(\vec{r},\omega) \exp(i\omega t) d\omega$$
(2.11)

In the same way the nonlinear polarisation is approximated to:

$$P^{\mathrm{NL}}(\vec{r},t) = p^{\mathrm{NL}}(\vec{r},t) \exp(-i(k_0 z - \omega_0 t)) + c.c. \qquad (2.12)$$

$$p^{\rm NL}(\vec{r},t) = \frac{1}{2\pi} \int \tilde{p}^{\rm NL}(\vec{r},\omega) \, exp(i\omega t) \, d\omega$$
(2.13)

With \mathbf{k}_0 the linear part of the wavector of the carrier frequency ω_0 .

The frequency-dependent field $\tilde{E}(\vec{r},\omega)$ is related to $\tilde{A}(\vec{r},\omega)$ by: $\tilde{E}(\vec{r},\omega) \approx \tilde{A}(\omega',t) \exp(i(k_0z))$, with $\omega' = \omega - \omega_0$. This allows Eq.(2.9) to be rewritten in terms of the field $\tilde{A}(\vec{r},\omega')$ and the polarisation $\tilde{p}^{\text{NL}}(\vec{r},\omega')$ amplitude:

$$\nabla_{\perp}^{2}\tilde{A}(\vec{r},\omega') + \frac{\partial^{2}\tilde{A}(\vec{r},\omega')}{\partial z^{2}} + 2ik_{0}\frac{\partial\tilde{A}(\vec{r},\omega')}{\partial z} + [k^{2}(\omega') - k_{0}^{2}]\tilde{A}(\vec{r},\omega') = -\frac{\omega^{2}}{\varepsilon_{0}c^{2}}\tilde{p}^{\mathrm{NL}}(\vec{r},\omega')e^{-ik_{0}z}$$

$$(2.14)$$

Where $k^2(\omega') = \frac{\omega^2}{c^2} \varepsilon(\omega')$. Next, $k(\omega')$ is approximated as a power series of the difference $\omega' = \omega - \omega_0$:

$$k(\omega) = k_0 + k_1(\omega - \omega_0) + D$$
 (2.15)

Where $D = \sum_{n=2}^{\infty} \frac{1}{n!} k_n (\omega - \omega_0)^n$ represents all the high-order dispersion terms. The contribution of D^2 will be neglected because it is invariably small.

Eq.(2.14) can now be Fourier-transformed back and a retarded time frame (moving reference frame) defined by z' = z and $\tau = t - \frac{1}{v_g}z = t - k_1z$ such that $\frac{\partial}{\partial z} = \frac{\partial}{\partial z'} - k'\frac{\partial}{\partial \tau}$ and $\frac{\partial}{\partial t} = \frac{\partial}{\partial \tau}$ is introduced:

$$\begin{bmatrix} \nabla_{\perp}^{2} + +2ik_{0}\frac{\partial}{\partial z'}\left(\mathbf{1} + \frac{ik_{1}}{k_{0}}\frac{\partial}{\partial t}\right) + 2k_{0}\widetilde{D}\left(\mathbf{1} + \frac{ik_{1}}{k_{0}}\frac{\partial}{\partial t}\right) \end{bmatrix} A(\vec{r},\tau)$$

$$= -\frac{\omega_{0}^{2}}{\varepsilon_{0}c^{2}}\left(\mathbf{1} + \frac{i}{\omega_{0}}\frac{\partial}{\partial t}\right)p^{\mathrm{NL}}(\vec{r},\tau)$$

$$(2.16)$$

With $\widetilde{D} = \sum_{n=2}^{\infty} \frac{1}{n} k_n \left(i \frac{\partial}{\partial t} \right)^n$ the differential operator.

In order to get an intuitive understanding of Eq.(2.16) and the different nonlinear processes associated with each individual term, only low-order contributions are considered. More specifically, since even order nonlinearities are equal to zero for the materials studied in this thesis, the third order term of the polarisation is the lowest-order nonlinearity. This is investigated in the following:

$$p^{NL}(\vec{r},\tau) = \mathbf{3}\varepsilon_0 \chi^{(3)} |A(\vec{r},\tau)|^2 A(\vec{r},\tau)$$
(2.17)

With the further approximation of neglecting the correction terms $\frac{ik_1}{k_0}\frac{\partial}{\partial t}$ and $\frac{i}{\omega_0}\frac{\partial}{\partial t}$, Eq.(2.16) becomes:

$$\frac{\partial A(\vec{r},\tau)}{\partial z'} = \left[\frac{i}{2k_0} \nabla_{\perp}^2 - \frac{ik_2}{2} \frac{\partial^2}{\partial \tau^2} + \frac{3i\omega_0}{2cn_0} \chi^{(3)} |A(\vec{r},\tau)|^2\right] A(\vec{r},\tau)$$
(2.18)

The expression above summarizes the nonlinear effects which act on the amplitude $A(\vec{r}, \tau)$ of a field propagating through a centrosymmetric nonlinear medium. The first term on the right represents the spreading of the beam in x- and y-direction due to diffraction. The second term, which contains the temporal second derivative, expresses the temporal distortion of the pulse due to group velocity dispersion. The last term represents the intensity-dependent distortion of the pulse phase, also known as *self-phase modulation*.

2.1.1 Parametric and Nonparametric Processes

Nonlinear processes can be divided into two categories: parametric and nonparametric. When the electronic population can be removed from the ground state only for a short period of time, the process is called parametric. In this period the electrons can reside in a virtual level only for a time $\delta t = \hbar \delta E$ given by the uncertainty principle, where δE is the energy difference between the virtual state and the nearest real state. This implies that after interacting nonlinearly with the pulse, the system returns to its ground state. The energy of the incident light wave is always conserved in the transmitted field and the medium behaviour can be described by a real susceptibility. Examples are second- or third-harmonic generation, self-phase modulation and self-steepening.

On the other hand, nonparametric processes involve population transfer in between real states like in the case of multi-photon absorption, saturable absorption or stimulated Raman scattering. In other words, the absorption of the radiation is needed to permit the population transfer from the ground state to the excited state. The susceptibility is a complex quantity and the energy of the electromagnetic field does not need to be conserved, but part of it can be transferred to or from the material.

The difference can also be explained in terms of the refractive index in his complex form $n = \tilde{n} + i\kappa$. The real part is behind parametric processes occurring inside the medium,

while the imaginary part, which corresponds to absorption, accounts for nonparametric processes [36].

2.1.2 Third-Order Nonlinearities

According to (2.3), the polarisation of a medium which undergoes only third-order nonlinearities can be expressed as [36,38]:

$$P^{\rm NL}(\vec{r}, t) = \varepsilon_0 \chi^{(3)} E^3(\vec{r}, t)$$
(2.19)

In the simplest case, the electric field propagates through an isotropic medium and is defined as a monochromatic wave $E(t) = Re\{E(\omega) \exp(i\omega t)\}$, with amplitude $E(\omega)$ and angular frequency ω . By replacing E(t) in Eq.(2.19) for the polarisation we get:

$$P^{\mathrm{NL}^{(3)}}(\omega) = \varepsilon_0 \chi^{(3)} E^3(\omega) + 3\varepsilon_0 \chi^{(3)} |E(\omega)|^2 E(\omega)$$
(2.20)

Which can be written as:

$$P^{\mathrm{NL}^{(3)}}(\omega) = P^{\mathrm{NL}}(3\omega) + P^{\mathrm{NL}}(\omega)$$
(2.21)

The first term represents a specific case of four-wave mixing were three photons with the same frequency ω get transformed into one photon of frequency $\mathbf{3}\omega$. This process is called *third-harmonic generation*. The second term is related to the intensity dependence of the refractive index of the medium (*Kerr effect*).

2.1.3 Kerr Effect and Self-Phase Modulation

The *optical Kerr effect* consists in a change of the medium's susceptibility at frequency ω when interacting with a strong light pulse with intensity $I(\omega) = \frac{1}{2}n\varepsilon_0 c|E(\omega)|^2$. It can be expressed as [38]:

$$\Delta \chi = \frac{P^{\rm NL}(\omega)}{E(\omega)} = 3\chi^{(3)} |E(\omega)|^2$$
(2.22)

If we derive $n^2 = 1 + \chi$, we get $\Delta \chi = 2n\Delta n$, so that Eq.(2.22) can be written as:

$$\Delta n = \frac{\mathbf{3}\chi^{(3)}}{n^2 \varepsilon_0 c} I \tag{2.23}$$

$$n(I) = n_0 + n_2 I \tag{2.24}$$

Where n_0 is the weak-field refractive index and $n_2 = \frac{3\chi^{(3)}}{n^2 \varepsilon_0 c}$ is the so-called *Kerr coefficient* and is typically on the order of $10^{-16} - 10^{-14}$ cm²/W.

Eq.(2.24) shows the linear dependence between the change of the material refractive index and the optical intensity. As a consequence of the Kerr effect, a wave propagating through the nonlinear medium will experience a modulation of its phase Φ_{NL} [38]:

$$\Phi_{\rm NL}(l) = k_0 z n(l) \tag{2.25}$$

which will also modify its instantaneous frequency ω of the amount $\partial \omega$:

$$\partial \omega = -\frac{d\Phi_{\rm NL}(l)}{dt}$$
(2.26)



Figure 2.1: a) Time-dependent nonlinear phase of a pulse undergoing self-phase modulation in a medium with $n_2 > 0$ b) Time-dependent change of instantaneous frequency of the carrier wave c) Electric field of the pulse as a function of time after interacting with the Kerr-active medium.

Figure 2.1, a) shows the nonlinear phase $\Phi_{NL}(t)$ induced in a medium with $n_2 > 0$ by a Gaussian pulse, which according to (2.25) is proportional to the pulse intensity. In panel b) the change of the instantaneous frequency of the carrier wave is plotted. Since in the first half of the pulse $\Phi_{NL}(t)$ goes from zero to its maximum, $\partial \omega$ is negative. The result is a red shift in the first half of the pulse and is depicted in panel c). When the nonlinear phase decreases from its maximum to zero, the situation is reversed: the instantaneous frequency is positive and the pulse is blue-shifted.

In general, the length on which a nonlinear effect takes place is a crucial measure for quantifying its impact on the pulse propagating through the nonlinear medium. For this purpose, the *nonlinear length* is introduced as a measure of self-phase modulation [36]:

$$L_{\rm NL} = \frac{c}{\omega n_2 I} \tag{2.27}$$

2.1.4 Self-Steepening

Besides the last term $\chi^{(3)} [A(\vec{r}, \tau)]^2$ of Eq.(2.18), which is related to self-phase modulation, the optical Kerr effect has a further factor which contributes to the light propagation in a nonlinear medium. In this section, the term $\frac{i}{\omega_0} \frac{\partial}{\partial t}$, which was previously

neglected, is taken into account [38]. According to the slowly-varying-amplitude approximation, it can be written as: $\frac{i}{\omega_0} \frac{\partial}{\partial t} \approx \mathbf{1} + \frac{2i}{\omega_0} \frac{\partial}{\partial \tau}$.

As the wavevector $k(\omega - \omega_0)$ in Eq. (2.15) is approximated as a power series of $\omega - \omega_0$, the third-order susceptibility can be expressed as a Taylor expansion:

$$\chi^{(3)}(\omega) = \chi^{(3)}(\omega_0) + (\omega - \omega_0) \frac{d\chi^{(3)}}{d\omega}$$
(2.28)

By considering the laboratory coordinates $z_1 t$, Eq.(2.16) becomes:

$$\frac{\partial A(\vec{r},t)}{\partial z} - k_1 \frac{\partial A(\vec{r},t)}{\partial t} = \frac{i}{2k_0} \nabla_{\perp}^2 A(\vec{r},t) - \frac{ik_2}{2} \frac{\partial^2 A(\vec{r},t)}{\partial t^2} +$$

$$3i \frac{\omega_0}{2n_0 c} \chi^{(3)}(\omega_0) [A(\vec{r},t)]^2 A(\vec{r},t) +$$

$$3i \frac{\omega_0}{2n_0 c} \chi^{(3)}(\omega_0) \left[2 + \frac{\omega_0}{\chi^{(3)}(\omega_0)} \frac{d\chi^{(3)}}{d\omega} \right] \frac{i}{\omega_0} \frac{\partial}{\partial t} [A(\vec{r},t)]^2 A(\vec{r},t)$$
(2.29)

The first three terms on the right are the ones responsible for diffraction, group velocity dispersion and self-phase modulation, as discussed previously. To simplify Eq.(2.29), the nonlinear coefficients $\gamma_1 = 3 \frac{\omega_0}{2n_0 c} \chi^{(3)}(\omega_0)$ and $\gamma_2 = 3 \frac{\omega_0}{2n_0 c} \chi^{(3)}(\omega_0) \left[1 + \frac{1}{2} \frac{\omega_0}{\chi^{(3)}(\omega_0)} \frac{d\chi^{(3)}}{d\omega}\right]$ are introduced. After solving the temporal derivative $\frac{\partial}{\partial t} |A(\vec{r}, t)|^2 A(\vec{r}, t)$, Eq.(2.29) becomes:

$$\frac{\partial A(\vec{r},t)}{\partial z} - \left[k_1 + \frac{4\gamma_2 c}{\omega_0} |A(\vec{r},t)|^2\right] \frac{\partial A(\vec{r},t)}{\partial t} =$$

$$\frac{i}{2k_0} \nabla_{\perp}^2 A(\vec{r},t) - \frac{ik_2}{2} \frac{\partial^2 A(\vec{r},t)}{\partial t^2} + 3i \frac{\omega_0}{2n_0 c} \chi^{(3)}(\omega_0) |A(\vec{r},t)|^2 A(\vec{r},t) + i\gamma_1 |A(\vec{r},t)|^2 A(\vec{r},t) - \frac{2\gamma_2}{\omega_0} A(\vec{r},t)^2 \frac{\partial A(\vec{r},t)}{\partial t}$$

$$(2.30)$$

The second term on the left contains the nonlinear group index $n_{\text{eff}}^{(g)} = n_0^{(g)} + \frac{4\gamma_2 c}{\omega_0} |A(\vec{r}, t)|^2 \equiv n_0^{(g)} + n_2^{(g)} I$ and is identified as the intensity-dependent contribution to the group velocity.

By using the definition of γ_2 , $n_2^{(g)}$ can be written in its explicit form:

$$n_{2}^{(g)} = 12 \frac{\omega_{0}}{n_{0}^{2} c \varepsilon_{0}} \chi^{(3)}(\omega_{0}) \left[1 + \frac{1}{2} \frac{\omega_{0}}{\chi^{(3)}(\omega_{0})} \frac{d \chi^{(3)}}{d \omega} \right]$$
(2.31)

From Eq.(2.31) it becomes clear how the intensity dependence of the group index $n_{\text{eff}}^{(g)}$ is given by both the medium susceptibility $\chi^{(3)}$ and its dispersion $\frac{d\chi^{(3)}}{d\omega}$.

As illustrated in Figure 2.2, for the general case of $n_2^{(g)} > 0$, the group velocity decreases linearly when the pulse intensity increases. This phenomenon is known as *self-steepening*. It leads to an increase of the slope of the pulse trailing edge caused by a reduced velocity of the pulse peak compared to its wings (case b). When the slope of the trailing edge tends to infinity, self-steepening becomes sufficiently strong that an optical shock wave is created (case c) [39]. This effect can take place when ultra-short pulses propagate through media without dispersion [40].

As for self-phase modulation, the *self-steepening distance* can be defined to quantify the effect:

$$L_{\rm SS} = \frac{c\tau}{2\sqrt{\ln 2}n_2^{(g)}I} \tag{2.32}$$

Where τ is the pulse duration.



Figure 2.2: Left: Time-dependent intensity profile of a Gaussian pulse. Right: Intensity profile of a Gaussian pulse in space a) Unperturbed pulse. b) Distorted intensity profile of the pulse undergoing self-steepening in a medium with $n_2^{(g)} > 0$ c) Optical shock wave generated in a medium with $n_2^{(g)} > 0$.

2.1.5 Saturable Absorption

In many materials the absorption of light depends on its intensity. This is described by the absorption coefficient α [36]:

$$\alpha = \frac{\alpha_0}{\mathbf{1} + \frac{I}{I_s}}$$
(2.33)

Where α_0 is the weak-field absorption coefficient and I_S is the saturation intensity which is a material-dependent parameter.

Figure 2.3 shows the band structure of nickel for the two cases of linear and *saturable absorption*. When the optical intensity *I* is much smaller than its saturation value I_S , the absorption coefficient is equal to the linear absorption coefficient α_0 (Figure 2.3, left). For

the opposite case of high intensities $I \gg I_S$, the absorption coefficient tends to zero i.e. the material is becoming more transparent. This is shown on the right side of Figure 2.3. An effect that could bring to saturable absorption is the Pauli blocking of charges above the Fermi level E_F . For intensities $I \gg I_S$, the high number of excited charges above E_F blocks further optical transitions. This effect results in the increase of transparency of the material.



Figure 2.3: Band-structure of nickel. Left: the case of linear absorption. Right: the case of saturable absorption. The states above the Fermi level are filled, therefore further electron transitions are not allowed.

2.1.6 Two-Photon Absorption

Two-photon absorption (2PA) is a third-order nonparametric effect where carriers get excited by absorbing simultaneously two photons. The absorption cross-section σ increases linearly with the intensity $\sigma = \sigma^{(2)}I$ where $\sigma^{(2)}$ is a coefficient that describes the strength of the process. The atomic transition rate *R* depends on the squared intensity and is defined as [36]:

$$R = \frac{\sigma I}{\hbar \omega} = \frac{\sigma^{(2)} I^2}{\hbar \omega}$$
(2.34)

As anticipated in 2.1.1, the process of two-photon absorption is related to the imaginary part of the susceptibility through the *two-photon absorption coefficient*:

$$\beta = \frac{3\pi}{\varepsilon_0 n^2 c \lambda} Im(\chi^{(3)})$$
(2.35)

 β is directly proportional to the absorption cross-section σ and can be used to define the number N_{2PA} of electrons excited through 2PA [41]:

$$N_{2PA} = (1 - R)F \frac{\beta I}{2\hbar\omega}$$
(2.36)

Where R is the reflectivity, $F = I \cdot \tau$ is the fluence of the laser pulse, I and ω its intensity and frequency, respectively.

2.1.7 Free-Electron Response: The Drude Model

The Drude and the Lorentz model were developed to describe classically the optical response of materials. The Drude model describes the collective motion of free electrons. In metals, the oscillation of free carriers are the main induced charge dynamics when interacting with a strong optical field. Even in a dielectric medium, the free carrier response becomes significant when the field is strong enough to excite a considerable fraction of electrons. The conduction electrons are not bound to any particular nucleus and can move freely through the lattice, hence any restoration force will be neglected in the equation of motion [42,43]:

$$m_e \frac{d^2 \vec{r}(t)}{dt^2} + m_e \gamma \frac{d \vec{r}(t)}{dt} = -e \vec{E}(t)$$
(2.37)

Where m_e is the electron mass, $\vec{r}(t)$ is the electron displacement induced by the external electric field $\vec{E}(t)$, e is the unit charge and γ is the damping coefficient which represents the energy loss due to collisions. γ can also be expressed in terms of the relaxation time τ , which is the average time between two collision events: $\gamma = 1/\tau$.

For a metallic system in thermal equilibrium, the damping coefficient can also be defined as the ratio v/l, where v represents the Fermi velocity and l is the mean free path between two successive collision events.

Solving Eq.(2.37) for a monochromatic wave $E(t) = Re\{E(\omega) exp(i\omega t)\}$ gives:

$$\vec{r}(\omega) = \frac{e}{m_e(\omega^2 + i\omega\gamma)}\vec{E}(\omega)$$
(2.38)

The total polarisation of all electrons per unit volume can now be expressed as:

$$\vec{P}(\omega) = -Ne\vec{r}(\omega) = -\frac{Ne^2}{m_e(\omega^2 + i\omega\gamma)}\vec{E}(\omega) = \frac{\chi(\omega)}{\varepsilon_0}\vec{E}(\omega)$$
(2.39)

With N the electron density per volume. The definition of polarisation in Eq.(2.2) and $n^2(\omega) = 1 + \chi(\omega) = \varepsilon_r(\omega)$ can be used to derive the frequency-dependent permittivity $\varepsilon_r(\omega)$:

$$n^{2}(\omega) = \varepsilon_{r}(\omega) = 1 - \frac{\omega_{\text{pl}}^{2}}{\omega^{2} + i\omega\gamma}$$
(2.40)

Where $\omega_{pl}^2 = \frac{Ne^2}{m_e \varepsilon_0}$ is the square of the plasma frequency. Eq.(2.40) defines the contribution of free electrons to the dielectric constant of the medium. An increase in free-electron density *N* leads to a smaller permittivity (and refractive index), since the

plasma frequency ω_{pl} increases. Therefore, for optical frequencies $\omega < \omega_{pl}$, the free electrons response becomes significant. Contrarily, for $\omega > \omega_{pl}$, the permittivity increases and the material becomes more transparent.

 $\varepsilon_r(\omega)$ can be rewritten by splitting its real and imaginary part:

$$\varepsilon_r(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \left(1 - \frac{\omega_{\rm pl}^2}{\omega^2 + \gamma^2}\right) + i\frac{\gamma\omega_{\rm pl}^2}{\omega(\omega^2 + \gamma^2)}$$
(2.41)

The imaginary part of the permittivity expresses the energy losses and is associated to the ohmic resistance of the material.

2.1.8 The Role of Bound Electrons: The Lorentz Model

The Lorentz model explains the mechanism behind transitions of electrons. In the case of our study, these interband transitions can take place in or out of resonance. In silicon, electrons can be transferred from the valence to the conduction band over the indirect band gap (1.12 eV) through single-photon absorption or over the direct band gap (3.4 eV) through multi-photon absorption. Also in metals interband transitions can be significant, since the overlap between filled valence bands and free conduction bands permits electrons to move freely.

Electrons which are bounded to the nucleus are treated as a harmonic oscillator. Therefore, the restoring force needs to be included. In fact, during the interaction with light, bound electrons will start oscillating with opposite phase with respect to the external field. The induced oscillations will generate an electric field which pulls the charges back to the position of equilibrium. In this discussion, the dipole of the electron-nucleus system is neglected.

The restoring force is defined as $\vec{F}_R(t) = m_e \omega_0^2 \vec{r}(t)$, with the natural frequency of the oscillator ω_0 . By adding $F_R(t)$ in Eq.(2.37), the equation of motion becomes [42]:

$$m_e \frac{d^2 \vec{r}(t)}{dt^2} + m_e \gamma \frac{d \vec{r}(t)}{dt} + m_e \omega_0^2 \vec{r}(t) = -e \vec{E}(t)$$
(2.42)

The general solution for a monochromatic wave is:

$$\vec{r}(\omega) = -\frac{e}{m_e(\omega_0^2 - \omega^2 - i\omega\gamma)}\vec{E}(\omega)$$
(2.43)

By using the same formalism as in the Drude model, the induced polarisation can be defined as:

$$\vec{P}(\omega) = -Ne\vec{r}(\omega) = \frac{Ne^2}{m_e(\omega_0^2 - \omega^2 - i\omega\gamma)}\vec{E}(\omega)$$
(2.44)

The frequency-dependent permittivity for bound electrons is obtained:

$$\varepsilon_r(\omega) = 1 + \frac{\omega_{pl}^2}{\omega_0^2 - \omega^2 - i\omega\gamma}$$
(2.45)

From the comparison of Eq.(2.45) with Eq.(2.40), it is evident that the effect of bound electrons has opposite sign with respect to the free-electrons contribution.

2.2 Linear Absorption as Probe: XUV Spectroscopy

When the intensity of an electromagnetic wave is not high enough to nonlinearly interact with a material, only linear effects occur. In one of the experiments performed in this work, the linear absorption of XUV radiation is brought into play for probing the electron dynamics induced by a laser pulse. Therefore, a short description of the effect is reported here.

In subsection 2.1.1, nonlinear absorption has been introduced as a nonparametric process which is related to the imaginary part of the refractive index. The same can be affirmed for the linear case. In the field of X-Ray spectroscopy, the notation for the complex refractive index is different compared to what can be seen in 2.1.1 for visible light [32]:

$$n(\omega) = \mathbf{1} - \delta(\omega) + i\beta(\omega)$$
(2.46)

Here, the real part $\delta(\omega)$ is related to refraction, while the imaginary part $\beta(\omega)$ is responsible for absorption. In particular, a polarisation-dependent $\beta(\omega)$ leads to the phenomenon of *dichroism* which will be discussed later.



Figure 2.4: Left: Exponential decay of the intensity when propagating through an absorptive medium. Right: X-Ray absorption as an example of linear absorption inside the absorptive medium. Since no virtual states are involved in the transition from the initial to the final state, absorption is a first order process.

Absorption can be described not only as a change in $\beta(\omega)$, but also as the attenuation of the light intensity while propagating through the medium. The intensity of an electromagnetic wave after linearly interacting with the absorptive material of length z is described by the phenomenological Lambert-Beer's law:
$$I(\omega_{I}z) = I_{0}(\omega)e^{-\alpha(\omega)z}$$
(2.47)

With $I_0(\omega)$ the frequency-dependent incident intensity and $\alpha(\omega)$ the absorption coefficient of the material. Eq.(2.47) exhibits the exponential decay of the intensity inside the medium whose strength is given by the $\alpha(\omega)$ of the material.

Another physical quantity which is related to the absorption coefficient is the *absorption cross-section*:

$$\sigma_{\rm abs}(\omega) = \frac{\alpha(\omega)}{N_{\rm atoms}}$$
(2.48)

Where *E* is the photon energy, *N* is the atomic number density and denotes the number of atoms per volume. The absorption cross-section is defined as the number of excited electrons per unit time divided by the number of incident photons N_{phot} per unit time and area [44]:

$$[\sigma_{abs}] = \frac{[\text{#excited electrons × illuminated area]}}{[\text{#incident photons]}}$$
(2.49)
=
$$\frac{[\text{#absorbed photons × illuminated area]}}{[\text{#incident photons × #atoms]}} = [length^2]$$

For instance, σ_{abs} is the probability of a photon with a certain energy to be absorbed in a certain portion of the medium dx:

$$\frac{dN_{\rm phot}}{dx} = -N_{\rm phot}N_{\rm atoms}\sigma_{\rm abs}$$
(2.50)

In the quantum-mechanical picture, a core-shell electron is excited from its initial state $|i\rangle$ with energy E_i to its final state $|f\rangle$ with energy $E_f = E_f + E$ when an XUV photon with energy E is absorbed by a material. X-Ray absorption is a first-order process where no intermediate virtual states $|n\rangle$ are involved [45]. According to (2.49), the absorption cross-section encloses the transition probability $\Gamma_{i \to f}$ and the flux of incident photons F_{phot} [44,46]:

$$\sigma_{\rm abs}(\omega) = \frac{\Gamma_{i \to f}}{F_{\rm phot}}$$
(2.51)

Where $\Gamma_{i \to f}$ is given by Fermi's Golden rule:

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} |\langle f | H_{\text{int}} | i \rangle|^2 \rho(E_f)$$
(2.52)

 $\rho(E_f)$ is the density of the final state and H_{int} is the perturbation term of the Hamiltonian operator *H* that describes the total energy of the matter-light system [47]. Consistent with the first-order perturbation theory, *H* is defined as the sum of the material steady-state Hamiltonian H_0 and the perturbative Hamiltonian H_{int} :

$$H(\vec{r},t) = H_0(\vec{r}) + H_{int}(t)$$
(2.53)

Given that $H(\vec{r}, t)$ represents the total energy of the system, it can be expressed as the sum of the kinetic $E_k(\vec{r}, t)$ and the potential energy $U(\vec{r}, t)$:

$$E_{k}(\vec{r},t) = \frac{\vec{p} \cdot \vec{A}}{2m} = \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} \vec{A}(\vec{r},t) \right)^{2}$$
(2.54)
$$U(\vec{r},t) = \varphi(\vec{r},t)$$
(2.55)

Here, \vec{p} is the momentum operator, $\vec{A}(\vec{r}, t)$ denotes the vector potential and $\varphi(\vec{r}, t)$ the scalar potential. Choosing the Coulomb gauge implies $\nabla \cdot \vec{A} = 0$. The Hamiltonian becomes:

$$H(\vec{r},t) = \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} \vec{A}(\vec{r},t) \right)^2 + \varphi(\vec{r},t)$$
(2.56)
$$= \frac{\hbar}{2mi} \nabla^2 - \frac{e}{2mc} \vec{A}(\vec{r},t) \cdot \frac{\hbar}{i} \nabla + \frac{e^2}{2mc^2} \vec{A}(\vec{r},t)^2 + \varphi(\vec{r},t)$$

The stationary and the perturbed Hamiltonians become:

$$H_0(\vec{r},t) = \frac{\hbar}{i2m} \nabla^2 + \varphi(\vec{r},t)$$
(2.57)

$$H_{\rm int}(\vec{r},t) = -\frac{e}{2mc}\vec{A}(\vec{r},t)\cdot\frac{\hbar}{i}\nabla + \frac{e^2}{2mc^2}\vec{A}(\vec{r},t)^2$$
(2.58)

The dynamics of the light-matter system is well-described by the time-dependent Schrödinger equation. At the beginning of this chapter it has been mentioned that the simplest solution is given by a plane wave. Hence the vector potential of the incoming photons can be expressed as $\vec{A}(\vec{r}, t) = A_0 \vec{\epsilon} e^{-i(\vec{k}\cdot\vec{r}-\omega t)}$, where $\vec{\epsilon}$ is the unit photon polarisation vector. By substituting this in (2.58) and neglecting the last term, the perturbed Hamiltonian can be written as:

$$H_{\rm int}(\vec{r},t) = -\frac{e\hbar}{i2mc} A_0 \vec{\varepsilon} e^{i(\vec{k}\cdot\vec{r}-\omega t)} \cdot \nabla$$
(2.59)

The exponential factor can be expanded as a series of $i\vec{k}\vec{r}$, giving higher terms of the electric and magnetic dipole. In the dipole approximation, the series is truncated after the first term:

$$H_{\rm int}(\vec{r},t) = -\frac{e\hbar}{i2mc}A_0\vec{\varepsilon}e^{-i\omega t}\cdot\nabla$$
(2.60)

The exponential factor of the vector potential $\vec{A}(\vec{r}, t)$ can be expanded, leading to the following expression:

$$\vec{A}(\vec{r},t) = A_0 \vec{\varepsilon} e^{-i(\vec{k}\vec{r}-\omega t)} = A_0 \vec{\varepsilon} e^{-i\omega t} \left(1 - i\vec{k}\vec{r} + \frac{1}{2}(i\vec{k}\vec{r})^2\right) \approx A_0 \vec{\varepsilon} e^{-i\omega t}$$
(2.61)

According to the dipole approximation, the series can be truncated after the first term which corresponds to the electric dipole transitions. From the transition probability given by Eq.(2.52), the perturbative Hamiltonian in Eq.(2.60), it is possible to obtain the X-Ray absorption resonance intensity [45]:

$$I_{\text{Res}} = \frac{2m}{\hbar^2} \frac{(E_f - E_i)^2}{\hbar\omega} |\langle f | \vec{\varepsilon} \cdot \vec{r} | i \rangle|^2$$
(2.62)

 I_{Res} has the dimension **[** $length^2 \times energy$ **]**. The product $\vec{\epsilon} \cdot \vec{r}$ is the polarisation dependent dipole operator \vec{P} , where \vec{r} is the electron position vector. Linearly polarised light is given by the angular momentum projection $m_l = 0$, while left- and right circularly polarised light correspond to $m_l = +1$ and $m_l = -1$, respectively. In the case of linearly polarised XUV pulses, the intensity of the XUV absorption is determined by the direction of the electric field vector, for example the z-direction. For circularly polarized XUV with the wavevector $k \parallel z$, the polarisation vector for left (-) and right (+) circularly polarised XUV is given by:

$$\varepsilon_z^{\pm} = \mp \frac{1}{\sqrt{2}} (\varepsilon_x \pm \varepsilon_y)$$
(2.63)

XUV-driven transitions excite electrons from the core levels, which are well localized. On the other hand, the final states are not as clearly determined. Several effects can influence the final state of electrons, such as electron-electron scattering or screening. In the simplest model of a single particle where these effects are neglected, the final states are determined by the selection rules. Given the quantum numbers $j_i m_i l$ and s, the permitted transitions in the dipole approximation are:

$$\Delta j = 0, \pm 1; \ \Delta s = 0; \ \Delta l = \pm 1; \ \Delta m_l = 0, \pm 1$$
 (2.64)

Given l = +1 and $m_l = 0, \pm 1$, the dipole operators for linear, left and right circularly polarised XUV radiation are expressed in terms of the spherical harmonics $Y_l^{m_l}(\theta, \varphi)$ [45,48]:

$$P_z^0 = \varepsilon_z^{\pm} \cdot \vec{r} = z = r \sqrt{\frac{4\pi}{3}} Y_1^0 = r C_1^0$$
(2.65)

$$P_{z}^{\pm} = \varepsilon_{z}^{\pm} \cdot \vec{r} = \mp \frac{1}{\sqrt{2}} (x \pm y) = r \sqrt{\frac{4\pi}{3}} Y_{1}^{\pm 1} = r C_{1}^{\pm 1}$$
(2.66)

The definition of the dipole operators has been simplified even further by introducing the Racah's spherical tensor operators $C_l^{m_l} = \sqrt{\frac{4\pi}{2l+1}} Y_l^{m_l}(\theta, \varphi)$. With Eq.(2.65) and (2.66) the polarisation dependent X-Ray absorption intensity can now be calculated.

2.3 Principles of Magnetism

When a light pulse interacts with a ferromagnetic material, the magnetic properties of the ferromagnet can be modified as well as its electronic properties. An effective technique for estimating and tracking the changes of the magnetic moment consists in measuring the Magnetic Circular Dichroism (MCD) of the material. Based on the formalism developed by E. C. Stoner [49], the concept of band-ferromagnetism is described in the first section. After, a theoretical overview of MCD is presented.

2.3.1 Ferromagnetism: The Band Model

Ferromagnets are materials exhibiting an intrinsic microscopic magnetisation, i.e. even in the absence of an external magnetic field [50]. The magnitude and orientation of the magnetisation are represented by the magnetic moment \vec{m} . Ferromagnets are characterised by small regions with aligned \vec{m} , which are denoted as *magnetic domains*. In Figure 2.5 left it is shown that if no magnetic field is applied, the domains inside the material are arbitrarily oriented.

Historically, the word "*ferromagnetism*" was used for all the materials exhibiting spontaneous magnetisation. However, this is not accurate. In **1953** L. Nèel first documented *ferrimagnetism* as the imperfect antiferromagnetic behaviour of certain materials [51]. Ferrimagnets show a small spontaneous magnetisation because of a partial alignment of magnetic moments. As a result, there are two classes of magnetic materials.

By applying an external magnetic field to a ferromagnet, the magnetic domains align with each other promoting the macroscopic magnetisation of the material (see Figure 2.5). The behaviour of ferromagnetic metals under the influence of a magnetic field is well explained by the *band model*, first employed by Mott [52] and Slater [53] in the **1930**s and later by Stoner [49]. The band model is based on the Bloch approach [54,55], where the electrons in a crystal are treated collectively. The kinetic energy dominates over the Coulomb repulsion between electrons and so they are interpreted as Bloch waves inside the crystal.



Figure 2.5: Magnetic domains inside a ferromagnet when no external magnetic field H_{ext} is applied (left) and with the application of H_{ext} (right). In the latter all spins align in the same direction.

In the case of atoms, electrons are fully localised and their properties can be described by quantum numbers. It follows that the spin *s* and the orbital magnetic moment *m* are both multiples of the Bohr magneton μ_B . Given the reduced Planck constant \hbar and the orbital momentum *l*, it applies [45]:

$$\vec{m} = (\mathbf{2}\vec{s} + \vec{l})\mu_B / \hbar \tag{2.67}$$

According to the Hund's second rule, the spins of unpaired electrons align parallel to maximise the total orbital momentum \vec{L} . For Hund's third rule, the total momentum $\vec{J} = \vec{L} + \vec{S}$ is maximised if the outer shell is more than half filled. In doing so, the total energy of the system is minimised. The electronic structure for the nickel atom is depicted in Figure 2.6, where the two unpaired electrons are in the 3d shell. The spin magnetic moment is $m_s = 2\mu_B$.



Figure 2.6: Electronic configuration of nickel. Ni is a 3d-transition metal, which implies that its unpaired electron spins reside in the 3d-shell.

In metals, the electrons in the conduction band are not localised, so that the atomic-like description with quantum numbers is not further valid. In fact, measuring the spontaneous magnetisation of nickel and dividing the value by the number of atoms leads to $m_s = 0.616\mu_B$. The spin magnetic moment of metals is not a multiple of the Bohr magneton, which suggests that a more accurate model is required. As previously mentioned, the band model was developed in several variants. The description presented here is the Stoner model. Non-localised electrons are pictured in a band-structure instead of being placed on discrete energy levels. Bands consist in a large number of closely spaced energy levels and originate when an electron is in the presence of a periodic potential. The electronic band-structure is usually given in the reciprocal space as a function of the wavevector \vec{k} . It represents the allowed energetic states and is characterised by periodic variations.

The description of the Stoner model given here doesn't account for a detailed \vec{k} -dependence of the band-structure [45]. Despite being a simple representation, it is sufficient for the treatment of ferromagnetism and, later, of magnetic circular dichroism.

Integrating the energy bands over all \vec{k} -states gives the number of energetic states that can be occupied for a specific energy. This is called *density of states* (DOS).

As shown in Figure 2.7 left, in non-magnetic materials the DOS as well as the electron density N is the same for spin-up $(|\uparrow\rangle = |+\rangle)$ and spin-down $(|\downarrow\rangle = |-\rangle)$ electrons:

$$D_{+}(E_{F}) = D_{-}(E_{F})$$
(2.68)

$$N_{+} = N_{-}$$
 (2.69)

With E_F the Fermi energy, defined as the difference between the Fermi level and the lowest occupied energy level at zero temperature. The origin of ferromagnetism can be found in the asymmetry of the DOS for spin-up and spin-down electrons (see Figure 2.7, right). Suppose the DOS for spin-up electrons gains one more electron which contributes to the total energy with δE . $D_+(E_F)$ becomes:

$$D_{+}(E_{F})\delta E = \frac{1}{2}D(E_{F})\delta E$$
(2.70)

Equally, the kinetic energy increases of the amount:

$$\Delta E_k = \frac{1}{2} D(E_F) \delta E \tag{2.71}$$



Figure 2.7: Left: density of states of a non-magnetic material. The DOS for spin-up and spin-down electrons is the same. Right: in a ferromagnetic material the DOS for spin-up and spin-down electrons is not balanced. The red band has the highest number of electrons (spin-up) and is called majority band. The blue band contains the spin-down electrons and is called minority band. The minority electrons are parallel to the external magnetic field H_{ext} , the majority electrons align antiparallel to H_{ext} .

In Figure 2.7, the band with spin-up electrons is called the *majority band* for having the highest number of populated states. In contrast, the band with spin-down electrons is called the *minority band*. The spin magnetic moment is antiparallel to the spin direction \vec{s} of the majority electrons accordant with $\vec{m}_s = -g\mu_B \vec{s}$, where g is the g-factor. As a result, also the external magnetic field is antiparallel to the majority spin.

In the electronic system, the coupling between electrons can be substituted by the meanfield of all electrons with paired spin acting on the unpaired one. This is the so-called *Mean-Field Approximation* (MFA) first introduced by P. Weiss and P. Curie to describe the temperature-dependent ferromagnetic behaviour of materials [50,56]. The mean-field *B* is related to the difference between spin-up and spin-down electrons and generates the microscopic magnetisation *M*. In fact, it can be expressed as $B = \lambda \mu_0 M$, where λ describes the strength of the mean-field and μ_0 is the vacuum permeability. The magnetisation *M* is directly proportional to the difference between the electron densities N_- and N_+ :

$$M = \mu_B (N_- - N_+)$$

$$= \mu_B \left(\frac{1}{2} N + \frac{1}{2} D(E_F) \delta E - \frac{1}{2} N + \frac{1}{2} D(E_F) \delta E \right) = \mu_B D(E_F) \delta E$$
(2.72)

Knowing *M*, the change in potential energy can be derived from the Helmhotz free energy [57], defined as $F = E_{pot} - TS$. Here, E_{pot} is the potential energy, *T* and *S* are respectively the temperature and the entropy of the closed thermodynamic system at constant temperature and volume. The free energy is related to the magnetisation through dF = -MdB. Assuming constant entropy and using Eq.(2.72), the change in potential energy is expressed as:

$$\Delta E_{\text{pot}} = -\int_0^M M' \,\lambda \mu_0 dM' = -\frac{1}{2} \lambda \mu_0 M^2 = -\frac{1}{2} U D(E_F) \delta E^2$$
(2.73)

With the constant $U = \lambda \mu_0 \mu_B^2$. The total change of energy caused by the spin flip of one electron is given by the sum of (2.71) and (2.73):

$$\Delta E = \Delta E_k + \Delta E_{\text{pot}} = \frac{1}{2} D(E_F) \delta E \delta E - \frac{1}{2} U D(E_F) \delta E^2$$

$$= \frac{1}{2} D(E_F) \delta E^2 (1 - U D(E_F))$$
(2.74)

 $\Delta E \leq \mathbf{0}$ is given only when the number of spin-up and spin-down electrons is unbalanced, which results in band splitting. Consequently, ferromagnetism is the most energetically favourable configuration for the electronic system. Mathematically, it has to apply:

$$UD(E_F) \ge 1 \tag{2.75}$$

Eq.(2.75) is known as the Stoner criterion for ferromagnetism.

2.3.2 Magnetic Circular Dichroism

In **1946** M. Faraday discovered that the polarisation of light changes after propagating through a transparent magnetic medium [58]. This phenomenon can be better understood if one considers the incident beam with linear polarisation as the sum of left- and right circular polarisation. The two polarisation components experience a different refractive index inside the material (*circular birefringence*), which results in a difference in time propagation and, consequently, in a phase shift between left- and right circular polarisation.

This discovery initiated the study of magnetic materials interacting with electromagnetic radiation. On one hand, the Faraday effect describes the difference in refraction for leftand right- circular polarised light. On the other hand, magnetic dichroism consists in the absorption of left- and right-circularly polarised light in different amounts. The first theoretical work demonstrating MCD by the use of X-Ray radiation dates back to **1975**, when Erskine and Stern simulated the absorption at the $M_{2,3}$ -edges of nickel [59]. The first experimental evidence was given almost fifteen years later by Schütz *et al.* by studying the K-edges of iron [60]. *Magnetic Circular Dichroism* (MCD) spectroscopy is based on the measure of radiation absorbed by a ferromagnetic material for circularly polarised incident light. The difference between the absorption intensities for left- and right circular polarisation is proportional to the difference of the spin-up and spin-down electrons number. This gives a measure for the material magnetic moment.

Dichroism in the One-Electron Model

The present section is based on the theoretical work of Stöhr [48]. The MCD process is treated quantum-mechanically in the one-electron scenario. This assumption simplifies the description but is equivalent to the Stoner band-model. Following the convention used in 2.2, right-circular polarised XUV possesses ellipticity $\epsilon = +1$, while left-handed polarisation has $\epsilon = -1$.

The absorption of XUV radiation is given by the transition probability from an initial core state $|i\rangle$ to a final state $|f\rangle$ in the valence band. Nickel is a **3***d*-transition metal, revealing the **3***d* vacancies as responsible for the material magnetic properties [61]. For the M_{2,3}-absorption edges of Ni, the XUV transition takes place from the spin-split **3***p* level (**3***p*_{1/2} and **3***p*_{3/2}) to the **3***d* valence states. The Coulomb interaction causes the splitting of the **3***d* band into spin-up \uparrow and spin-down \downarrow component. For the quantum-mechanical description given here, the direction of the applied magnetic field is chosen parallel to the spin-down direction, which results in the sample magnetisation direction parallel to the one of the spin-up electrons. As a consequence, the spin-up band is completely filled, while the spin-down band has one vacancy, according to the one-electron picture.

The XUV transition probability can be calculated by taking the wave functions projected on the basis $|l,m_l,s,m_s\rangle$ as well as the product between the spherical harmonics $Y_l^{m_l}(\theta,\varphi)$ and a spin-dependent function. Electrons with spin-up are denoted with the function α , while spin-down electrons are represented by β . The **3***d* valence states are degenerate due to spin-orbit coupling, which implies $m_l = -2, -1, 0, +1, +2$. Therefore, the transition probability is given by the average over all the possible transitions to the five **3***d* energy levels where the vacancy could reside. Since the dipole operator does not act on the spin component of initial and final states, the basis for the initial and the final state can be considered only in their angular part:

$$|i\rangle = |n_l, n_l\rangle \tag{2.76}$$

$$|f\rangle^{\uparrow} = |n', l + \mathbf{1}, m_l + \mathbf{1}\rangle \tag{2.77}$$

$$|f\rangle^{\downarrow} = |n', l + \mathbf{1}, m_l - \mathbf{1}\rangle$$
(2.78)

The transition probability is derived from the matrix element $\langle f | P_{\pm 1}^{(U)} | i \rangle$ where $P_{\pm 1}^{(U)}$ is the dipole operator given by Eq.(2.66) for left- and right circular polarisation. Assuming l = 1:

$$\langle n', l+1, m_l+1 | P_{+1}^{(1)} | n, l, m_l \rangle = -\sqrt{\frac{(l+m_l+2)(l+m_l+1)}{2(2l+3)(2l+1)}}R$$
 (2.79)

$$\langle n', l+1, m_l-1|P_{-1}^{(1)}|n, l, m_l\rangle = -\sqrt{\frac{(l-m_l+2)(l-m_l+1)}{2(2l+3)(2l+1)}}R$$
 (2.80)

Here $R = \int R_{nl}^*(r)R_{n'l'}(r)r^3dr$ denotes the radial matrix element. Under the assumption that all the degenerate final states have the same radial component, the $3p \rightarrow 3d$ matrix elements are calculated [62].

Based on Eq.(2.79) and (2.80) it must be highlighted that reversing the polarisation direction of the incident XUV radiation is equivalent to switching the direction of the external magnetic field.

$$\left\langle n', l+1, -m_l+1 \middle| P_{+1}^{(1)} \middle| n', l, -m_l \right\rangle = \left\langle n', l+1, m_l-1 \middle| P_{-1}^{(1)} \middle| n', l, m_l \right\rangle$$
(2.81)

For instance, changing the circular polarisation from right $P_{+1}^{(1)}$ to left $P_{-1}^{(1)}$ is analogous to changing the magnetisation of the sample from m_l to $-m_l$. This is of fundamental importance, as experimentally it is often easier to switch the magnetic field direction.

An approach for understanding this analogy can be the following: reversing the magnetic field reverses the alignment of the spins, which implies a switch of spin direction for the vacancies in the 3d-valence state. On the other hand, changing the polarisation of the exciting XUV changes the coupling with the electrons spin residing in the spin-split 3p levels, since right-circularly polarised light likely excites more spin-up electrons and spin-down electrons are more likely to be excited by left-circularly polarised XUV.

From the matrix elements calculated above, the selection rules for $p \rightarrow d$ transitions are obtained: $\Delta n = 0$, $\Delta l = 1$, $\Delta m_l = \pm 1$ for right- and left circular polarisation. The case where $\Delta l = -1$ corresponds to the $p \rightarrow s$ transitions and are not considered here, as they are less probable than the $p \rightarrow d$ transitions.

In the present consideration of one spin-down vacancy in the **3***d* valence states, the initial and final state are given by the spin-down function β :

$$|i\rangle = |l = \mathbf{1}, s = \frac{\mathbf{1}}{\mathbf{2}}, m_l, \beta \rangle = a_{m_l} Y_1^{m_l} \beta$$
(2.82)

$$|f\rangle^{\downarrow} = |l = \mathbf{2}, s = \frac{\mathbf{1}}{\mathbf{2}}, m_l, \beta \rangle = Y_2^{m_l} \beta$$
(2.83)

Where a_{m_l} are the Clebsch-Gordan coefficients for normalising the change of basis and m_l varies from -l to l.

The XUV absorption strength associated with the $\mathbf{3}p_{\frac{1}{2}} \rightarrow \mathbf{3}d$ is given by the sum over all the initial *i* and final states *f*:

$$A_{i \to f}^{\pm} = \sum_{i,f} \left| \left\langle f \left| P_{\pm 1}^{(1)} \right| i \right\rangle \right|^2$$
(2.84)

For the transition $3p_{\frac{3}{2}} \rightarrow 3d$, corresponding to the M_3 absorption-edge of nickel, it follows:

$$A_{3p_{3} \to 3d}^{+} = \frac{1}{3}R^{2} \qquad A_{3p_{3} \to 3d}^{-} = \frac{5}{9}R^{2}$$
(2.85)

While for $3p_{\frac{1}{2}} \rightarrow 3d$ i.e. the M_2 absorption-edge:

$$A_{3p_{\frac{1}{2}} \to 3d}^{+} = \frac{1}{3}R^{2} \qquad A_{3p_{\frac{1}{2}} \to 3d}^{-} = \frac{1}{9}R^{2}$$
(2.86)

The intensity for right-circularly polarised XUV is the same for both transitions, while it differs for left-circularly polarised radiation. The MCD signal can now be defined as the difference between the absorption intensities for the two polarisation directions: $I_{MCD} = A^+ - A^-$.

Calculating I_{MCD} for the two possible transitions $\mathbf{3}p_{\frac{1}{2}\frac{3}{2}} \rightarrow \mathbf{3}d$ leads to $I_{MCD}^{M_3} = -\frac{2}{9}R^2$ and $I_{MCD}^{M_2} = \frac{2}{9}R^2$. These signals are identical in amplitude but with opposite sign, as a direct consequence of the one-electron model where only one vacancy in the $\mathbf{3}d$ valence states is assumed. However, from experiments on various metals [60,63] it is evident how the ratio between the two MCD signals is nearer to 2:1 than 1:1. The source for the disparity is the spin-orbit splitting and the presence of more than one vacancy in the final state.

Dichroism in the Two-Step Model

The so-called *two-step model* for dichroism can be developed by making use of the results obtained from the one-electron model described above. It consists of two successive stages where in the first step the XUV transition from the initial to the final state occurs without a necessary spin selection. Therefore, the d-shell is assumed not to be spin-split. In the subsequent step, the spin dependence is introduced so that only electrons with a certain spin can complete the transition.

With Eq.(2.81) it has been shown how switching the magnetic field \vec{H}_{ext} with a fixed XUV circular polarisation is identical to reversing the polarisation direction and keeping the magnetic field in one direction. More specifically, right circularly polarised XUV with

 \vec{H}_{ext} in down direction delivers the same MCD absorption signal as left circularly polarised XUV with \vec{H}_{ext} oriented up. Here, the circular polarisation is kept in the right direction and one vacancy for each spin direction of the electrons is assumed in the $\mathbf{3}d$ valence states. From Eq.(2.81) and (2.85) the $\mathbf{3}p_{\frac{3}{2}} \rightarrow \mathbf{3}d$ transition probabilities with \vec{H}_{ext} pointing down for spin up \uparrow and spin down \downarrow electrons are:

$$A_{3p_{\frac{3}{2}} \to 3d}^{\downarrow} = \frac{1}{3}R^2 \qquad A_{3p_{\frac{3}{2}} \to 3d}^{\uparrow} = \frac{5}{9}R^2$$
(2.87)

This results in **62.5%** for spin up and **37.5%** probability for spin down electrons. Applying the same for the $3p_{\frac{1}{2}} \rightarrow 3d$ transitions leads to **25%** and **75%**, respectively. By changing the direction of the magnetic field to up, the transition probabilities are reversed. As a consequence, the absence of spin selection in the **3***d* states cancels out the dichroic signal.

In the second part of the two-step model, the spin-splitting in the 3d states due to spinorbit coupling is introduced and only spin-down electrons can be excited to the final state. As a result, for each initial state only one excitation path is allowed, the one for spindown electrons.



Figure 2.8: Two-step model for a fixed external magnetic field oriented down. The minority electrons are aligned to \vec{H}_{ext} . For right-circularly polarised XUV, the probability for electrons to complete a transition to the **3***d*-valence states is highest for spin-down electrons of the **3** $p_{\frac{1}{2}}$ level. For left-circularly polarised XUV, the situation is reverse: spin-down electrons from the **3** $p_{\frac{3}{2}}$ level are more likely to be excited. The spin-selectivity of the **3***d*-valence states gives a non-zero MCD signal.

In summary, according to the two-step model, the initial inner-shell is seen as a source of spin-polarised electrons, while the final 3d-shell is considered to work as a spin-sensitive detector by properly aligning the magnetisation and the XUV polarisation direction.

The macroscopic spin disparity is the characteristic feature of ferromagnets. It is responsible for the dichroic signal and its strength is related to the level of magnetisation of the material. In fact, the MCD signal is given by the difference between the number of vacancies for spin-up N_h^+ and spin-down electrons N_h^- , which is proportional to the magnetic moment *m* of the material [48,50]:

$$I_{\rm MCD} = N_h^+ - N_h^- \propto m \tag{2.88}$$

For a fully magnetised material, $N_h^- = 0$ and the MCD signal is maximised. If the sample is partially magnetised, then the final state has a small number of vacancies for spin-down electrons $N_h^- \neq 0$ and I_{MCD} is weaker.

In Figure 2.8, the two-step model is illustrated for a fixed magnetisation direction. Leftand right- circularly polarised XUV is applied for obtaining the two absorption spectra μ_+ and μ_- , depicted in Figure 2.9 a) and c) for the L- and M-edges, respectively. In the lower panels b) and d) the MCD signal given by the difference $\mu_+ - \mu_-$ is shown.

Sum Rules and Applicability to the M-edges

The quantitative determination of the material magnetic moment from the experimental MCD signal requires the application of the sum rules. In 1991 Thole *et al.* [64] developed the first method for calculating the orbital component of the magnetic moment, given by the expectation value of the orbital angular momentum $\langle L_z \rangle$:

$$\frac{\int_{j_{+}+j_{-}} dE(\mu_{+}-\mu_{-})}{\int_{j_{+}+j_{-}} dE(\mu_{+}-\mu_{-}+\mu_{0})} = \frac{1}{2} \frac{l(l+1)+2-c(c+1)}{l(l+1)(4l+2-n)} \langle L_{z} \rangle$$
(2.89)

Where μ_+ and μ_- are the MCD absorption spectra for right- and left circularly polarised light, respectively. The term $\mu_0 = \frac{1}{2}(\mu_+ + \mu_-)$ is called the *white-line* and corresponds to the absorption of linearly polarised XUV. *n* is the principal quantum number, while *l* and *c* denote the orbital quantum number for the initial and final state of the transition. The integral is over the sum $j_+ + j_-$, where $j_{\pm} = c \pm \frac{1}{2}$ is the quantum number for the total momentum of the final states with low (+) and high (-) binding energy.

In 1992 Carra *et al.* [65] extended the magneto-optical sum rule to determine also the spin component of the magnetic moment by calculating the expectation value of the spin momentum $\langle S_z \rangle$:

$$\frac{\int_{j_{+}} dE(\mu_{+} - \mu_{-}) - \frac{c+1}{c} \int_{j_{-}} dE(\mu_{+} - \mu_{-})}{\int_{j_{+}+j_{-}} dE(\mu_{+} - \mu_{-} + \mu_{0})}$$

$$= \frac{l(l+1) - 2 - c(c+1)}{3c(4l+2-n)} \langle S_{z} \rangle$$

$$+ \frac{l(l+1)[l(l+1) + 2c(c+1) + 4] - 3(c-1)^{2}(c+2)^{2}}{6lc(l+1)(4l+2-n)} \langle T_{z} \rangle$$
(2.90)

With $\langle T_z \rangle$ the magnetic dipole operator. This model represents a powerful tool for the determination of the magnetic moment. However, Thole and Carra's approach is based on the single ion picture with a partially filled valence shell. This simplified model has questionable validity for real magnetic materials with hybridized multi-bands. Wu *et al.* [66,67] suggested a different approach where the ratio between $\langle L_z \rangle$ and the sum of $\langle S_z \rangle$ and $\langle T_z \rangle$ is taken to eliminate the errors related to the denominators:

$$\frac{\langle L_z \rangle}{2 \langle S_z \rangle + 7 \langle T_z \rangle} = \frac{2}{3} \frac{\int_{j_+ + j_-} dE(\mu_+ - \mu_-)}{\int_{j_+} dE(\mu_+ - \mu_-) - 2 \int_{j_-} dE(\mu_+ - \mu_-)}$$
(2.91)

The applicability of Eq.(2.91) is limited by the fact that $\langle L_z \rangle$ and $\langle S_z \rangle$ can't be directly determined in a separate way, but only their ratio. The separation between orbital and spin contribution to the magnetic moment requires further assumptions.

An additional constraint of both Carra's and Wu's model is the determination of $\langle T_z \rangle$, which can't be neglected for anisotropic materials. In the works of Stöhr and König in 1995 [68,69] it was suggested to calculate the magnetic dipole operator from the average of several measurements performed at different orientations of the sample. In the case of isotropic magnetic materials such as nickel, iron or cobalt, the contribution of T_z is around **10%** [65,70] and can therefore be considered negligible.

The theoretical value of $\langle L_z \rangle$ and the one obtained with the sum rules were found to agree within ~10%, while a comparison of $\langle S_z \rangle$ gave a margin of error up to 50% [66,67].

Experimentally, the sum rules were applied for the characterisation of the L-edges of transition metals undergoing static excitations [25,71] as well as for studying the timeevolution of L_z and S_z in the presence of a laser pulse [25,72,73]. Therefore, they represent a beneficial tool for the interpretation of experimental results. By contrast, the efficacy of the sum rules is restrained by several challenges. To give an example, they have not been applied to the M-edges of transition metals because of their small spinorbit coupling. This becomes clearer by looking at Figure 2.9, where the comparison between the L- and the M-absorption edges is shown.



Figure 2.9: a) Absorption spectra for left-circularly (μ_{-}) , right-circularly (μ_{+}) and linearly (μ_{0}) polarised XUV when the *L*-edges are probed. The peaks corresponding to L_{2} and L_{3} are energetically separated. The corresponding MCD signal is shown in b). c) and d) represent the absorption spectra and the MCD signal when electrons are excited from the M-absorption edges. Here, M_{2} and M_{3} overlap, as the spin-orbit splitting is smaller than the bandwidth of the density of states.

The first step for determining $\langle S_z \rangle$ and $\langle L_z \rangle$ is to calculate the area under the peak of the absorption edges given by the absorption spectra μ_0 , μ_+ and μ_- :

$$\Delta Q_i = \int_{j_i} dE(\mu_+ - \mu_-) \qquad Q_i = \int_{j_i} dE\mu_0$$
(2.92)

With i = 2,3. Eq.(2.89) and (2.90) can be simplified in the following expressions:

$$\langle L_z \rangle = \frac{2}{3} \frac{N_h}{\epsilon cos\theta} \frac{\Delta Q_3 + \Delta Q_2}{Q_3 + Q_2}$$
(2.93)

$$\langle S_z \rangle = \frac{1}{3} \frac{N_h}{\epsilon cos\theta} \frac{\Delta Q_3 - 2\Delta Q_2}{Q_3 + Q_2} - \frac{7}{2} \langle T_z \rangle$$
(2.94)

Where N_h is the number of holes, ϵ is the ellipticity of the circularly polarised light and θ is the angle between the magnetisation direction of the sample and the \vec{k} -vector of the incident beam.

It becomes now comprehensible how the spin-orbit coupling plays a crucial role in the determination of $\langle S_z \rangle$. If the SO coupling is not strong enough, as in the illustrated case of the M-edges (Figure 2.9), the absorption peaks $p_{\frac{1}{2}}(M_2)$ and $p_{\frac{3}{2}}(M_3)$ are not well energetically separated. As a consequence, the limits of integration for Eq.(2.92) are not

properly defined. This does not constitute a problem for the evaluation of $\langle L_z \rangle$, since here the integrals are summed. On the other hand, it strongly influences the evaluation of $\langle S_z \rangle$ where the areas of the two absorption edges are subtracted [74,75].

A further factor which affects the quantitative estimation of $\langle S_z \rangle$ is the presence of background contribution. For instance, the way the spectra are normalised modifies the estimation of the spin component, since with the normalisation factor N the radial component should be cancelled. Nevertheless, N is spin- and energy dependent [76], so that it can linearly change of about **30%** from the top to the bottom of the *d*-band of nickel [67,77,78]. The spin-orbit coupling is proportional to the radial component, but the orbital momentum is proportional to the spin-orbit coupling energy [78]. Therefore, it should not be affected by energy variations.

One last limitation that needs to be highlighted is the presence of competing transition channels. For the M-edges there are two possible transitions that can happen: $3p \rightarrow 3d$ and $3p \rightarrow 4s$. The first one has the highest probability, as the levels have the same quantum number [79]. As a result, this does not constitute a limit for the applicability of the sum rules to the M-edges [32].

Chapter 3

Investigation of Time-integrated Optical

Nonlinearities

The time-integrated measurement of nonlinearities is the first step for identifying their nature. Of particular significance is the investigation of the change of the material's refractive index and the number of charges excited by the NIR pulse. Their intensity dependence reveals important information about the nonlinear effects setting in inside the medium.

In the work of this thesis, a few-cycle laser pulse with a duration of about 4 fs is used, which excludes any dynamics with a greater characteristic time constant and sets the electronic response as the major contributor to the material nonlinearities [80]. The solids under investigation are silicon as a semiconductor and nickel as a metal. In the following it is shown how the investigation of the medium's time-integrated nonlinearities is possible only in silicon. The measurement technique used in this case is the well-known Z-scan established in **1990** by M. Sheik-Bahae [81].

3.1 Z-Scan in Silicon

The results presented in this section are obtained by measuring a **200** nm thick silicon membrane with an open aperture Z-scan. A similar analysis was performed by [32,82]. The technique consists of measuring the power transmitted through a material for different intensities of the incident pulse. The intensity is given by:

$$I = \frac{E_{\text{peak}}}{\tau A} \tag{3.1}$$

where E_{peak} is the peak energy and τ is the pulse duration. Since *I* is inverse proportional to the area of the beam profile *A*, the variation of the intensity is achieved by simply moving the sample along the propagation direction of the beam (see Figure 3.1). For this purpose, the sample is fixed on a movable stage. The maximum intensity is obtained by putting the sample in focus, where the beam size is the smallest. If the maximum intensity is not high enough to induce nonlinearities in the material, no change in the transmitted

power is expected. The transmitted intensity can then be expressed by the Lambert-Beer's law:

$$I = I_0 e^{-\alpha z} \tag{3.2}$$

Where \mathbf{I}_0 is the incident intensity, z is the propagation length in the medium and α its frequency dependent absorption coefficient. When the maximum intensity is high enough to promote the nonlinear response of the sample (> $\mathbf{10}^{11}$ W/cm² in the case of silicon), Eq.(3.2) has to be rewritten as [83]:

$$I = I_0 e^{-\alpha z - \beta(I)z} \tag{3.3}$$

Where β is the intensity dependent two-photon absorption coefficient described by Eq.(2.35).



Figure 3.1: Setup of an open aperture Z-scan. The sample is fixed on a movable stage and is moved along the propagation direction z of the beam. At the same time, the transmitted power is recorded with a powermeter (orange curve). The intensity profile of the pulse is plotted in red as a function of z.

3.1.1 Intensity-dependent Transmission

The peak energy transmitted through silicon for an incident $E_{\text{peak}} = 4 \,\mu\text{J}$ is shown in Figure 3.1 and Figure 3.2 (orange curve). When nonlinear effects set in (sample in focus), the transmission drops to **65.5%** of the infalling peak energy. When the sample is moved away from the focus, the incident intensity decreases and the transmission rises equally in both left and right direction. Here, the sample's response is essentially linear and the maximum relative transmission is **84%**.

The open aperture Z-scan is performed for three different peak energies (Figure 3.2, left). It is evident how an increase in peak energy results in a greater drop in transmission when the silicon sample is positioned in focus, giving **66.85%** transmission for **3.8** μ J and **69.7%** for **3** μ J. In the linear case, the maximum transmission value is similar for all three measurements (around **84%**). Different than the nonlinear polarisation, the linear

response of the material increases linearly with the incident electric field. Therefore, it is not measurable in a time-integrated measurement.



Figure 3.2: Left: Open-aperture Z-scan performed on silicon for three different peak energies. The transmission of the sample in focus decreases by increasing the peak energy. Right: Intensity-dependence of the relative transmission.

3.1.2 The Beta coefficient

Liu et al. developed a formalism to describe two-photon absorption in UV transmitting materials. According to this, the transmitted intensity can be expressed as [83,84]:

$$I = \frac{I_0 (1 - R)^2 e^{-\alpha z}}{1 + \frac{\beta}{\alpha} I_0 (1 - R) (1 - e^{-\alpha z})}$$
(3.4)

Where *R* is the reflectivity under normal incidence. It should be observed that this formalism gives a simplified description of silicon nonlinearities where only two-photon absorption takes place. This model is not exhaustive for the parameters of the pulse (broadband spectrum and higher intensity) used in this experiment, since further effects as tunnelling and multiphoton absorption could play a crucial role. Nevertheless, an estimation of β can still be given.

From Eq.(3.4) the 2PA Coefficient β can be retrieved:

$$\beta = \frac{\alpha \left(e^{-\alpha z} - \frac{l(z)}{l_0} \right)}{l(z)(1 - e^{-\alpha z})}$$
(3.5)

Eq. (3.5) was obtained by taking R = 0, since the sample was positioned under Brewster angle. The value of β for **750** nm, the central wavelength of the laser used in this work, is not known in literature. Additionally, the absorption coefficient α strongly depends on temperature and frequency, which also leads to large variations in the value of β . The spectrum of the laser pulse covers wavelengths from about **400** nm to **1050** nm, a spectral range in which silicon's absorption coefficient changes from **102500** cm⁻¹ to **15.610** cm⁻¹ [85]. One can recognize how the absorption coefficient rapidly increases when the photon energy of the exciting pulse gets closer to the band gap of silicon (**1.1** eV). A weaker dependence of α on the temperature is reported by Vuye et al. [86]. At **750** nm, α varies from **640.88** cm⁻¹ at **20** °C to **188.5** cm⁻¹ at **300** °C.

Despite the high variance of α in the available literature, the calculation of the 2PA coefficient is presented here for the purpose of estimating the 2PA contribution in the nonlinear dynamics of silicon (see Figure 3.3, left). For intensities in the range of 10^{12} W/cm² and $\alpha = 511.6$ cm⁻¹ (at 850 nm [85]), a mean value of $\beta = 1.065 \pm 0.228$ cm/GW is calculated.

Bristow *et al.* calculated β for wavelengths up to **850** nm. For $\alpha = 500$ cm⁻¹, they obtained $\beta = 2.1 \pm 0.4$ cm/GW at **850** nm [87], which is reasonably near to the value found from the measurements presented here. Sabbah and Riffe found a value of $\beta = 6.8$ cm⁻¹ with $\alpha = 1020$ cm⁻¹ at **800** nm [41]. Finally, for wavelengths between **1.2** µm and **2** µm, Lin et al. obtained $\beta < 1$ cm/GW [88].



Figure 3.3: Left: 2PA coefficient β obtained with $\alpha = 500$ cm-1 by taking the measured transmission at incident intensities above $3.4 \cdot 10^{12}$ W/cm2. Right: Number of excited carriers per atom in case of one-photon absorption (1PA, red) and two-photon absorption (2PA, green) as a function of intensity.

3.1.3 The Contribution of One- and Two-photon Absorption

With β obtained from the mesurements, the number of excited carriers can be investigated. In subsection 2.1.6 the number of excited charges through 2PA is reported. The total number per atom, which includes both one and two photon absorption, is given by:

$$N = \frac{1}{\rho_{\text{atom}}} (N_{1\text{PA}} + N_{2\text{PA}}) = \frac{1 - R}{\rho_{\text{atom}}} F\left(\frac{\alpha}{\hbar\omega} + \frac{\beta I}{2\hbar\omega}\right)$$
(3.6)

Where the atom density ρ_{atom} is $5 \cdot 10^{22}$ atoms/cm³. As previously mentioned, this formalism gives only a simplified description of the silicon nonlinearities induced by a strong, few-cycle laser pulse. The number of excited carriers N_{1PA} and N_{2PA} per atom are calculated from Eq.(3.6) by neglecting the reflectivity. In Figure 3.3, right, one can notice the intensity threshold for the two different processes responsible of charge excitation.

For intensities below 10^{12} W/cm², the dominant process is single photon absorption over the indirect band gap. For intensities above 10^{12} W/cm², the laser-induced electron excitation takes place mostly through two-photon absorption over both the direct and the indirect band gap. The total number of excited charges per atom reaches ~2.55 \cdot 10⁻³ at $4 \cdot 10^{12}$ W/cm², inducing a significant change in the refractrive index of silicon. According to the Drude model, the free-carrier contribution to the refractive index can be expressed as [41]:

$$\Delta n_{FC}(N,T_e) = -\frac{2\pi e^2}{n_0 \omega^2} \frac{N}{m^*(T_e)}$$
(3.7)

Where n_0 is the refractive index of silicon at the central frequency of the laser, ω is the central angular frequency and $m^*(T_e) = 0.156 m_e$ is the temperature-dependent effective mass.

3.1.4 Change of Refractive Index

Eq.(3.6) gives access to the total number of charges excited through 1PA and 2PA. By substituting N in Eq.(3.7), it is possible to calculate the change of silicon's refractive index due to the free carriers generated through 1PA and 2PA. As shown on the left of Figure 3.4, in the range of 10^{11} W/cm² the refractive index does not reduce considerably due to the presence of free charges, reaching a maximum chenge of $\sim -1.85\%$. This result agrees with the values reported in [32,82]. On the other hand, an intensity of $4 \cdot 10^{12}$ W/cm² already induces a change of $\sim -25\%$ for n = 3.63 at 850 nm. At 10^{13} W/cm², silicon's refractive index tends to zero. A possible explanation might be the erroneous assumption of the sample still considered at room temperature for intensities near the material damage threshold ($\sim 10^{13}$ W/cm²). Subsequently, an underehestimation of the effective mass in Eq.(3.7) is expected. A further aspect that might play a role is the behaviour of silicon near its damage threshold: the material could start melting before actually showing deterioration.



Figure 3.4: Left: Intensity-dependent change of the refractive index in silicon due to the free carriers generated through 1PA and 2PA. Inset: Zoom over the intensity interval $3 - 15 \cdot 10^{11}$ W/cm². Right: Intensity-dependent change of the refractive index due to the Kerr effect for $n_2 = 4.6 \cdot 10^{-14}$ cm²/W [87]. Inset: Zoom over the intensity interval $3 - 15 \cdot 10^{11}$ W/cm².

The negative contribution to the refractive index due to the free carriers is partially balanced by the positive contribution given by the Kerr effect. According to Bristow *et al.* [87], the value of the nonlinear refractive index n_2 , determined by measuring with a **200** fs pulse at **850** nm, is **4.7** \cdot **10**⁻¹⁴ cm²/W. Using Eq.(2.24), the change of n_2 can be calculated (Figure 3.4, right). For an intensity of $4 \cdot 10^{12}$ W/cm², $\Delta n_{\text{Kerr}} = n - n_0 =$ **0.184** is obtained, which corresponds to an increase of about **5%**. In consequence, the Kerr effect couteracts **1/5** of the refractive index change caused by 2PA. This value is higher than what found by [32], but probably underestimated by the literature value of n_2 . Its numerical value strongly depends on the spectral profile of the exciting pulse.

3.2 Time-integrated Measurement of Nickel's Transmission

Because of their intrinsic nature of being opaque materials, metals have a high reflectivity and a low transmissivity of visible light. The high number of free electrons creates an electron plasma which absorb and re-emit photons. The sample used in the work of this thesis is a **8** nm thick nickel film coated on a **10** μ m thick fused silica substrate. The thickness of Ni is chosen in order to have a) enough intensity for the transmitted field to be detected and at the same time b) have enough absorption for retrieving Nickel's electronic properties from the transmitted waveform. SiO₂ is inert to any nonlinearity at the intensities applied to measure Ni's nonlinear response. Moreover, it is transparent to visible light. This makes it the best candidate as a substrate.



Figure 3.5: Setup for measuring nickel's transmission difference between in and out of focus. The sample is fixed on a movable stage and is moved along the propagation direction \mathbf{z} of the beam. At the same time, the transmitted signal is recorded with a photodiode and a boxcar averager, then read out with an oscilloscope. The expected profile of Ni's transmission curve is plotted in orange. The intensity profile of the pulse is plotted in red as a function of \mathbf{z} .

In the spectral range of the laser, the linear transmission of the Ni/SiO₂ sample is about **43%**, making the performance of the experiment more challenging with respect to silicon.

The conventional Z-scan performed with a powermeter does not detect any change in transmission. Therefore, the transmitted signal is recorded with a photodiode and a boxcar averager (Figure 3.5). The difference between the transmitted signals in and out of focus, for an incident peak energy of **1.1** μ J, amounts to only **~2%**, a quantity comparable to the systematic error of the powermeter. It is meaningful to notice that nickel shows higher transmission for higher intensity (in focus). In other words, it transmits more when the nonlinear effects set in, suggesting different physical processes as their origin compared to the silicon case. Further study of the intensity-dependent transmission in nickel is treated in Chapter 6 with the time-resolved investigation of its nonlinearities. Here, it will be shown that the main effect which causes a change in Ni's transmission is saturable absorption.

3.3 Main Findings of the Time-Integrated Study

The present chapter provides a first study of the nonlinearities in silicon and nickel. The time-integrated transmitted power is measured as a function of the sample position. Silicon is highly transparent, hence it is possible to extract the characteristic parameters of its nonlinear behaviour from a z-scan [81]. First, Si shows an exponential decrease of transmission when the sample moves nearer to the focus position, i.e. when the intensity gets high enough for nonlinear effects to set in. More specifically, it is found that for intensities > 10^{12} W/cm² two-photon absorption takes over one-photon absorption. The free carriers generated through 2PA cause the reduction of silicon's refractive index of 25% at the incident intensity of $4 \cdot 10^{12}$ W/cm². At the same intensity, the Kerr effect acts on n with an increment of 5%. This value is expected to be underestimated by an incorrect literature value of n_2 , which strongly depends on the spectral and temporal profile of the exciting pulse. In the field-resolved study of silicon's nonlinearities (see 5.3), this aspect is further investigated.

On the other hand, in the case of nickel a position-scan with a standard powermeter is not applicable. As it is an opaque material, the **8** nm thick Ni film transmits only **40%** of the incident power. The change in transmission between in and out of focus is detected here with a photodiode and a boxcar averager, exhibiting only a 2% transmission difference between high and low intensity. Interestingly, nickel's transmission increases at high intensity, suggesting saturable absorption as the main nonlinear process taking place. This effect is further discussed in section 6.3.

By using a lock-in amplifier for detecting the signal, an accurate z-scan of nickel is possible. However, this thesis is focussed on the time-resolved study of the electronic response to optical excitation, as it enables a much deeper investigation of nonlinearities in solids.

Chapter 4

Experimental Methods for the Study of Charge

and Spin Dynamics

Optoelectronic and plasmonic devices represent a possible alternative to standard electronics for pushing signal processing to petahertz clock rates. Therefore, tracking light-matter interaction in real-time is of fundamental importance to study the charge dynamics underlying nonlinear processes induced in a solid by a strong optical pulse. A further alternative route to conventional electronics is given by spintronics, which relies on both charge and spin degrees of freedom. A feasible approach is the optical control of electronic and magnetic properties through ultra-short laser pulses. Many open questions need to be addressed before extending modern optoelectronic and spintronic devices to petahertz frequencies. One such unsolved problem is how light could be used to manipulate materials on sub-fs time scales, to enable gate switching at ultra-high clock frequencies. A following challenge is to identify the physical processes underlying the materials' nonlinear behaviour.

Time-resolved Measurement Technique	Accessible Dynamics
Polarisation Sampling	Induced electron current
Transient Absorption	Carrier population transfer
Atto-MCD	Magnetic Moment (Spin)

Table 4.1: The three different measurement techniques applied in the work of this thesis and the corresponding charge and spin dynamics which can be studied.

In the present work, three time-resolved techniques are performed for the study of strongfield induced charge and spin dynamics (Table 4.1). Polarisation Sampling (PS) [1] spectroscopy is used to investigate nonlinearities induced by intraband electronic motion in silicon and nickel. On the other hand, the study of the carrier redistribution due to interband transitions inside Si, Ni and SiO₂ is performed with Transient Absorption (TA) spectroscopy. By applying these complementary techniques, we present an extensive description of the electronic properties of a semiconductor and a metal under the influence of a strong electric field.

Finally, a novel technique based on TA is introduced for observing the optically-induced spin transfer in Ni/Pt multilayer samples on a sub-femtosecond time scale. This method is called Attosecond Magnetic Circular Dichroism (Atto-MCD) [90] and gives access to the magnetic and electronic properties of the material at the same time.

4.1 Transient Absorption Spectroscopy and Streaking

When a light pulse interacts with a medium, electrons can be excited from the valence (VB) to the conduction band (CB) or they can be accelerated within the same band. As TA represents a powerful technique for studying the change in the electronic population distribution due to electron excitation, a wide range of materials have been examined such as semiconductors [16,17], dielectrics [19,91] and transition metals [92].



Figure 4.1: Band-structure of silicon (based on Fig.1 of [16]). The few-cycle NIR pulse excites electrons from the VB to the CB, while the XUV pulse excites the deep-bound electrons to the CB. The XUV transitions are sensitive to the change of carrier population distribution induced by the NIR pulse.

Figure 4.1 shows the principle of a TA measurement for a band-gap material, for example silicon. The few-cycle NIR pump pulse excites electrons from the valence to the conduction band. The attosecond XUV pulse works as the probe pulse, exciting the deepbound electrons to the CB. These XUV excitations are sensitive to the change in the population distribution induced by the NIR pulse. Therefore, the XUV radiation transmitted through the sample carries information about the electron population change induced by the NIR pulse. In TA, the transmitted XUV is measured as a function of the

delay between pump and probe pulses to time-resolve the electronic motion. According to the Lambert-Beer's law, the absorption coefficient of a medium of length *z* is expressed by:

$$\alpha(\omega) = -\frac{1}{z} ln \frac{l(\omega, z)}{l(\omega, z0)}$$
(4.1)

Where ω is the central angular frequency of the laser pulse. The absorbance can be defined as:

$$\mu(\omega) = -\ln \frac{l(\omega, z)}{l(\omega, z\mathbf{0})}$$
(4.2)

Specifically for the case of a TA experiment, the change in XUV absorbance is obtained from the ratio between the transmitted intensity in presence of the pump pulse $I_{pumped}(\omega, \tau)$ and the intensity of the incident XUV pulse $I_{XUV}(\omega)$:

$$\Delta \mu_{\rm XUV}(\omega,\tau) = -ln \frac{I_{\rm pumped}(\omega,\tau)}{I_{\rm XUV}(\omega)}$$
(4.3)

The change in the occupation is defined as the difference between the XUV absorbance in presence of the NIR pump pulse and the XUV absorbance without the NIR pulse. It is given by:

$$\Delta DOS_{XUV}(\omega, \tau) = -ln \frac{I_{\text{pumped}}(\omega, \tau)}{I_{XUV}(\omega)} + ln \frac{I_{\text{unpumped}}(\omega, \tau)}{I_{XUV}(\omega)}$$

$$= ln \frac{I_{\text{pumped}}(\omega, \tau)}{I_{\text{unpumped}}(\omega)}$$
(4.4)

In Figure 4.2 the set-up of transient absorption spectroscopy is depicted. The few cycle near-infrared (NIR) pulse is focused into a gas target to generate a train of attosecond XUV pulses through High-Harmonic Generation (HHG). Depending on the photon energy of the material absorption edges, argon (Ar) or neon (Ne) are used for HHG in the present experiments. For probing the M-edges of nickel around **66** eV, Ar is used, while Ne is suitable for probing the L-edges of silicon (~**100** eV) and SiO₂ (~**109** eV).

The NIR and the XUV pulses are spatially separated by a perforated mirror in order to create a Mach-Zehnder interferometer. A delay between the two is introduced by putting a movable stage into the NIR arm. In the XUV arm, an Al/Zr+Si/Mo filter (depending on the XUV photon energy) is located in order to block the residual NIR radiation and spectrally filter the XUV radiation. The XUV pulse train is turned into isolated XUV pulses with the filter and a mirror. Also here, the type of coating depends on the XUV energy required to probe. For measuring the electron dynamics in nickel, a Mo/Si multilayer mirror is used. In the case of silicon and SiO₂, a set of three XUV mirrors coated with rhodium (angle of incidence 15°) is needed.

The two beams are recombined with a second perforated mirror and focussed with a toroidal mirror (Jobin Yvon HORIBA) into the sample. The transmitted XUV radiation is measured as a function of energy and delay between pump and probe pulse. It is detected with an XUV spectrometer consisting of a grating and a XUV-sensitive CCD

camera (Princeton Instrument, PIXIS XO400B). In front of this, a slit is positioned to prevent the NIR light transmitted through the sample from reaching the camera.

In this work, the intraband carrier dynamics given by TA are measured in parallel with the waveform of the exciting electric field given by attosecond streaking spectroscopy [93,94]. It is possible to directly compare the electronic response to the NIR excitation and the NIR field, giving access to their absolute timing. The temporal relation reveals if the electronic system responds instantaneously or with a time-delay to the NIR excitation. This is of great relevance for understanding the physical processes underlying the optically-induced dynamics.



Figure 4.2: Set-up of transient absorption spectroscopy. A train of attosecond XUV pulses are generated through HHG by focussing the few-cycle NIR pulse into a gas target. The XUV and the NIR beam are separated with a perforated mirror to introduce a delay between the two pulses. For eliminating the remaining NIR radiation in the XUV arm and isolate the attosecond XUV pulses, a filter is positioned in the beam path. After recombining XUV and NIR with a second perforated mirror, they are focussed with a toroidal mirror into the sample. The transmitted XUV radiation is measured with a spectrometer as a function of the delay between pump and probe pulse. In parallel, the waveform of the electric field is measured with streaking spectroscopy.

The streaking set-up is also shown in Figure 4.2. The XUV radiation ionizes Ne atoms emitted by the gas nozzle. The ionized electrons get accelerated by the NIR pulse and their velocity is measured with a Time-Of-Flight (TOF) spectrometer. The amount of gained momentum depends on the difference between the time $t_0 = 0$ of the birth of the free electrons and the time $t > t_0$ of the interaction with the NIR field. In other words, it depends on the delay $\Delta t = t - t_0$ between the XUV and the NIR pulse. The electrons

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momentum is proportional to the NIR pulse vector potential, thus the electric field is obtained from: $E(t) = \frac{\partial A(t)}{\partial t}$.

4.2 Polarisation Sampling

Attosecond Polarisation Sampling (APS) is a measurement technique first introduced by Sommer et al. [1]. The basic idea is to directly detect the electric field after interacting with a medium. This carries the information about the induced polarisation and the amount of energy deposited inside the material. Otherwise speaking, APS is sensitive to the electron currents within the same band. The temporal resolution, as for transient absorption, is on the attosecond scale.

The materials under study are silicon and nickel. The samples are the same used for performing the time-integrated analysis described in Chapter 3.

Different than in [1], where the waveform is detected with an attosecond Streak camera, Linear Petahertz Photo-conductive Sampling (LPPS) in gas is used in this work [95]. The working principle of LPPS is similar to the one of streaking, although it has the advantage of having a higher dynamic range. The central idea is to measure a current J(t) which is proportional to the vector potential A(t) of the field. Therefore, instead of measuring the modified electron momenta as streaking spectroscopy, LPPS measures the charge separation in an external circuit.

The basic concept of polarisation sampling is depicted in Figure 4.3. It consists of three measurements where the spatial properties of a Gaussian beam are utilized. This is identical to the Z-scan working principle described in 3.1. The first step is to detect the unperturbed pulse; this is considered the reference. In the second measurement, the sample is positioned in the beam focus and the transmitted electric field is detected. This is equivalent to measuring the strong field after propagating through the medium. The third measurement consists of recording the waveform transmitted through the sample located out of focus. This is clearly analogous to measuring the perturbed weak field. The transmitted strong and weak fields carry information about the nonlinear and the linear response of the medium, respectively. Knowing the waveform of the unperturbed pulse (reference), both the nonlinear and the linear polarisation of the material can be extrapolated.

As shown in Figure 4.4, the few cycle near-infrared (NIR) pulse is focused into an Ar target to generate a train of attosecond XUV pulses centred at **20** eV through HHG. As in TA, the NIR and the XUV are separated by a perforated mirror to introduce a delay between the two pulses. The sample is located in the NIR arm. Different from the case of transient absorption, no spectral filtering with a metallic filter is applied in the XUV arm. The reason is the fact that low energy XUV photons are necessary for measuring LPPS, these would be filtered out as well. After the first perforated mirror, the XUV radiation gets reflected by an unprotected gold mirror at **45**° to maximize reflection around **20** eV. After, the two beams are recombined with the second perforated mirror and focussed with the toroidal mirror into the LPPS set-up. As in streaking, the XUV pulse ionizes the neon atoms coming from the gas nozzle. The electrons get accelerated by the NIR electric field and the amount of gained momentum depends on the delay between the XUV and the NIR pulse. Two electrodes read out the generated current, which is then pre-amplified with two pre-amplifiers (Femto, fast optical power meter series OE-200) and measured

with a lock-in amplifier (Zurich Instruments, MFLI, 500 kHz/5 MHz). The current signal is proportional to the vector potential of the NIR pulse, giving complete access to its waveform. The adjustable amplification of the current allows to detect smaller signals compared to streaking. Similarly, the upper limit of the pulse intensity is limited, in principle, only by the damage threshold of the sample under analysis. On the other hand, the field detection with streaking has two main limits: if the intensity of the NIR pulse is not high enough, the electrons don't gain sufficient momentum to reach the TOF. On the other hand, if the intensity is too high, the NIR pulse starts ionising the gas by multiphoton absorption or tunnelling, causing electron screening.

As mentioned before, the XUV pulses for LPPS are centred at **20** eV. These harmonics lie in the plateau region of the XUV spectrum. Therefore, the used XUV pulses are not isolated. The temporal resolution of the LPPS detection technique is given by the envelope of the XUV pulse train. Consequently, the temporal profile of the XUV radiation represents the main limitation to the high-frequency detection of the NIR pulse.



Figure 4.3: Schematic picture of the working principle of PS. As an example, the results on silicon are shown. The 1st Measurement consists in measuring the unperturbed electric field. In the second and the third measurement, the field is detected after propagating through the sample positioned in (strong field) and out (weak field) of focus.



Figure 4.4: Set-up of polarisation sampling. Attosecond XUV pulses are generated through HHG by focussing the few-cycle NIR pulse into an Ar target. The XUV and the NIR beam are separated with a perforated mirror. In the NIR arm, a delay is introduced and the sample is positioned in the beam path. After recombining XUV and NIR with a second perforated mirror, they are focussed with a toroidal mirror into the LPPS set-up. Here, the waveform of the electric field is detected.

4.3 Attosecond Magnetic Circular Dichroism

The magnetic properties of matter can be manipulated with light on different time scales. In the past years, several experiments have been reported where optical pulses were able to reduce the magnetic moment of the material causing demagnetisation [25,73,96–98]. Some of the leading effects are spin-orbit coupling, which happens on a time scale of a few tens of femtoseconds; thermalization of charges and spins, with a characteristic time of $\sim 10^2$ fs; electron-phonon coupling and dissipation of angular momentum to the lattice, which take place on a picosecond time scale. It is noticeable how the time window in which the light pulse coherently interacts with the magnetic sample has stayed unexplored. Theoretical work has been done on tailored systems where the demagnetisation channel is the spin transfer between a ferromagnetic (FM) and a paramagnetic (PM) layer [99,100]. The predicted time scale of the intersite spin migration is given by the temporal length of the laser pulse. Accordingly, the investigation of demagnetisation in its early stage requires few-femtosecond laser pulses and sub-femtosecond time resolution.

Aiming to explore the coherent spin dynamics in tailored FM/PM systems, a novel technique called "Attosecond Magnetic Circular Dichroism" (Atto-MCD) was developed in this work [90]. It combines transient absorption spectroscopy with circularly polarized attosecond XUV pulses to measure the magnetic circular dichroism (MCD) with sub-femtosecond time resolution. In synchrony to the spin dynamics, atto-MCD allows to

track the charge dynamics as well, making the technique unique. As explained in 2.3, XMCD is the polarisation-dependent XUV absorption of a magnetic material. Namely, a magnetised sample shows different absorption spectra $\mu^{-}(\omega)$ and $\mu^{+}(\omega)$ for left- and right-circularly polarised XUV pulses. The difference $\mu^{-}(\omega) - \mu^{+}(\omega)$ is the conventional MCD signal $\Delta_{MCD}^{conv}(\omega)$ (Figure 4.5), which is a measure of the magnetic moment of the material.

As previously mentioned, changing the circular polarisation of the XUV pulse is analogous to reversing the direction of the external magnetic field applied to the sample, which has the advantage of being facilely implementable in the experimental set-up. If the magnetic system gets excited with a NIR pulse, this will induce a reduction of the magnetic moment of the ferromagnetic material. Measuring the XUV transmission as a function of the delay between the NIR and the XUV pulse enables the time-track of the laser-induced demagnetisation.



Figure 4.5: Schematic concept of MCD. The XUV radiation transmitted through a magnetised sample is measured for the both directions of the external magnetic field, $\mu^+(\omega)$ in a) and $\mu^-(\omega)$ b). In c) the XUV absorbance for the two cases is shown. The difference delivers the MCD signal, which is a measure of the magnetic moment of the material. The sample is a tailored system of FM/PM layers developed by the group of M. Münzenberg at the university of Greifswald.

In Figure 4.6 the set-up for the Atto-MCD experiment is depicted. From a comparison with Figure 4.2, it is evident that the main differences with a conventional TA set-up is the XUV phase retarder and, clearly, the application of a magnetic field to the sample. In the experiments presented below, the external magnetic field amounts to **50** mT. Attosecond XUV pulses centred at **66** eV are generated in a argon target to probe the M-absorption edges of Nickel.



Figure 4.6: Set-up of Atto-MCD. Attosecond XUV pulses centred at **66** eV are generated through HHG by focussing the few-cycle NIR pulse into an Ar target. The XUV and the NIR beam are separated with a perforated mirror to introduce a delay between the two pulses. Spectral filtering is applied by an Al filter and a multilayer mirror. In the XUV arm, the phase retarder is positioned to turn the XUV polarisation from linear to circular and isolate the attosecond XUV pulses. After recombining XUV and NIR with a second perforated mirror, they are focussed with a toroidal mirror into the sample where an external magnetic field is applied. The transmitted XUV radiation is measured with a spectrometer as a function of the delay between pump and probe pulse.

4.3.1 XUV Phase Retarder to generate circular polarisation

Probing the dynamics of the magnetic moment requires circular polarised XUV pulses to couple with the spin of electrons. The transformation of the polarisation from linear to circular for attosecond XUV pulses is not a trivial procedure. Transmission polarisers are troublesome to apply because of the high material absorption of XUV radiation. Therefore, reflection optics are more suitable. Furthermore, depending on the XUV photon energy, special multilayer mirrors have to be realized for maximizing the reflectivity over a wide energy range. In the work of this thesis, the polarisation was rotated with a multiple-reflection phase shifter first introduced by T. Koide and T. Shidara [101]. The device was used for synchroton sources [102,103] as well as for extreme ultraviolet (EUV) pulses generated with HHG [104]. Albeit the reached ellipticity is close to **100%**, the total reflection is only of a few percent and could use further improvement.

The XUV phase retarder used in this experiment is developed by Yi-Ping Chang [105] and is shown in Figure 4.7. It consists in a set of four Mo/Si multilayer mirrors which changes the polarisation of the XUV pulse from linear to circular by introducing a phase shift between the two components E_{\parallel} and E_{\perp} of the XUV electric field. According to the Fresnel equations, the reflectivity for the parallel and the perpendicular components can be expressed as a function of the incident angle [102]:

$$\widetilde{r}_{s} = r_{s}e^{i\delta_{s}} = \frac{\cos\theta_{i} - \sqrt{\varepsilon_{r} - \sin^{2}\theta_{i}}}{\cos\theta_{i} + \sqrt{\varepsilon_{r} - \sin^{2}\theta_{i}}}$$
(4.5)

$$\widetilde{r_p} = r_p e^{i\delta_p} = \frac{\varepsilon_r \cos\theta_i - \sqrt{\varepsilon_r - \sin^2\theta_i}}{\varepsilon_r \cos\theta_i + \sqrt{\varepsilon_r - \sin^2\theta_i}}$$
(4.6)

The phase difference between s and p is given by:

$$\Delta \varphi = \delta_s - \delta_p \tag{4.7}$$

It becomes clear how $\Delta \varphi$ can be controlled by varying the angle θ_i between the surface normal and the infalling beam, and the type of reflecting material ε_r . To this extent, circular polarisation can be achieved. An additional factor that contributes to the ellipticity is the extinction ratio. This is defined as the intensity ratio between the two polarisation components R_s/R_p . In the ideal case, this should be equal to one and can be controlled by rotating the polariser mount by the angle θ_{pa} (see Figure 4.8).



Figure 4.7: CAD drawing of the phase retarder. The mount was fabricated in aluminium by the workshop at MPQ.



Figure 4.8: Side view and front view of the phase retarder. θ_{pa} is the angle between the normal of the mirrors' surface and the polarisation axis of the pulse. It can be changed by rotating the phase retarder mount. θ_i is the angle between the normal of the mirrors' surface and the incident beam. This can be tuned by adjusting the mount of the mirrors.

The polarisation status of the XUV after the phase retarder is measured with a Rabinovitch detector [106]. It acts as a rotating linear polarizer. The beam is reflected by a multilayer mirror positioned at **45°** such that the extinction ratio is maximized. In other words, only the XUV in one polarisation direction, *s* or *p*, gets reflected and recorded by a reverse-biased XUV sensitive photodiode (AXUV100G, OptoDiode Corp.). The detector (multilayer mirror and photodiode) is rotated and the signal is recorded as a function of the rotation angle for different polariser angles θ_{na} .

Figure 4.9 shows the experimental results (left) and the theoretically predicted values (right). The plotted signals oscillate along the rotation angle of the Rabinovitch detector. For each θ_{pa} , the maximum I_{max} and the minimum intensity I_{min} are taken to define the ellipticity:

$$\epsilon = \sqrt{\frac{I_{\min}}{I_{\max}}}$$
(4.8)

Linear polarised light gives $\epsilon = 0$, while if $\epsilon = 1$ the pulse is perfectly circular polarised and the recorded signal is a flat line instead of an oscillating curve. The maximum ellipticity $\epsilon \approx 0.5$ is achieved at $\theta_{pa} = 36^{\circ}$. This value is in good agreement with the theory which predicts $\epsilon \approx 0.549$ [105].

The pulse duration is not significantly affected by the reflecting phase retarder. In fact, by applying a FROG-like algorithm to the measured streaking spectrogram a duration of $\tau_{XUV} = 310 \pm 20$ as is obtained [32].



Figure 4.9: Left: Experimental results of the signal amplitude measured with the photodiode as a function of the detector's angle of rotation. The different curves correspond to different rotations of the polariser. Right: Theoretical prediction of the signal amplitude as a function of the rotation angle.
Chapter 5

Experiments: Strong-Field Induced Charge

Dynamics in Silicon

Pushing the frontiers of signal processing, in terms of speed, requires a different approach compared to standard electronics, which can be given by the manipulation of electron currents with ultrashort optical pulses. Current electronic devices mostly rely on silicon-based chips. Therefore, the application of optoelectronic devices, based as well on silicon (Si), represents an appealing alternative, as it is possible to use the same underlying technology. In view of this, the interaction of Si with a strong and ultrashort optical pulse needs to be exhaustively studied.

The present chapter is dedicated to the time evolution of the silicon nonlinearities induced by a strong laser field. In the first part, the interband electron dynamics are investigated by performing Transient Absorption (TA) spectroscopy. Here, the absolute timing between the laser electric field and the change in carrier density is measured by combining TA with attosecond streaking spectroscopy. The second part regards the intraband electron transitions. Polarisation sampling is used to time-resolve the induced polarisation as well as the work applied to silicon by the laser electric field.

5.1 Interband Electronic Motion in Silicon

Transient absorption experiments have been performed in the past on semiconductors with both direct [17,107] and indirect [16] band gaps. If for the case of direct band gap materials the electronic response was measured in parallel with the waveform of the pump electric field, for indirect band gap semiconductors this synchronous comparison has not been done yet.

The setup of the transient absorption experiment is described in section 4.1. The samples under analysis are a **50** nm and a **200** nm thick membrane of monocrystalline silicon (fabricated by Norcada), placed at Brewster angle to minimise reflection losses. Si is an indirect band-gap material with a band-gap of **1.11** eV at **300** K [50]. Its band structure is illustrated in Figure 4.1.

The XUV pulses are generated in neon through High Harmonic Generation (HHG) and are spectrally filtered by a zirconium and a silicon filter together with three rhodium-coated mirrors set at **16°** incidence. The XUV spectrum covers the energy range from **80**

eV to **110** eV with the purpose of probing the $L_{2,3}$ -edges of silicon at **98.72** eV and **98.32** eV.

Figure 5.1 shows the TA trace of **50** nm thick silicon for a pump intensity of $5 \cdot 10^{12}$ W/cm². In general, the normalised XUV transmission $\Delta T(\omega, t)$ is calculated as:

$$\Delta T(\omega, t) = \frac{T_{\text{Pumped}}(\omega, t)}{T_{\text{Unpumped}}(\omega, t)}$$
(5.1)

At each time step of the measurement, the spectrum of the XUV transmitted through the sample is alternatingly acquired with (T_{Pumped}) and without $(T_{Unpumped})$ the NIR pump. This procedure makes it possible to cancel out possible fluctuations in the XUV spectrum due to small pressure changes in the HHG target or drifts in the laser system. On the other hand, a set of two acquisitions per time step extends the total time of the measurement by more than a factor of two. Therefore, long-term alterations of the XUV spectrum and counts are more likely to set in. Additionally, quick fluctuations can take place only during the measurement of T_{Unpumped} and hence be introduced in the evaluation of ΔT . In view of this, in some cases it is required to average T_{Unpumped} over time. A further alternative is to replace the unpumped transmitted XUV spectrum with the time-averaged incident XUV spectrum T_{XUV} (without the sample) in the calculation of ΔT . This is measured separately and has the advantage that it requires a shorter integration time as well as less time steps. In the measurements presented in this work, the cleanest TA signal, with the most salient sub-cycle features, is obtained by dividing T_{Pumped} with $T_{\rm XIIV}$ averaged over time. It shall be noticed that ΔT derived from Eq.(5.1) is equivalent to the transmission obtained from the definition of absorption given by Eq.(4.2).



Figure 5.1: Normalised XUV transmission change of **50** nm thick silicon as a function of the delay between pump and probe and the XUV photon energy. The pump intensity is $5 \cdot 10^{12}$ W/cm². It is noticeable how the signal changes with the arrival of the NIR pump pulse.

The TA signal plotted in Figure 5.1 indicates how the arrival of the NIR pulse induces a change in the XUV transmission which is photon-energy dependent. Above ~99.4 eV, which corresponds to the bottom of the conduction band, the XUV transmission increases. On the other hand, for energies corresponding to the top of the valence band (~98.3 eV) the XUV transmission decreases. The energy dependence of the induced change in the XUV signal is discussed more in details below.

5.1.1 Time-integrated Observation of the Band-Gap Narrowing

Before examining the time-evolution of the XUV transmission, it is worthwhile to investigate the time-integrated transmission signals. Figure 5.2 left shows the measured spectra T_{Unpumped} (blue) and T_{Pumped} (dark red) for the **50** nm thick silicon membrane. The green curve is the XUV absorbance of silicon calculated from Eq.(4.2). The sudden rise at ~99.4 eV is resonant to the XUV transition from the L₃-level to the X-point of the conduction band (see Figure 4.1). The transition from the L₂-level to the X-point corresponds to **99.8** eV. Unfortunately, the energy resolution of the XUV spectrometer is about **40** meV, which does not allow one to sharply distinguish L₂ from L₃ as in the literature [16]. Nevertheless, a kink is noticeable.

The right panel of Figure 5.2 shows the pumped and the unpumped spectrum on a smaller energy scale. The area marked with the red circle highlights the spectra around 99 - 99.5 eV. It is noticeable how the presence of the NIR pump pulse shifts the spectrum to lower energies of about 67 meV. This effect is known as *band-gap narrowing*, also observed by M. Schultze *et al.* [16] for similar intensities. The strong laser pulse induces a Stark splitting of the energy levels inside silicon and hence broadening of the levels' substructures. However, the coupling with the quasi-free electrons of the conduction band is stronger compared to the coupling with localised core electrons of the L-edges. Therefore, the interaction with the laser electric field results in a visible reduction of the band-gap and permits electron excitations at lower energies than the minimum of the X-valley.

The sub-structure broadening is partially counteracted by a further effect induced by the laser electric field: the blue shift of the L-edge transition. It consists of a reversible shift to higher energies of about **80** meV. It is exhaustively described in Ref.[16] and won't be further discussed here.

It shall be noticed that the electrons are excited through single and multi-photon absorption, enabling NIR transitions over the direct and indirect band gaps. The z-scan experiment demonstrates that when the intensity reaches $\sim 1 \cdot 10^{12}$ W/cm² (subsection 3.1.3), two-photon absorption dominates over one-photon absorption. However, for intensities above $5 \cdot 10^{11}$ W/cm², the main excitation channel is tunnelling through the direct band gap, as the Keldysh parameter γ is smaller than 1 [16]. For the intensities applied here, tunnelling is the primary excitation process.

The black circle in Figure 5.2 marks the area around **101.4** eV, which is identified as the XUV transition from the L-edges to the L-point of the conduction band. Here, the NIR pulse induces an evident increase in XUV transmission due to the electrons being excited from the valence to the conduction band, resulting in the final state blocking of the XUV transitions. In the time-resolved measurement shown in Figure 5.1, the increase is observable at all photon energies above ~99.5 eV, corresponding to all electron transitions to the conduction band.



Figure 5.2: Left: XUV spectra transmitted through silicon in presence (dark red) and in absence (blue) of the NIR pump pulse. The green curve is the calculated absorbance according to Eq.(4.2). The measured silicon membrane is **50** nm thick. Right: Zoomed view of the transmitted spectra with and without NIR pump pulse.

5.1.2 Evolution of the Silicon's Response on Long Time Scale

To investigate the time evolution of ΔT at a specific photon energy, the signal is integrated over an energy window of **200** – **300** meV. In Figure 5.3, the XUV transmission change at different photon energies is plotted on a long time scale. Here, the **200** nm thick silicon sample is studied. During the interaction with the laser pulse, the change in transmission is dominated by the electronic response of the system. After, the lattice response sets in with a characteristic time constant corresponding to the fastest phonon in silicon (~64 fs) [108,109].

The blue curve represents the time evolution of the black marked area in Figure 5.2, right. The increase in XUV transmission at the central photon energy of **101.4** eV indicates an increase in electronic population inside the conduction band due to the NIR excitations.

The XUV photons probing the top of the valence band have an energy that corresponds to the lowest absorption edge. In this case, it corresponds to the L_3 edge at ~98.32 eV. In fact, the red curve displayed in Figure 5.3 exhibits a drop/increase in XUV transmission/absorption, suggesting that states are emptied with the arrival of the NIR pulse. Interestingly, both curves do not show a complete recovery from the NIR excitation in the time window of 600 fs. The typical time scale for electron-hole recombination in band-gap materials is usually in the range of some picoseconds [110].

It should be taken into consideration that the XUV transmission out of resonance is influenced by several effects that cause energy shifts. As mentioned above, the laser electric field deforms the band structure of silicon, resulting in reversible and irreversible modifications of the XUV transmission.



Figure 5.3: XUV Transmission change of silicon for two different photon energies. The blue curve corresponds to **101.4** eV and exhibits an increase that is in synchrony with the arrival of the NIR pulse at *Delay* = **0**. This behaviour of the XUV transmission is visible at all energies above \sim **99.4** eV. Here, electrons from the conduction band are probed. The red curve is the time evolution of the transmitted XUV at \sim **98.4** eV. At this energy, the NIR pulse induces a drop in the XUV transmission, suggesting that the electrons in the top of the valence band are being probed.

5.1.3 Absolute Timing of the Laser-induced Electron Dynamics

As previously discussed, the characteristic time of interaction with the laser electric field is dominated by the electronic response of the material. In Figure 5.4, the depicted XUV transmission change shows an oscillating behaviour in the few femtosecond time window when the pulse is present. This effect is visible in the **50** nm thick silicon membrane. The **200** nm Si demonstrates to be too thick for the XUV propagation length, causing the modulations to vanish. The period of the observed oscillations corresponds to half the period of the laser electric field, which motivates further investigation of the phase relation between the oscillating electronic response and the electric field.

The determination of the absolute timing is of great importance for understanding the physical processes underlying optical electron excitation. Moreover, it defines the response time of the electronic system which is demonstrated to be smaller than a half-cycle of the laser pulse. In fact, a retarded response would smear out the oscillating behaviour.

For the purpose of investigating the absolute timing, TA spectroscopy is combined with streaking spectroscopy, a well-established technique which delivers the waveform of the laser pulse. The TA signal is recorded with **0.1** fs time steps. The measurements are performed in a "sandwiched" manner: a streaking trace is taken before and after the TA measurement to take into account possible delay drifts intrinsic to the laser system. Then, the two measured fields are averaged and compared with the TA trace. To optimise the total time of the measurement set, only the spectrum in presence of the NIR field is recorded with the TA measurement. Therefore, the XUV spectrum instead of the

unpumped spectrum T_{Unpumped} is taken for the evaluation of ΔT given by Eq.(5.1). Figure 5.4 displays the XUV transmission change at **100.4** eV with an incident intensity of 4. 10^{12} W/cm². The plot shows perfect synchrony with the extrema of the mean electric field E(t). For instance, the oscillations of the electronic population redistribution in silicon, at resonance, are caused by the instantaneous response to the oscillating electric field, i.e. by the induced polarisation. In fact, the XUV transmission change can be considered as a combination of two effects: the transient population transfer, which increases in a stepwise fashion while the electronic system interacts with the NIR pulse, and the induced polarisation, which results in the strong oscillations of the TA signal. In the first, the maximum slop of each step is in synchrony with each of the extrema of the NIR field. On the other hand, in the oscillations induced by the instantaneous response of the electronic system, the maxima are expected to be in synchrony with the extrema of the NIR electric field. It can be concluded that the NIR excitation is not strongly influenced by the current generated from the excited electrons residing in the CB. In fact, it is confirmed in section 6.1 that the presence of electrons in the conduction band (as in the case of a metal) introduces a $\pi/2$ -shift in the phase of the oscillating electronic response.



Figure 5.4: a) Normalised XUV transmission change of **50** nm thick silicon as a function of the delay between pump and probe and the XUV photon energy. The pump intensity is $5 \cdot 10^{12}$ W/cm². It is noticeable how the arrival of the NIR pulse induces oscillations in the XUV signal. b) XUV transmission change of silicon at **100.4** eV (blue curve) with the incident electric field (red curve) measured with streaking. The energy interval of integration corresponds to the area marked in black in a). The applied intensity measured from the beam profile at the focus is $4 \cdot 10^{12}$ W/cm². From the measured field strength $I_{peak} = 1.2 \cdot 10^{13}$ W/cm² is obtained.



Figure 5.5: Streaking spectrogram for the measurement of the pulse waveform performed at a central photon energy of **100** eV. The trace gives the vector potential of the pulse.

The behaviour of silicon appears to be typical for band-gap materials probed at the resonance, as it is also observed in fused silica (see section 5.1.5 and [19]). However, F. Schlaepfer *et al.* [17] have performed TA spectroscopy on Gallium Arsenide (GaAs) with partially contradicting results. It was found that for this direct band-gap semiconductor the modulations of the electronic response inside the CB are affected by the intraband dynamics. The TA measurement was compared in the same way with the streaking spectrogram. Nevertheless, the comparison was performed at photon energies 1 - 3 eV above the CB minimum, i.e. out of resonance. Here, intraband dynamics might play a more significant role with respect to interband transitions. In general, they have observed an energy-dependent phase relation with the exciting pulse, indicating a strong atomic response of GaAs.

In the silicon measurements presented here, the modulations of the XUV transmission change are not observed deep in the conduction band, but at the bottom of the CB (**100.4** eV) and the top of the VB (**98.4** eV). Here, both signals are in synchrony with $E^2(t)$. More specifically, the two TA signals show complementary oscillations where the maxima at **98.4** eV correspond to the minima at **100.4** eV (Figure 5.6, left). This behaviour appears obvious, as both changes in transmission are caused by the same electron transitions observed at different photon energies. In other words, the holes are probed at **98.4** eV, while the electrons at **100.4** eV. The correlation is confirmed by the theoretical simulations presented below.



Figure 5.6: Left: XUV transmission change at **100.4** eV in blue and **98.4** eV in red. The two signals corresponding to the bottom of the CB and the top of the VB, respectively, show complementary oscillating behaviour. Right: XUV transmission change at **100.4** eV for three different incident peak energies. With increasing E_{incident} , the change in transmission gets bigger and steeper.

5.1.4 Comparison with the Elk Simulations

The experimental data discussed above for silicon are compared with the computational results shown in Figure 5.7. The simulations are performed by S. Sharma et al. using the Elk code [111], an all-electron full-potential linearised augmented plane-wave (LAPW) code for determining the properties of crystalline solids (further details are presented in Appendix A). The code is used to calculate the change in the dielectric function $\varepsilon(\omega, t)$ which can be directly compared with the measured change in the XUV absorption. $\varepsilon(\omega, t)$ is obtained from the total number of excited charges n_{ex} . The plot in Figure 5.7 shows the change in the dielectric function for an incident intensity of $1.5 \cdot 10^{12}$ W/cm² integrated over 96 - 99 eV (red curve) and 100 - 101.5 eV (blue curve). The integration intervals are broad, as the calculated signal does not change qualitatively in these energy ranges. As in the experiment, the XUV absorption is expected to increase for photon energies below the maximum of the VB (hole signal) and decrease for energies above the minimum of the CB (electron signal). The theoretical results show modulations of the change of the dielectric function with twice the laser frequency. The phase between the modulations and the incident field does not show any photon-energy dependence. Furthermore, the phase of the oscillations is shifted by $\pi/2$ with respect to the measured XUV transmission change, showing perfect synchrony with the vector potential of the exciting laser pulse.

The disagreement between experiment and theory derives from the erroneous definition of the number of excited charges used in the Elk code for deriving $\varepsilon(\omega, t)$: n_{ex} is calculated using the ground-state orbital, which takes into account also the linear contribution when the electric field interacts with the electronic system. On the other hand, by projecting the states onto a Houston basis, this linear contribution is not considered and it follows that $\varepsilon(t)$ is in synchrony with the extrema of the electric field [112,113]. The experimental results reported here agree with the choice of projecting the states onto a Houston basis.



Figure 5.7: Simulated dielectric function for an incident intensity of $1.5 \cdot 10^{12}$ W/cm², integrated over 96 - 99 eV (red curve) and 100 - 101.5 eV (blue curve). The green curve is the vector potential of the incident pulse.

5.1.5 Comparison with a wide Band-Gap Material: Fused Silica

The optical manipulation of the carrier population distribution is presented in the work of this thesis for several materials. Silicon is analysed as a semiconductor, while nickel is studied as an example of a transition metal (Chapter 6). With the aim of presenting a complete picture of the electron dynamics in solids, the previous study of Schultze *et al.* [19] on fused silica is revisited. The band-gap of SiO₂ is 8.9 eV at **300** K [114]. Therefore, for probing the Si L-states of SiO₂, the XUV spectrum needs to be shifted to higher energies compared to the study of the Si L-edges in a pure silicon sample. In other words, it has to be centred at **105** eV. This is achieved by decreasing the pressure in the HHG target from **165** mbar to **152** mbar. Furthermore, a molybdenum filter is used for spectrally filtering the XUV pulses. The sample under analysis is a **125** nm thick SiO₂ membrane, the same used by Schultze *et al.* [19].

Figure 5.8 depicts the XUV absorption change $\Delta \mu_{XUV}$ of the L-edges of Si at an incident intensity of **2.45** · **10**¹³ W/cm². $\Delta \mu_{XUV}$ is calculated according to (4.3). As the band-gap is much larger compared to silicon, the required intensities to excite electrons into the conduction band is at least one order of magnitude greater. The XUV absorption decreases with the arrival of the NIR pulse. In other words, resonant to the L-edges, the final states of the NIR transitions are probed in the conduction band, as in silicon. On the other hand, the electronic system of SiO₂ recovers from the NIR excitation within the duration of the pulse, which is not observed in Si. This behaviour shows how the status of a dielectric material can be switched in the few femtoseconds of interaction with the strong-field. The reason for the reversible NIR excitation observed in SiO₂ can be found in the adiabatic nature of the NIR transitions [19]: when an insulator with a band gap ΔE_{gap} interacts with a weak optical field with frequency ω such that $\hbar \omega \gg \Delta E_{gap}$ is valid, the electronic system reacts adiabatically (instantaneously) to the optical excitation. When the field strength approaches its critical value $F_C \approx \frac{\Delta E_{gap}}{ea}$ (where *a* is the lattice constant and *e* the electron charge), the electrons residing in the valence band undergo Zener-type transitions and populate the conduction band. Therefore, the ultimate speed limit of reaction to weak and strong fields is given by the band gap of the insulator $\tau \ge \frac{1}{\Delta E_{gap}}$. As a result, insulators react faster than semiconductors to the optical excitation.

The plot shows remarkable oscillations in the measured XUV signal. By comparing with the waveform of the pulse measured with streaking, it results evident how the maxima of the modulations are synchronous to the extrema of the NIR electric field. From this perspective, band-gap materials appear to respond in the same fashion to the NIR excitation: the change in XUV absorption in silicon and in SiO₂ represents the instantaneous change in electronic population distribution. While in silicon it is an irreversible change on a time-scale of hundreds of femtoseconds, in SiO₂ the electronic population redistribution recovers within the second half of the exciting pulse.



Figure 5.8: XUV absorption change of fused silica at **108.9** eV (blue curve) with the incident electric field (red curve) measured with streaking. The applied intensity measured from the beam profile at the focus is **2.45** · **10**¹³ W/cm². From the measured field strength $I_{peak} = 1.96 \cdot 10^{13}$ W/cm² is obtained.

Figure 5.9 depicts the XUV absorption change of fused silica above resonance ($\sim 109 \text{ eV}$, corresponding to $\sim 1.3 \text{ eV}$ above the conduction band minimum) and below resonance ($\sim 105.9 \text{ eV}$, corresponding to $\sim 1.8 \text{ eV}$ below the conduction band minimum). The change in the XUV signal at energies smaller than the conduction band minimum at $\sim 107.7 \text{ eV}$ might be caused by the virtual excitation of electrons into the band-gap.

The two plotted curves oscillate with the same phase. For instance, they do not show an energy dependence of the phase relation with the electric field. In [19] it is demonstrated that this is valid also for energies greater than 109 eV, i.e. deeper in the conduction band.



Figure 5.9: XUV absorption change at **108.9** eV (above the conduction band minimum) in blue and **105.85** eV (below the conduction band minimum) in red. The two signals exhibit synchroneous oscillations, and thus the phase with the NIR field does not show any energy dependence at resonance and below.

5.2 Intraband Dynamics in Semiconductors: Theoretical Overview

Attosecond polarisation sampling is a measurement technique which permits the direct access and tracking of polarisation of an electronic system excited by a laser field. As a result, it makes it possible to study the induced nonlinearities in a time-resolved way. In the following section, the technique is applied to measure the induced polarisation and the transferred energy in the few femtoseconds of interaction between a NIR pulse and silicon. The energy dissipation of the optical pulse while it propagates through the medium and the induced polarisation are both essential information for the future realisation of optoelectronic devices.

As described in 4.2, the electric field transmitted through a material carries the information about its linear and nonlinear response to the laser excitation. For a better understanding of the experimental data analysis of silicon, a theoretical overview is given in the present subsection and is based on the formalism given by K. Yabana *et al.* for band-gap materials.

5.2.1 Linear Propagation

When the field is weak, only linear processes take place in the medium. As previously mentioned in Chapter 2, the polarisation in case of linear interaction is defined according to Eq. (2.2). By considering a pulse propagating only in *z*-direction, the linear polarisation can be expressed in the frequency domain as follows:

$$P_{\text{Linear}}(z,\omega) = \varepsilon_0 \chi(\omega) E(z,\omega)$$
(5.2)

It applies that $1 + \chi(\omega) = \varepsilon(\omega) = n^2(\omega)$, where $\chi(\omega)$ is the susceptibility, $\varepsilon(\omega)$ the permeability and $n(\omega)$ the refractive index.

In Chapter 2, the basic description of light-matter interaction is presented by starting from the Maxwell equation. When only linear processes are taken into account, Eq. (2.9) becomes:

$$\frac{\partial^2}{\partial z^2} E(z,\omega) = -\frac{\omega^2}{c^2} (1 + \chi(\omega)) E(z,\omega) = -\frac{\omega^2}{c^2} n^2(\omega) E(z,\omega)$$
(5.3)

Where *c* is the speed of light and ω is the frequency.

A general solution for Eq.(5.3) is the electric field $E(z, \omega)$ written as the sum of its transmitted and reflected component:

$$E(z,\omega) = F(\omega) \exp(ik(\omega)z) + G(\omega)\exp(-ik(\omega)z)$$
(5.4)

With $k(\omega)$ the wavevector, $F(\omega)$ and $G(\omega)$ the amplitudes of the forward and backward propagating wave. Since the silicon sample is set at Brewster angle, the back-propagating term can be neglected.

Considering a sample of length L, the incident and the transmitted field in the linear regime can be defined as:

$$E_{\text{weak}}(z = \mathbf{0}, t) = \int F(\omega) \exp(-i\omega t) d\omega$$
(5.5)

$$E_{\text{weak}}(z = L, t) = \int F(\omega) \exp(-i\omega t) \exp(ik(\omega)L) d\omega$$
(5.6)

From these relations it follows:

$$exp(ik(\omega)L) = \frac{\int exp(i\omega t) E_{weak}(L,t)d\omega}{\int exp(i\omega t) E_{weak}(0,t)d\omega}$$
(5.7)

This equation permits direct access to the refractive index $n(\omega) = ck(\omega)/\omega$ from the experimentally measured fields.

5.2.2 Nonlinear Polarisation

If the incident electric field is strong enough, nonlinearities set in. In this case, the total polarisation defined by Eq.(2.4) becomes:

$$P(z,t) = \varepsilon_0 \int \chi(t-t')E(z,t') + P_{\rm NL}(z,t)$$
(5.8)

By Fourier-transforming P(z, t) and substituting $P(z, \omega)$ in Eq.(5.3) gives:

$$\frac{\partial^2}{\partial z^2} E(z,\omega) = -\frac{\omega^2}{c^2} n^2(\omega) E(z,\omega) - \frac{\omega^2}{\varepsilon_0 c^2} P_{\rm NL}(z,\omega)$$
(5.9)

Which is analogous to Eq.(2.9). For solving Eq.(5.9), the backward propagating term in Eq.(5.4) can still be neglected. Nonlinear effects are spatially dependent and so a spatial dependency of the forward propagating term $F(z, \omega)$ needs to be introduced. Nevertheless, if the z-dependence is small, the second derivative of $F(z, \omega)$ can be neglected:

$$\frac{\partial^2}{\partial z^2} E(z,\omega) = \frac{\partial^2}{\partial z^2} F(z,\omega) e^{ik(\omega)z} + 2ik(\omega) \frac{\partial}{\partial z} F(z,\omega) e^{ik(\omega)z}$$

$$-k^2(\omega)F(z,\omega) e^{ik(\omega)z}$$

$$\approx 2ik(\omega) \frac{\partial}{\partial z} F(z,\omega) e^{ik(\omega)z} - k^2(\omega)F(z,\omega) e^{ik(\omega)z}$$
(5.10)

Eq.(5.9) simplifies to:

$$2ik(\omega)\frac{\partial}{\partial z}F(z,\omega)e^{ik(\omega)z} = -\frac{\omega^2}{\varepsilon_0 c^2}P_{\rm NL}(z,\omega)$$
(5.11)

As for the linear regime, the incident and the transmitted electric field can be defined as:

$$E_{\text{strong}}(\mathbf{0}, t) = \int F(\mathbf{0}, \omega) \exp(-i\omega t) d\omega$$
(5.12)

$$E_{\text{strong}}(L,t) = \int F(L,\omega) \exp(-i\omega t) \exp(ik(\omega)L) d\omega$$
(5.13)

In order to directly link the nonlinear polarisation $P_{\text{NL}}(z, t)$ of Eq.(5.11) with the strong electric field $E_{\text{strong}}(z, t)$, the inverse Fourier transforms of Eq.(5.12) and (5.13) are taken:

$$F(\mathbf{0},\omega) = \frac{1}{2\pi} \int E_{\text{strong}}(\mathbf{0},t) \exp(i\omega t) dt$$
(5.14)

$$F(L,\omega) = \frac{1}{2\pi} \int E_{\text{strong}}(L,t) \exp(i\omega t) \exp(-ik(\omega)L) dt$$
(5.15)

Substituting in Eq.(5.11) leads to the determination of $P_{\rm NL}(z,\omega)$ with the measured incident and transmitted field [1]:

$$P_{\rm NL}(z,\omega) \approx -2ik(\omega) \frac{\varepsilon_0 c^2}{\omega^2} \frac{F_{\rm strong}(L,\omega) - F_{\rm weak}(L,\omega)}{L} e^{ik(\omega)z}$$
(5.16)

With $E(z = L, \omega) = F(z = L, \omega) exp(ik(\omega)L)$ it becomes:

(5.17)

$$P_{\rm NL}(z,\omega) \approx -2ik(\omega) \frac{\varepsilon_0 c^2}{\omega^2} \frac{E_{\rm strong}(L,\omega) - E_{\rm weak}(L,\omega)}{L} e^{ik(\omega)(z-L)}$$

Eq.(5.17) describes how the nonlinear polarisation in silicon can be obtained from the measured fields. The definition is analogous to the one used in [1] for fused silica.

5.2.3 Energy Transfer

Once the polarisation inside the material is known, it is possible to determine the amount of energy transferred from the electric field to the medium. This is defined as the product of the incident electric field and the generated electron current density J(t) integrated over time. Since $J(t) = \frac{dP(t)}{dt}$, the energy transfer is given by:

$$W(t) = \int_0^t E(t') \cdot \frac{dP(t')}{dt'} dt'$$
(5.18)

This formula can be applied for determining the linear and the nonlinear work done on the sample.

5.3 Strong-Field Induced Multi-Photon Absorption in Silicon

In 3.1 it is shown how the time-integrated study of silicon's transmission can deliver information about the physical phenomena behind its nonlinear response. From the analysis of the intensity dependence, it is demonstrated that for intensities above 10^{11} W/cm² two-photon absorption (2PA) dominates over one-photon absorption (1PA). The latter can originate from phonon-assisted transitions to the X-valley (indirect band gap) or from transitions to trap states within the band gap. Furthermore, at $4 \cdot 10^{12}$ W/cm² the refractive index of silicon is expected to be reduced by **25%** due to the free carriers injected by 2PA. The decrease is partially balanced by a **5%** increase of *n* due to the Kerr effect, which is suspected to be underestimated by the literature value of n_2 , due to its strong dependence on the spectral profile of the pulse.

In the following, these effects will be further investigated by measuring the electric field transmitted through silicon. The field-resolved measurement technique is called "Polarisation Sampling" (PS) and the same experiment was performed by [32,82] at lower intensities, where streaking spectroscopy was used for detecting the electric field. The detection method used in the work of this thesis is Linear Petahertz Photo-conductive Sampling (LPPS) in neon and is described in section 4.2, dedicated to the polarisation sampling setup. As previously mentioned, it has the advantage of having a higher dynamic range compared to streaking. On the other hand, it gives access only to the relative amplitude of the detected electric fields. For the comparison of the transmitted waveforms this does not play a crucial role, as the intensity can be determined with Eq.(3.1) by measuring the incident peak energy and the beam size.

Each set of measurements contains the acquisition of the electric field without the sample (reference), the transmitted electric field when the sample is out of focus (weak field) and the transmitted field when the sample is positioned in focus (strong field). In the fourth measurement, the incident field is detected a second time. The comparison between the two reference fields permit the recognition of drifts of the laser system. All the

measurements are performed with **0.1** fs time steps. To compensate for long-term fluctuations of the signal, the measured waveforms are normalised on a short time window before or after the arrival of the pulse.

The sample under analysis is the same used in the z-scan and in some of the TA measurements, a **200** nm thick silicon membrane. It is positioned at Brewster angle so that reflections can be neglected.

Figure 5.10 shows the two transmitted waveforms in the presence of the strong $(3.4 \cdot 10^{12} \text{ W/cm}^2)$, blue curve) and the weak $(1.8 \cdot 10^{12} \text{ W/cm}^2)$, red curve) field. In the time windows where the pulses oscillate weakly, the two waveforms perfectly overlap, confirming the fact that at low intensity only linear effects set in. On the other hand, silicon exhibits smaller transmission in its strongest half-cycles for high incident intensity, especially in the first half of the pulse. The total transmitted amplitude decreases by 25% when the field strength is increased by 37.5%. This behaviour is confirmed by the *z*-scan measurements presented in 3.1. If the 2PA and the Kerr effect weren't balanced, an intensity-dependent phase shift between the transmitted and the incident pulse would be expected. However, this phase shift is not visible at any intensity, suggesting a balanced action of 2PA and Kerr effect to within the accuracy of the measurement.



Figure 5.10: The blue and the red curves are the electric fields transmitted through the sample positioned in and out of focus, respectively. The green dashed line is the reference pulse. The incident peak energy is **2.5** μ J, which corresponds to an intensity of **3.4** \cdot **10**¹² W/cm² in focus and **1.8** \cdot **10**¹² W/cm² out of focus.

5.3.1 Correction of the Pulse Propagation

Before investigating silicon's electron dynamics, it is essential to make some considerations regarding the analysis of the measured waveforms. First, it shall be remarked that the Gouy phase doesn't play any role for the evaluation of the transmitted fields. Even if the sample experiences different pulse phases if located in or out of focus, the detection of the waveforms through LPPS images the focus position. Moreover, if the sample responds only linearly when positioned out of focus, the phase of the pulse does

not play a role in its interaction with the material. Therefore, phase corrections are not considered to be relevant.

If the incident peak energy is high enough, the field transmitted through the sample out of focus could already contain the nonlinear response of the material. A possible way for verifying if nonlinearities are setting in is the numerical propagation to the mid-point of the sample [1], which corrects for material dispersion. The transmitted pulses are numerically back-propagated to the middle point and in the same way, the incident field is forward propagated. If the transmitted pulse contains only the linear contribution, the corrected incident and transmitted waveforms should be identical.

Figure 5.11 shows the comparison between the numerically corrected pulses for low (left) and for high (right) intensity. For the evaluation, the literature value for the refractive index given by [115] is taken. In the right panel it can be seen how the numerical propagation can't take into account the nonlinear response of the system. At the incident intensity of $3.4 \cdot 10^{12}$ W/cm², the transmitted back-propagated pulse clearly contains the nonlinear response of silicon, as it underestimates the transmission. This is visible where the pulse strongly oscillates. On the other hand, the numerically corrected pulses perfectly coincide before and after the arrival of the pulse, indicating a purely linear response.

The left panel shows the forward propagated incident pulse and the back-propagated pulse transmitted through silicon positioned out of focus. The high agreement between the two waveforms suggests the small presence of nonlinearities. Furthermore, the perfect overlap of the waveforms before and after the pulse are a sign for an excellent signal-to-noise ratio and stability of the laser system.



Figure 5.11: Numerically propagated pulses for an incident peak energy of 2.5μ J, which corresponds to an intensity of $3.4 \cdot 10^{12}$ W/cm² in focus and $1.8 \cdot 10^{12}$ W/cm² out of focus. The left panel shows the comparison of the forward propagated incident field with the back-propagated field transmitted through silicon out of focus (low intensity). The two waveforms almost perfectly overlap. On the right, the same is plotted for the case of transmission through the sample in focus (high intensity). Here, nonlinearities set in and the correction of dispersion can't compensate them.

5.3.2 Linear and Nonlinear Polarisation

As presented in 5.2.2, the transmitted waveforms in the presence of a strong and a weak field are the required information for the determination of the linear $P_{\rm L}$ and the nonlinear polarisation $P_{\rm NL}$. Figure 5.12 shows the incident electric field together with the induced

 $P_{\rm L}$ and $P_{\rm NL}$ calculated from the fields plotted in Figure 5.11. The linear polarisation oscillates in synchrony with the electric field, which implies that no energy is transferred from the pulse to the medium. On the other hand, according to its definition given by (5.17), the nonlinear polarisation is shifted forward by $\pi/2$ with respect to the incident electric field. Consequently, there is a constant and unidirectional flow of energy from the electric field to the electronic system.

In Figure 5.13 left, $P_{\rm NL}$ is plotted for different incident intensities. The maximum value of $P_{\rm NL}$ is depicted on the right as a function of the field strength. When the field strength is increased by a factor of ~1.45, i.e. the intensity increases from $1.2 \cdot 10^{12}$ W/cm² to $2.65 \cdot 10^{12}$ W/cm², the nonlinear polarisation grows by a factor of ~2. If $P_{\rm NL}$ is caused only by third-order nonlinear processes, it is meant to follow E^3 and therefore increase by a factor of $1.45^3 \approx 3$. As silicon is a centrosymmetric material, second-order nonlinear polarisation is smaller than a factor of 3. The weaker intensity scaling indicates that additional higher order terms are setting in and counteracting the lowest order (third-order) nonlinearities. As mentioned in 5.1, electron tunnelling from the valence to the conduction band dominates over two-photon absorption in the considered range of intensities. In fact, approaching the tunnelling regime results in a significant contribution of higher order terms of the nonlinear polarisation which are of similar magnitude of its third order term.

When the intensity exceeds $2.65 \cdot 10^{12}$ W/cm², the exponential scaling factor of $P_{\rm NL}$ drops below 2. This is further discussed in 5.3.4 by comparing the experimental results with the theoretical predictions.



Figure 5.12: The measured incident electric field with **2.5** μ J peak energy is plotted in red. The blue and the green curve represent the nonlinear and the linear polarisation of silicon, respectively. Both $P_{\rm L}$ and $P_{\rm NL}$ last for the duration of the pulse. $P_{\rm L}$ oscillates in synchrony with the incident field, while $P_{\rm NL}$ is shifted forward by $\pi/2$.



Figure 5.13: Left: nonlinear polarisation $P_{\rm NL}$ for different intensities of the incident field calculated from the measured fields Right: Dependence of the maximum value of $P_{\rm NL}$ near $Delay \approx 0$ fs from the applied field strength.

5.3.3 Energy Transfer

With the measured fields and the theoretical analysis of K. Yabana et al., it is possible to determine the amount of energy that the exciting pulse transfers to the sample. This transferred energy (or work) can also be decomposed in its linear and nonlinear contributions, as plotted in Figure 5.14. The nonlinear work $W_{\rm NL}$ shows a stepwise behaviour where the steps are in synchrony with the zero-crossings of the electric field, equally true for $P_{\rm NL}$. The nonlinear transfer of energy is an irreversible process, as $W_{\rm NL}$ stays in silicon even after the interaction with the pulse. This behaviour is similar to what is seen in 5.1.2 for the XUV transmission, as the life-time of the excited state is longer than the interaction time with the exciting field. By contrast, the linear contribution W_{Linear} oscillates synchronous to the extrema of the electric field and returns to zero when the pulse is over. On one hand, single-photon absorption dominates over twophoton absorption below $\sim 10^{12}$ W/cm². On the other hand, the contribution of tunnelling is significant already at intensities > $5 \cdot 10^{11}$ W/cm². The outcome on the linear contribution is that no linear energy is stored in silicon after interacting with the electric field. For instance, W_{Linear} represents how the pulse propagates through the sample or, in other words, the electronic displacement induced by the NIR field.



Figure 5.14: Linear, nonlinear and total energy transferred to silicon for an incident intensity of $3.4 \cdot 10^{12}$ W/cm². The curves are normalized over the total incident energy.

The energy transfer is obtained for the same range of intensities at which the nonlinear polarisation is calculated and plotted in Figure 5.13, left. It is noticeable in Figure 5.15, how the increase in intensity does not change the steepness of the total work, i.e. of its nonlinear component. The total transferred energy exhibits an overshoot which is given by its linear component. Consequently, it scales with the electric field. Sommer *et al.* [1] observed a similar feature in the energy transfer of fused silica. However, the overshoot in the total transferred energy of SiO₂ originates from the Kerr effect. This reversible nonlinearly occurs in fused silica on a larger scale compared to silicon and increases linearly with the intensity, i.e. with the squared electric field. Therefore, the two observed overshoots have different origin in the two band gap materials. Moreover, the nonlinear energy transferred to fused silica evolves from being reversible, due to the Kerr effect, to being irreversible once absorption also starts occurring. Conversely, it is observed in silicon that the amount of nonlinear transferred energy keeps the same qualitative behaviour for all the analysed intensities.

A further aspect which should be highlighted in the two dielectrics is the intensity scaling of the irreversible component of their transferred energy, which is induced by the excitation of real carriers, i.e. by absorption. According to (5.18), the measured energy transfer scales with $\sim \frac{dP_{\rm NL}}{dt} \cdot E$, where $\frac{dP_{\rm NL}}{dt} \propto x \cdot E^{x-1}$. Fused silica has a band gap of **8.9** eV, which implies that the real carrier excitation occurs via five- or six-photon absorption. Therefore, the irreversible transferred energy is observed to scale steeply at high intensities.

The situation is different in silicon, where real carriers are excited over the direct band gap by absorbing two photons or by tunneling. In fact, as observed in subsection 5.3.2, the nonlinear polarisation scales linearly with E^2 for intensities until **2.65** · **10**¹² W/cm², and decreases for higher intensities due to the dominance of higher order nonlinearities. This is further observed in the energy transferred to the sample.



Figure 5.15: Total transferred energy for different incident intensities. The curves are normalized over the total incident energy.

5.3.4 Comparison with the SALMON Simulations

The experimental results of silicon's light-induced electron dynamics are supported by the full *ab-initio* TD-DFT calculations performed with SALMON [113,116,117] by the group of K. Yabana.

Transmitted Waveforms and Energy Transfer

Figure 5.16 left shows the transmitted fields for $5 \cdot 10^{12}$ W/cm² and $1 \cdot 10^{12}$ W/cm² simulated with the SALMON code. The intensities are similar to the ones used for measuring the fields plotted in Figure 5.10. As with the experimental fields, the calculated fields are normalised on a time window before the appearance of the first pulse oscillations. In the same way, the incident and the transmitted fields are propagated to the mid-point of the sample.

The pulse transmitted at high intensity is truncated at its strongest half-cycles due to the nonlinear response of silicon, while before and after the strong oscillations, the two waveforms perfectly overlap. The behaviour is analogous to the experimentally measured fields. The linear and the nonlinear polarisation obtained from the calculated fields is depicted in Figure 5.16, right, while the transferred energy is shown in Figure 5.17. As in the experiment, $P_{\rm NL}$ exhibits a $\pi/2$ retardation with respect to the exciting pulse, while $P_{\rm L}$ is simultaneous to the exciting field. In view of this, it is clear that TDDFT-calculations show perfect qualitative agreement with the experimental results.



Figure 5.16: Left: electric fields transmitted through silicon at the intensity of $5 \cdot 10^{12}$ W/cm² (blue curve) and $1 \cdot 10^{12}$ W/cm² (red curve). Right: the red curve represents the incident electric field, while the green and the blue curve are the linear and the nonlinear polarisation, respectively.



Figure 5.17: Total, linear and nonlinear work done on the sample by the exciting electric field. The theoretical results are plotted on the left, while the plot on the right depicts the experimental results shown in Figure 5.14.

Intensity Dependence of the Nonlinear Order

For a deeper understanding of the nature of silicon's nonlinearities, the exponential factor, which relates the nonlinear polarisation to the electric field through $P_{\rm NL} \propto E^x$, needs to be further investigated. For the estimation of x, the maximum value of $P_{\rm NL}$ corresponding to the maximum of the electric field E is taken (at $t \approx 0$ fs). In Figure 5.18, the exponent x is plotted as a function of the intensity in the theoretical and in the experimental case. The perfect agreement (within the error bars) of the intensity scaling is of great significance, as it confirms that the observed nonlinear effects occurring in silicon are fully described by the TD-DFT calculations. From Figure 5.18 it is clear how the order of the nonlinearities decreases from **3** to < **0.5** by increasing the intensity of one order of magnitude. As mentioned in 5.1.1, the Keldysh parameter γ is smaller than **1** for

intensities above $\sim 5 \cdot 10^{11}$ W/cm² [16], suggesting that the interaction is becoming increasingly non-perturbative towards 10^{13} W/cm². A further aspect is the plasma response of silicon which becomes significant at the mentioned intensities. As a consequence, the characteristic features of the lowest-order nonlinearities (2PA and the Kerr effect) are increasingly suppressed.



Figure 5.18: Nonlinear order as a function of the incident intensity. The orange points are the experimental data, while the blue line is obtained from the TD-DFT simulations.

5.4 Main Findings of the Field-Induced Electronic Motion in Silicon

In this chapter, two main aspects of the optically-induced electron dynamics are investigated in silicon. By use of transient absorption spectroscopy, the change of electronic population density induced by an ultrashort NIR pulse has been studied. For the first time, distinct oscillations in the XUV transmission change of silicon have been observed, which demonstrates a response time of the electronic system smaller than a half-cycle of the pulse. By combining TA with streaking spectroscopy, it is possible to set the absolute timing between the oscillating electronic response and the waveform of the exciting NIR pulse, exhibiting perfect synchrony with the extrema of the electric field. As the instantaneous electric field excitation is responsible for the induced polarisation of the material, the observed timing suggests that the electron dynamics in silicon are dominated by the transient population transfer and the induced polarisation.

The sub-cycle carrier response to optical excitation is observed also in wide band gap materials [19,91]. In order to present an exhaustive description of the dynamics in solids with a band gap, the results of the transient absorption experiment on SiO_2 are shortly reported. The XUV transmission change at resonance shows a similar behaviour as

silicon: the transmission increases and exhibits oscillations with twice the frequency of the NIR pulse. These oscillations are in synchrony with the NIR electric field. Different than in silicon, SiO_2 recovers from the NIR excitation already in the second half of the pulse. On the other hand, Si does not recover within a time window of hundreds of femtoseconds. The different behaviour between SiO_2 and Si origins from the size of the band gap, which determines the response time of the material [19].

A more extensive study of the phase relation between the exciting pulse and the sub-cycle carrier response of silicon could be reached by investigating the dependence of the oscillations in the XUV signal from the XUV photon energy. For this purpose, it would be worthwhile for silicon to be probed with a broader XUV pulse in future experiments.

The measured XUV transmission is compared with the time-dependent dielectric function simulated with the Elk code [111], which is a measure for the XUV absorption change. The theoretical results show a $\pi/2$ shift of the phase between the oscillating dielectric function and the electric field, which does not correspond to the experimental results. In the simulations, the phase difference is determined by the choice of the definition of the number of excited charges n_{ex} . The Elk code makes use of the ground state in its definition, while in the SALMON code the states are projected on the Houston basis. The difference in defining n_{ex} introduces a $\pi/2$ shift in the phase between the exciting field and the number of excited charges, i.e. between the field and the change in the dielectric function. The experimental results presented here demonstrate to agree with the formalism based on the Houston function, proving the non-arbitrariness of the definition of n_{ex} . Both the Elk and the SALMON code are able to simulate the current induced by the pulse, which allows to compare the two codes with different definitions of n_{ex} . However, with the Salmon code, it is not possible to determine the change in the dielectric function as with the Elk code.

In the second part, the intraband electronic motion is investigated with polarisation sampling. PS is a field-resolved measurement technique which permits to directly access the polarisation and the amount of energy transferred to the material. In the past, PS has been applied with streaking as a method for detecting the field. Here, Linear Petahertz Photo-conducting Sampling (LPPS) in gas [95] is used, as it allows a higher dynamic range. Measuring the fields transmitted through silicon at low and high incident intensity permits one to recognise the balanced action of two-photon absorption and the Kerr effect. In fact, no phase shift is observed in the transmitted field, which suggests for an equal contribution of nonlinear effects acting with opposite sign on the refractive index.

From the analysis of the intensity dependence it is clear how the exponential field-strength scaling of silicon's nonlinear polarisation is smaller than a factor of 3, which is indeed expected for third-order nonlinear effects (Kerr effect and two-photon absorption). The weaker scaling indicates that higher-order nonlinearities are occurring and have similar magnitude to the lowest order (third-order) nonlinearities. The observed effect is consistent with the theoretical predictions of Schultze *et al.* [16], who suggest tunnelling as the main excitation process in silicon. In other words, the electron transitions occur mostly over the direct band gap. The experimental results demonstrate that the nonlinear response of silicon is considerably larger than its linear response. As a result, by exciting Si with an ultra-short and intense laser pulse, the material turns from a linear absorber to a nonlinear, direct band-gap absorber.

The comparison with *ab-initio* TD-DFT calculations [117] showed excellent agreement with the experimental results. This is found to be crucial for understanding the origin of silicon's nonlinearities.

An alternative experiment for further investigating the role of 2PA in silicon could involve an exciting pulse with lower frequencies. The contribution of 1PA would be reduced, as single photons are not energetic enough to allow electron transitions. As a result, the contribution of 2PA and the disentanglement from electron tunnelling could become more straightforward.

The high signal-to-noise ratio of LPPS, compared to Streaking spectroscopy, permits measurements on a wide time range with a short integration time, which should allow a high spectral resolution of the measured signal. However, it is not possible to retrieve the frequency-dependent refractive index of silicon from the transmitted fields, as LPPS is not sensitive enough at high frequencies. The detection technique requires XUV pulses with a photon energy of **20** eV. Those harmonics lie in the plateau region of the XUV spectrum. Here, the XUV pulses are not isolated and their long temporal profile limits the observation of fast oscillations, i.e. of high frequencies. Streaking spectroscopy has shown to be more adequate for determining the frequency-dependence of nonlinearities [32]. Nevertheless, the superior dynamic range of LPPS compared to streaking gives access to the nonlinear response of materials with low transmittance at optical frequencies, as for example nickel. Therefore, an advantageous approach is the improvement of the spectral resolution of LPPS to higher frequencies.

In conclusion, the experimental results reported in this chapter give evidence of the subcycle control of silicon's electronic properties. Moreover, the investigation of the amount of energy dissipated into the sample and its intensity dependence enabled the recognition of a reversible and an irreversible component of the transferred energy. These findings constitute a fundamental aspect of the interaction between a strong optical field and silicon, which is at the basis for the future realisation of silicon-based optoelectronic circuits at petahertz clock-rates.

Chapter 6

Experiments: Strong-Field Induced Charge

Dynamics in Nickel

The application of strong, few-cycle laser pulses has enabled the control of the electronic properties of band-gap materials on the sub-femtosecond time scale . On account of this, the optical manipulation of electronic motion has inevitably been demonstrated to open new perspectives in the field of signal processing at petahertz clock-rates [12]. A question which arises from the present and the past studies on seminconductors and dielectrics, is if electrons in metals (materials without a band gap) can be manipulated with light in the same way. Of particular interest in the fields of optelectronics and plasmonics are thin metallic films. For this reason, the present chapter is dedicated to the investigation of the optically-induced change of the electronic properties of nickel (Ni) in a **8** nm thick film.

The first part is dedicated to the study of the electronic population redistribution (interband transitions) in Ni while interacting with a strong laser pulse. For this purpose, transient absorption spectroscopy is applied. In the second part, the field-induced intraband carrier dynamics in Ni is inspected by sampling the transmitted electric field with polarisation sampling spectroscopy.

6.1 Interband Electronic Motion in Nickel

The sub-femtosecond control of electronic population in transition metals still remains a narrowly explored field in attosecond transient absorption or reflection spectroscopy. Some work has been done on nickel for longer time-scales of some tens of femtoseconds [121] or on the picosecond time-scale [122]. Obviously, no sub-cycle electronic response could be observed. In the work of this thesis, nickel is investigated in the few femtoseconds of interaction with the strong electric field. As for the study of the spin dynamics (Chapter 7), the attosecond XUV pulses are centred at **66** eV to probe the Ni $M_{2,3}$ -edges with binding energies of **68** eV and **66.2** eV, respectively. The sample under analysis is an **8** nm thick nickel coated on a **200** nm thick silicon substrate. Silicon has no resonant transitions at the photon energies covered by the XUV pulses. Therefore, it is a good candidate as a substrate.

Figure 6.1 depicts the XUV transmission change as a function of the energy and the delay between pump and probe pulse. The XUV signal is calculated according to Eq.(5.1), by

taking the ratio between the spectrum in presence of the NIR pulse T_{Pumped} and the XUV spectrum T_{XUV} . It can be noticed in Figure 6.1 that the strongest change in XUV signal is located around **65** – **66.5** eV, corresponding to the M₃ absorption edge. In Figure 5.1, it is shown how the XUV transmission in silicon increases resonant to the L-edges. In nickel, the XUV transmission at the M-edges decreases. Above 68 eV, the opposite trend is observed: the XUV transmission increases with the arrival of the NIR pulse. The dependence of the change in the XUV signal from the photon energy is discussed in the subsections below.



Figure 6.1: XUV transmission change in nickel as a function of the photon energy and the delay between pump and probe pulse. The incident intensity is $7.3 \cdot 10^{12}$ W/cm².

6.1.1 Time-integrated Observation of the Valence Band Reduction

The transmitted XUV spectra in the presence (T_{Pumped}) and in the absence ($T_{Unpumped}$) of the NIR pulse already carry certain information about the strong-field induced effects taking place in the material. Figure 6.2 depicts the measured T_{Pumped} and $T_{Unpumped}$ together with the absorbance (green curve) calculated according to (4.2) and averaged over the delay axis. Even if the two absorption edges M₃ (**66.2** eV) and M₂ (**68** eV) lie under the same peak, one can recognise them in the plotted absorbance. The right of Figure 6.2 illustrates two interesting differences in the transmitted spectra. Around **65** eV, the NIR pulse shifts the conduction band towards lower energies by about **170** meV. This is similar to the band-gap narrowing observed in silicon, but originates from different physical processes. Stamm *et al.* [25] reported the same effect at the L-edges of nickel and their explanation can be adapted to the energy shift observed at the M-edges in the present experiment. They interpret the measured energy shift of **130** meV as being caused by the reduction of the valence band width. The underlying physics includes several effects as electron scattering and the preservation of the charge neutrality. The in-depth description of the origin of the energy shift can be found in [25,123].

The blue shift visible at ~ 65 eV is coupled to the smaller XUV transmission in presence of the NIR pulse. This is clearly visible in the time-evolution of the XUV transmission presented below.

The marked area around **68.3** eV shows the broadening of the XUV spectrum of **~100** meV in presence of the NIR field. The reason for this effect measured in nickel is not clear, but could be related to the broadening of the sub-structures due to the presence of the oscillating electric field. Furthermore, the transmitted XUV spectrum in the presence of the NIR pulse is larger at photon energies above **~68.5** eV. The two mentioned effects merge and are hard to disentangle in a time-integrated study.



Figure 6.2: Left: XUV spectra transmitted through the nickel in presence (dark red) and in absence (blue) of the NIR pump pulse. The green curve is the calculated absorbance according to Eq.(4.2). Right: Zoomed view of the transmitted spectra with and without NIR pump pulse.

6.1.2 Evolution of the Nickel's Response on Long Time Scale

As already mentioned above, the M_2 absorption edge of nickel is weak compared to the M_3 edge. Furthermore, Ni's absorption features in the presence of the NIR pulse are spread over the energy, due to possible broadening of the levels' substructures. As a result, the change in XUV transmission is visible mostly near the M_3 edge and can be integrated over a relatively broad energy range (**1** or **2** eV).

Figure 6.3, left shows the XUV transmission change as a function of time at $2.9 \cdot 10^{12}$ W/cm². The signal is evaluated as the ratio between the pumped spectrum T_{Pumped} and the XUV spectrum T_{XUV} . The XUV signal is integrated in the energy interval of 65.8 ± 0.1 eV (blue curve) and 68.6 ± 0.2 eV (red curve). Here, the choice of the photon energy intervals is based on the strongest optically-induced change of the XUV transmission. Resonant to the M₃ edge, the XUV transmission drops by ~4% when the NIR pulse arrives at *Delay* ≈ 0 fs. This decrease suggests that states are emptied by the NIR pulse, permitting more XUV transitions from the core levels and therefore higher XUV absorption. On the other hand, at 68.6 eV the XUV pulse probes the final states of the NIR transitions, i.e. where the electron occupation increases. As a result, the XUV transmission increases. The broad energy difference between initial and final state

suggests that the excitation channel of the considered transitions could be multi-photon absorption.

One can notice that the electronic response of nickel recovers to more than the half of the maximum signal in the time interval of **550** fs, different to what shown in Figure 5.3 for silicon. Figure 6.3, right shows the XUV transmission change at **65.8** eV for different pump intensities ranging from $1.4 \cdot 10^{12}$ W/cm² to $4.9 \cdot 10^{12}$ W/cm². The three curves are fitted with an exponential decay function to obtain the following time constants: **316.42 ± 47.50** fs for $1.4 \cdot 10^{12}$ W/cm², **224.78 ± 27.30** fs for $2.9 \cdot 10^{12}$ W/cm² and **321.92 ± 33.86** fs for $4.9 \cdot 10^{12}$ W/cm². The evaluated time constants reveals how, within the errors, the time of recovery from the NIR excitation does not significantly depend on the incident intensity.



Figure 6.3: Left: XUV transmission change for $2.9 \cdot 10^{12}$ W/cm² at 65.8 eV (blue) and 68.6 eV (red). Right: XUV Transmission change of nickel at 66.5 eV for three different pump intensites: $4.9 \cdot 10^{12}$ W/cm² (3.7 µJ) in green, $2.9 \cdot 10^{12}$ W/cm² (2.7 µJ) in blue and $1.4 \cdot 10^{12}$ W/cm² (1.7 µJ) in red.

6.1.3 Absolute Timing of the Laser-induced Electron Dynamics

On long time scales, non-coherent effects such as thermalisation processes set in, making it challenging to disentangle the electronic response from the lattice contributions [16,121]. The coherent control of the electronic properties of a material occurs during the time of interaction with the laser electric field. In this time window of a few femtoseconds, the change in the population distribution can be studied on a sub-cycle level using attosecond metrology and has been widely applied on band-gap materials.

With the aim of answering the question if there is a universal response of matter to optical excitation, the ultrafast rearrangement of electronic population in a transition metal is studied in the following. Figure 6.4 shows the XUV transmission change of nickel at **64** eV (slightly below resonance) at the incident intensity **7.3** \cdot **10**¹² W/cm². The TA signal is recorded with **0.1** fs time steps. It can be noticed that the XUV signal is modulated with twice the frequency of the exciting electric field. This is the first proof for the sub-cycle, instantaneous response of the electronic system inside a transition metal to the strong field excitation. At this energy, the XUV signal drops only of **2%**, while at resonance it decreases of **~5%** (see Figure 6.3). However, the oscillations are more distinct at **64** eV in the considered measurement. As in the study of silicon, the electronic response given by the TA measurement is compared with the NIR electric field measured with streaking

spectroscopy (Figure 6.5). The comparison gives full access to the origin of the opticallyinduced modulations. The measurements are performed in a sandwiched manner, where the streaking spectrogram is measured before and after the TA measurement. Then, the two streaking traces are averaged and directly compared with the TA signal. In such manner, possible delay drifts in the laser system are taken into consideration. The results in Figure 6.4 show the perfect synchrony of the oscillating XUV transmission change with the oscillation peaks of the vector potential of the NIR pulse. In other words, the modulated behaviour of the carrier population redistribution is affected by the intraband electron currents induced by the NIR pulse. This intraband electronic motion causes a phase shift of $\pi/2$ of the sub-cycle carrier response with respect to the electric field of the exciting pulse, i.e. the modulations are synchronous with the pulse vector potential. The observed effect is not surprising, as in a metal the electrons are delocalised and free to move. A further aspect which can be noticed in Figure 6.4 is the symmetry breaking in the oscillations of the TA signal: the minima of the vector potential induce much stronger oscillations compared to the maxima of the vector potential. This asymmetric modulation is not observed in all the performed measurements and not confirmed by theory (see subsection 6.1.4), hence it is not further subject of discussion.



Figure 6.4: Timing of the carrier response of nickel (left) and silicon (right). The blue curve represents the XUV transmission change of nickel at **64** eV, while the green curve is the vector potential of the NIR pulse measured with streaking. The applied intensity measured from the beam profile at the focus is **7.3** · **10**¹² W/cm². From the measured field strength $I_{peak} = 2.4 \cdot 10^{13}$ W/cm² is obtained.



Figure 6.5: Streaking spectrogram for the measurement of the pulse waveform performed at a central photon energy of 66 eV. The trace gives the vector potential of the pulse.

Figure 6.6 is the equivalent on a short time-scale of Figure 6.3, but for slightly different peak energies. As in the measurement of Figure 6.4, the biggest change in the XUV signal is measured at resonance (~66 eV), while the modulations of the XUV signal are the strongest below resonance. On the left, the XUV transmission change at 65.2 ± 1 eV (hole signal) and 69 ± 0.2 eV (electron signal) is plotted. Even if the oscillations at 69 eV are not as pronounced as the ones observed at 65.2 eV, it is possible to recognise the synchrony between the maxima in the hole signal and the minima in the electron signal, similar to silicon. It implies that the two XUV signals refer to the same NIR-induced transition probed at different photon energies. The plot on the right of Figure 6.6 shows the XUV transmission change at 66 eV for three different peak energies of the pump pulse. It can be noticed how the reduction of the XUV transmission becomes stronger by increasing the peak energy.



Figure 6.6: Left: XUV transmission change at **65.2** eV in blue and **69** eV in red. The two curves corresponding to the hole and the electron signal, respectively, show complementary oscillating behaviour. Right: XUV transmission change at 66 eV for three different incident peak energies. With increasing $E_{incident}$, the change in transmission gets larger and steeper.

6.1.4 Comparison with the Elk Simulations

The change in the population distribution, quantified by the measured change in XUV transmission, is backed up by the computational results of the Elk code [111] obtained by S. Sharma *et al.* The code is used as well to support the transient absorption results of silicon (Chapter 5) and the magnetisation dynamics in nickel (Chapter 7). More computational details can be found in Appendix A.

The code is able to deliver the dielectric function $\varepsilon(\omega, \tau)$ of the material as a function of the photon energy and the delay between pump and probe pulse. $\varepsilon(\omega, \tau)$ is proportional to the number of excited charges, and can be directly compared with the experimentally measured XUV absorption. Figure 6.7 shows the dielectric function integrated over two energy intervals, **61** – **68** eV and **68.5** – **72** eV. As observed in the experiment, the absorption signal resonant to the M₂-edge increases when nickel interacts with the NIR electric field. When the XUV pulse probes at higher photon energies, corresponding to the final state of the NIR transitions, the XUV absorption decreases. Both hole and electron signal show a sub-cycle response to the NIR excitation. The oscillations are in synchrony with the vector potential, as also observed in the experiment.

It has been mentioned that the Elk code makes use of the ground state for the determination of the number of excited charges $n_{ex}(t)$. A different approach is given by the use of the Houston function [113]. In subsection 5.1.4 it is shown that in silicon, the use of the two different definitions results in a $\pi/2$ difference in the calculation of the phase. On the other hand, the choice does not influence the phase relation between the NIR field and $n_{ex}(t)$ when the material is a metal. This implies that the experimental results can be well described by the theoretical calculations performed with the Elk code.



Figure 6.7: Simulated dielectric function for an incident intensity of $1.5 \cdot 10^{12}$ W/cm² integrated over 61 - 68 eV (blue curve) and 68.5 - 72 eV (red curve). The green curve is the vector potential of the incident pulse.

6.2 Intraband Dynamics in Thin Metal Films: Theoretical Overview

In Chapter 5, the strong-field induced inter-band dynamics in silicon are investigated with the field-resolved measurement technique of polarisation sampling [1]. The same experiment is reported here for analysing the nonlinearities in nickel given by the laserinduced intraband transitions of electrons. Linear Petahertz Photo-conductive Sampling (LPPS) in gas [95] is used likewise to detect the electric field. In the following, it is shown for the first time, that the tecnique can be applied to a transition metal.

6.2.1 Nonlinear 2D Macroscopic Electromagnetism

Light propagation through thin films requires a different formalism compared to bulk materials. The theoretical description in the present section is developed by K. Yabana et al., based on the work of S. Yamada *et al.* [124].

To set up the problem, the one-dimensional light propagation through a thin film is considered. As shown in Figure 6.8, the nickel thin film is located in the *xy*-plane between z = 0 and z = a, and the beam propagation direction is z. In the following, the incident pulse is p-polarised and the incidence is taken normal to the surface of the sample. For z < 0, the pulse propagates through the fused silica substrate with dielectric constant ε_1 , while for z > a there is vacuum (ε_2).



Figure 6.8: Illustration of the setup for calculating the induced current and the transferred energy in nickel.

The propagation of the electric field through the medium can be described with the Maxwell equation:

$$\frac{1}{c^2} \frac{\partial^2 A(z,t)}{\partial t^2} - \frac{\partial^2 A(z,t)}{\partial z^2} = \frac{4\pi}{c} J(z,t)$$
(6.1)

Where A(z,t) is the vector potential and J(z,t) is the electric current density in a bulk material. Assuming the thickness a of the sample sufficiently small, J(z,t) can be approximated to:

$$J(\boldsymbol{z},t) = \theta(-\boldsymbol{z})J_1(\boldsymbol{z},t) + \delta(\boldsymbol{z})J_{2D}(\boldsymbol{z},t) + \theta(\boldsymbol{z})J_2(\boldsymbol{z},t)$$
(6.2)

With $J_{2D}(z, t)$ the current density inside the thin nickel film, which can be considered as two-dimensional, $J_1(z, t)$ and $J_2(z, t)$ the current densities before (in the SiO₂ substrate) and after (in vacuum) the nickel layer, respectively. J(z, t) can be taken constant along z so that $J_{2D}(z, t)$ can be written as:

$$J_{2D}(z,t) = \int_0^a dz \ J(z,t) \approx a J(0,t)$$
(6.3)

The described formalism for 2D macroscopic electromagnetism can be extended to the nonlinear case. According to (2.3), the induced polarisation in the SiO₂ substrate and in the nickel film is given by:

$$P(z,t) = \chi E(z,t) = -\frac{\chi}{c} \frac{dA(z,t)}{dt}$$
(6.4)

P(z,t) is linked to the current density:

$$J(\boldsymbol{z},t) = \frac{dP(\boldsymbol{z},t)}{dt} = -\frac{\chi}{c} \frac{d^2 A(\boldsymbol{z},t)}{dt^2}$$
(6.5)

The simplest solution of (6.1) is given by a plane wave, thus the total vector potential of the pulse propagating along z is expressed as:

$$A(z,t) = \begin{cases} e^{i(k_1z-\omega t)} + Ae^{i(-k_1z-\omega t)} & z < \mathbf{0} \\ Ce^{i(k_2z-\omega t)} & z > a \end{cases}$$
(6.6)

The coefficients A and C are determined by using the boundary condition at z = 0. For the continuity of the fields 1 + A = C is given. The second expression to find the coefficients A and C can be obtained by integrating the Maxwell equation (6.1) on a small interval $-\delta < z < \delta$ with an infinitely small δ :

$$-\frac{\partial A(\boldsymbol{z},t)}{\partial \boldsymbol{z}}\Big|_{-\delta}^{+\delta} = \frac{4\pi}{c} J_{2D}(\boldsymbol{z},t)$$
(6.7)

It follows that:

$$-ik_2C + ik_1(1 - A) = a(\varepsilon - 1)\frac{\omega^2}{c^2}C$$
(6.8)

With $\varepsilon - \mathbf{1} = n^2 - n_2^2$, where *n* and n_2 are the refractive indexes for nickel and vacuum, respectively. Now *A* and *C* can be obtained:

$$A = \frac{k_1 - k_2 + ia(\varepsilon - 1)\frac{\omega^2}{c^2}}{k_1 + k_2 - ia(\varepsilon - 1)\frac{\omega^2}{c^2}}$$
(6.9)

$$C = \frac{2k_1}{k_1 + k_2} \left(1 - \frac{ia(\varepsilon - 1)}{k_1 + k_2} \frac{\omega^2}{c^2} \right)$$
(6.10)

The general solution (6.6) assumes a more physical meaning by introducing the incident $A^{in}(t)$, the reflected $A^{re}(t)$ and the transmitted pulse $A^{tr}(t)$. Using the relation $n = \sqrt{\varepsilon}$, Eq.(6.6) becomes:

$$A(z,t) = \begin{cases} A^{in}e^{i\left(t-\frac{n_{1}z}{c}\right)} + A^{re}e^{i\left(t+\frac{n_{1}z}{c}\right)} & z < 0 \\ A^{tr}e^{i\left(t-\frac{n_{2}z}{c}\right)} & z > a \end{cases}$$
(6.11)

Substituting A(z, t) in (6.7) with the definition (6.11) and using the relation $A^{in}(t) + A^{re}(t) = A^{tr}(t)$ leads to the following expression for $A^{tr}(t)$:

$$-\frac{1}{c}\frac{dA^{tr}}{dt} = -\frac{1}{c}\frac{2n_1}{n_1 + n_2}\frac{dA^{in}}{dt} - \frac{1}{c}\frac{4\pi}{n_1 + n_2}J_{2D}(z,t)$$
(6.12)

It is important to notice that the current density $J_{2D}(z,t)$ depends only on the transmitted electric field. With the assumption of a weak incident field, the current $J_{2D}(z,t)$ of a thin nickel film can be defined by the linear response formula:

$$J_{2D}(\boldsymbol{z}, \boldsymbol{t}) = a \int dt' \boldsymbol{\sigma}(\boldsymbol{t} - \boldsymbol{t}') E^{tr}(\boldsymbol{t})$$
(6.13)

Where $\sigma(t)$ is the time-dependent conductivity of the thin-film. By Fourier-transforming Eq. (6.12), $E^{tr}(\omega)$ is obtained as a function of the incident field $E^{in}(\omega)$:

$$E^{tr}(\omega) = \left\{ \mathbf{1} + \frac{\mathbf{1}}{n_1 + n_2} \frac{\mathbf{4}\pi a}{c} \sigma(\omega) \right\}^{-1} \frac{\mathbf{2}n_1}{n_1 + n_2} E^{in}(\omega)$$
(6.14)

Which leads to the following definition of $\sigma(\omega)$:

$$\sigma(\omega) = \frac{c}{4\pi a} \left\{ 2n_1 \frac{E^{in}(\omega)}{E^{tr}(\omega)} - (n_1 + n_2) \right\}$$
(6.15)

6.2.2 Energy Transfer

For calculating the amount of energy deposited from the pulse into the material it is necessary to examine the total energy balance given by the standard expression of the energy conservation in electromagnetism:

$$\frac{\partial u}{\partial t} = \frac{1}{4\pi} \left(\vec{E} \frac{\partial \vec{D}}{\partial t} + \vec{H} \frac{\partial \vec{B}}{\partial t} \right)$$
(6.16)

From the Maxwell equations, (6.16) can be rewritten as:

$$\frac{\partial u}{\partial t} + \frac{4\pi}{c} \nabla \vec{S} = -\vec{E} \cdot \vec{J}$$
(6.17)

Where \vec{S} is the Poynting vector defined as: $\vec{S} = \frac{c}{4\pi} \vec{E} \times \vec{H}$. In the geometry shown in Figure 6.8, \vec{S} has only the **z**-component, while the magnetic field is only along **y**:

$$\vec{H}^{in}(\vec{r},t) = \hat{y}n_1 E^{in}\left(t - \frac{n_1 z}{c}\right)$$
(6.18)

The Poyinting vector can now be written as:

$$\vec{S} = \begin{cases} S^{in}(z,t) = \frac{cn_1}{4\pi} E^{in} \left(t - \frac{n_1 z}{c} \right)^2 \\ S^{re}(z,t) = \frac{cn_1}{4\pi} E^{in} \left(t + \frac{n_1 z}{c} \right)^2 \\ S^{tr}(z,t) = \frac{cn_1}{4\pi} E^{in} \left(t - \frac{n_2 z}{c} \right)^2 \end{cases}$$
(6.19)

Using Eq.(6.19) and integrating Eq.(6.17) over a volume **V** composed by a unit area in the **xy**-plane and an infinitesimally small interval $-\delta < z < \delta$ results in the following expression:

$$\frac{\partial}{\partial t} \int_{V} d\vec{r} u + \frac{4\pi}{c} \{ S^{tr}(+\delta, t) - S^{re}(-\delta, t) - S^{in}(-\delta, t) \}$$

$$= -E^{tr}(t) \cdot J_{2D}[E^{tr}(t)](t)$$
(6.20)

The physical meaning of each term is obvious. The first term on the left represents the change of field energy density inside the thin film. The second term including the Poynting vector describes the energy balance between the infalling and the transmitted electric field. The term on the right side of the equation is the energy transferred from the electric field to the medium. It follows that the definition of the time-dependent electronic excitation energy per unit area is given by:

$$W(t) = \int_0^t dt' E^{tr}(t') \cdot J_{2D}[E^{tr}(t)](t')$$
(6.21)

According to Eq. (6.12), the transmitted electric field is given by:

$$E^{tr}(t) = \frac{2n_1}{n_1 + n_2} E^{in}(t) + \frac{1}{n_1 + n_2} \frac{4\pi}{c} J_{2D}(t)$$
(6.22)

From this equation $J_{2D}(t)$ can be retrieved as a function of the measured fields $E^{in}(t)$ and $E^{tr}(t)$. Replacing it in (6.21) leads to a more explicit expression for the excitation energy:

$$W(t) = \frac{c}{4\pi} \int_0^t dt' E^{tr}(t') \{ (n_1 + n_2) E^{tr}(t') - 2n_1 E^{in}(t') \}$$
(6.23)

In the specific case pictured in Figure 6.8, $\mathbf{n}_1 = \mathbf{1.45}$ and $\mathbf{n}_2 = \mathbf{1}$.

The linear component $W^{\text{Linear}}(t)$ is obtained by taking E^{tr} in the presence of a weak incident field. The total work $W^{\text{TOT}}(t)$ is determined by taking E^{tr} for a strong incident field. The difference between $W^{\text{TOT}}(t)$ and $W^{\text{Linear}}(t)$ gives the nonlinear energy transferred to the sample.

6.3 Strong-Field Induced De-Metallization in Nickel

The study of the intraband dynamics in a metallic material, with means of sampling the transmitted electric field, exhibits several challenges due to its intrinsic high reflectivity and low transmissivity.

The use of a thin metallic film together with the application of LPPS in gas for detecting the transmitted electric field, make it possible to apply polarisation sampling for studying nickel's intraband electronic motion. As mentioned in section 4.2, LPPS has a higher dynamic range compared to streaking and therefore permits a measurement with smaller integration time. In other words, LPPS has the advantage of taking a set of measurements in less time and/or with a higher signal-to-noise ratio.



b) Without Nickel: Reference

Figure 6.9: The illustration shows the sample under analysis for applying polarisation sampling at nickel. The half of a **10** μ m thick SiO2 substrate is coated with **8** nm nickel. The pulse transmitted through the substrate is taken as the reference. The pulse transmitted through SiO₂ coated with Ni is measured for a weak and a strong incident field by positioning the sample out of focus and in focus, respectively. The three pulses carry all the information to retrieve nickel's linear and nonlinear response.

In the transient absorption experiment, the 8 nm thick nickel is deposited on a silicon substrate, as Si is inert in the spectral range covered by the XUV probe pulses. In polarisation sampling, both the linear and the nonlinear response of the sample are directly retrieved from the transmitted electric fields. As silicon gets nonlinearly polarised in a similar range of intensities as nickel, it can't be used as a substrate in this experiment. The **8** nm thick nickel film is coated on a **10** μ m thick SiO₂ substrate. The nonlinear response of SiO₂ sets in at intensities on the order of **10**¹⁴ W/cm². As Ni is studied in the intensity range of **10**¹¹ – **10**¹² W/cm², fused silica shows to be a suitable substrate. SiO₂
has a two orders of magnitude smaller thermal conductivity compared to Si [125,126]. Accordingly, the thermal damage threshold of the Ni/SiO₂ sample is lower compared to the Ni/Si sample.

As illustrated in Figure 6.9, the sample consists in half SiO_2 coated with nickel and half just SiO_2 without coating. Further details about the sample preparation can be found in the Appendix A. This design makes it possible to separately measure the electric field transmitted through fused silica, which is treated as the reference pulse, and the electric field transmitted through nickel for a weak and a strong incident field. As theoretically described above, the three detected fields allow for the subtraction of the linear response of the substrate from the linear and nonlinear signal of nickel.

The sample is positioned with SiO_2 in front at ~10° with respect to the incident beam. Furthermore, all the PS measurements reported in the following are performed with 0.1 fs time steps.

6.3.1 Transmitted Fields: Amplitude and Phase Modulation

The left plot of Figure 6.10 depicts the set of the three measured pulses for the evaluation of nickel's nonlinear response: the reference through the SiO₂ substrate (green curve), the pulse transmitted through the sample out of focus (red curve) and in focus (blue curve). Here, the measurements are performed in the range of 10^{11} W/cm². Interestingly, nickel becomes 8.2% more transparent when the field strength is increased by 24.7%. This effect is observed on a smaller scale in the time-integrated measurement of the transmitted power (see section 3.2). The strong-field induced transparency is related to a decrease of the imaginary part of the dielectric function, i.e. of the extinction coefficient κ ($\kappa = Im(n)$). This can be understood as a reduction of the ability to absorb energy caused by the presence of the strong field. The origin can be found in the saturation of absorption: with increasing intensity, the number of excited electrons above the Fermi level is sufficiently high to saturate the NIR absorption by Pauli-blocking. Accordingly, further electron transitions are not allowed.

What can't be detected in a simple time-integrated measurement of the transmitted power is the time-dependent phase shift that the NIR pulse undergoes after propagating through nickel. In the inset of Figure 6.10, the phase difference between the incident and the transmitted fields is plotted in the time region corresponding to the main oscillations of the pulse. It is calculated as the phase angle of the ratio between the complex envelope of the reference and the transmitted pulse. The most reliable value of the phase shift is obtained where the signal-to-noise ratio is maximised, i.e. at the strongest half-cycle of the transmitted field. For the incident intensity of $4.5 \cdot 10^{11}$ W/cm², the phase difference at the strongest half-cycle amounts to -0.437 ± 0.050 rad, while for $7 \cdot 10^{11}$ W/cm² it corresponds to -0.486 ± 0.050 rad. It can be noticed that the phase difference at the lowest intensity already starts to increase considerably within the strongest half-cycle of the pulse. On the other hand, the phase at $7 \cdot 10^{11}$ W/cm² stays almost constant during the pulse and starts rising at the end of the pulse. The recovery of the optically induced phase shift is observed only at the lowest measurable intensity and its origin remains unclear.

The measured increase in the phase velocity of the incident pulse after propagating through Ni corresponds to a decrease of the real part of the dielectric function. A small fraction of the phase shift is caused by the linear response of the material, i.e. by its refractive index. According to the theoretical predictions of K. Yabana *et al.* (subsection 6.3.4), the solely linear response of Ni occurs at the intensity of 10^{10} W/cm². However,

as the thin Ni film transmits only $\sim 40\%$ of the incident radiation, small changes in the transmitted fields for extremely weak incident intensities can't be measured reliably. Therefore, all the measurements performed in the present experiment are in the nonlinear regime.

The nonlinear component of the measured phase shift is a direct consequence of saturable absorption. In a metal, the induced current is directly proportional and in phase with the incident field (*conducting phase*). On the other hand, the induced current inside a dielectric is directly proportional to the time-derivative of the polarisation, i.e. of the incident electric field (*insulating phase*) and hence phase shifted by $\pi/2$ with respect to the incident (driving) field [112]. When the strong pulse interacts with the sample, nickel becomes more transparent, which results in the transition from a conducting to a semiconducting behaviour. One can interpret this transmutation as the building of a band-gap, i.e. of an energetically forbidden region due to the optically-induced state blocking. The observed mutation is confirmed by the optically induced current which is calculated from the measured fields. This is presented and discussed in subsection 6.3.2.

Figure 6.11, left shows the same set of three measurements but for higher incident intensity: $1.2 \cdot 10^{12}$ W/cm² and $1.7 \cdot 10^{12}$ W/cm² for the weak and the strong field, respectively, in addition to the reference. Surprisingly, the transmittance of nickel decreases by **24%** when the field strength is increased by **19%**. For intensities approaching the damage threshold, the saturable absorption effect is reversed and Ni exhibits a higher absorption. This phenomenon can be explained by the NIR excitation of electrons from the initial excited state to a higher state into the conduction band.

While the amplitude of the transmitted pulse gets lower when the intensity is increased from $1.2 \cdot 10^{12}$ W/cm² to $1.7 \cdot 10^{12}$ W/cm², the phase shift of the transmitted pulse continues to increase almost linearly with the intensity. In the inset of Figure 6.11, it can be seen how the phase stays mostly constant during the pulse for both intensities. Even though at $1.2 \cdot 10^{12}$ W/cm² the phase difference return to zero at the end of the pulse, this does not happen at higher intensity. The values estimated at the strongest half-cycle are -0.562 ± 0.050 and -0.605 ± 0.050 rad, respectively. At $1.7 \cdot 10^{12}$ W/cm², the phase difference reaches its maximum which corresponds to almost a $\pi/5$ shift. The intensity dependence of the transmission change and of the phase shift are further discussed in subsection 6.3.4, when compared to the theoretical predictions.

The observed intensity-dependent behaviour of a thin metallic film reveals to be considerably appealing for manipulating the phase and amplitude of optical pulses at the same time. The effect of saturable absorption and reverse saturable absorption was observed as well in platinum nanoparticles [127] and MoTe₂ nano-films [128]. However, the authors reported the time-integrated study of the transmitted power by performing a conventional *z*-scan [81]. Consequently, they observed only the change of the pulse amplitude as a function of the intensity. The theoretical work done by M. Uemoto *et al.* [112] has shown a similar behaviour in graphite thin films. The required field strength for observing a strong phase shift approaches $2.7 \cdot 10^{-1}$ V/Å, which is two orders of magnitude greater than the field strengths applied in the present experiment.



Figure 6.10: Incident field (green curve) and transmitted fields at $4.5 \cdot 10^{11}$ W/cm² (red curve) and $7 \cdot 10^{11}$ W/cm² (blue curve). The measured fields exhibit a higher transmission of nickel for higher incident intensity. Inset: the set of three measured pulses is plotted together with the calculated phase difference between reference and transmitted field for $4.5 \cdot 10^{11}$ W/cm² (red curve) and $7 \cdot 10^{11}$ W/cm² (blue curve).



Figure 6.11: Incident field (green curve) and transmitted fields at $1.2 \cdot 10^{12}$ W/cm² (red curve) and $1.7 \cdot 10^{12}$ W/cm² (blue curve). The measured fields exhibit a lower transmission of nickel for higher incident intensity. Inset: the set of three measured pulses is plotted together with the calculated phase difference between reference and transmitted field for $1.2 \cdot 10^{12}$ W/cm² (red curve) and $1.7 \cdot 10^{12}$ W/cm² (blue curve).

6.3.2 Induced Current

The three measured pulses provide all the necessary information for the evaluation of the optically induced current and therefore the energy transferred to the nickel film. Similar to the experiment in silicon, the detected fields are normalised on the field oscillations of a small delay interval after the main pulse. Moreover, no Gouy correction is applied to the phase of the pulses. LPPS images the focus position of the beam, which is to say that the different pulse phases experienced by the sample in and out of focus does not play a role. On the other hand, the measured pulses are not numerically propagated to the midpoint of the sample like in Si, as the chosen Ni film is extremely thin (**8** nm).

Figure 6.12 depicts the nonlinear (green curve) and the total (blue curve) current induced by the NIR pulse (red curve). The evaluation is performed by retrieving the current from Eq.(6.22) for the case of a weak and a strong incident field. As described in section 4.2, the nonlinear current originates from the interaction with a strong field, where the material's behaviour is both linear and nonlinear. The nonlinear component can then be obtained by subtracting the linear response of the material for a weak incident field. However, due to the experimental limitations mentioned in 6.3.1, the weak field still contains a small amount of the nonlinear contribution. This leads to an underestimation of the nonlinear component of the current evaluated from the transmitted fields.

In Figure 6.12 it can be noticed that the nonlinear current is phase shifted forward with respect to the incident pulse. As reported in the previous subsection, the optically induced saturation of absorption induces an increase in the phase velocity of the laser pulse after propagating through the thin metallic film. In other words, it results in the transition of nickel from being a conductor to being a semi-conductor. This effect is observed in the phase-shifted nonlinear and total current which is induced by the pulse to the sample.



Figure 6.12: Incident electric field (red curve), nonlinear (green curve) and total (blue curve) induced current at $1.3 \cdot 10^{12}$ W/cm².

Figure 6.13 depicts the total induced current retrieved from the fields plotted in Figure 6.10 and Figure 6.11, i.e. for different intensities. The inset highlights the area around the

strongest half-cycle. By increasing the intensity from $4.5 \cdot 10^{11}$ W/cm² to $1.7 \cdot 10^{12}$ W/cm², the amplitude of the current increases as well. On the other hand, the phase shift increases until $1.2 \cdot 10^{12}$ W/cm² and decreases when the intensity reaches $1.7 \cdot 10^{12}$ W/cm². This is indicated by the black arrows in the inset.

The observed increase of the phase shift until $1.2 \cdot 10^{12}$ W/cm² is indicative for the semiconductor metamorphosis of nickel caused by saturable absorption. The reversion of this effect, which is observed in the fields plotted in Figure 6.11, emerges here in the change of phase shift direction of the induced current at $1.7 \cdot 10^{12}$ W/cm².



Figure 6.13: Total induced current retrieved from the measured fields at $4.5 \cdot 10^{11}$ W/cm² (blue curve), $7 \cdot 10^{11}$ W/cm² (purple curve), $1.2 \cdot 10^{12}$ W/cm² (red curve) and $1.7 \cdot 10^{12}$ W/cm² (green curve).

6.3.3 Energy Transfer

With the thin-film formalism introduced by Yabana *et al.* and described above, the work applied from the NIR field to the sample can be determined according to Eq.(6.21). It is clear how the applied work mainly depends on the phase between the induced current and the field transmitted at low and high intensity. Figure 6.14 shows the total work at $1.15 \cdot 10^{12}$ W/cm², together with its linear and nonlinear components. As Ni's response is not solely linear for the weak incident field, the linear energy transfer still contains a minor nonlinear contribution which causes an underestimation of the nonlinear component of the energy transfer.

All three curves are modulated at twice the frequency of the NIR field. In particular, the linear and the total transferred energy oscillate with a $\pi/2$ shift forward with respect to the electric field. On the other hand, the more-stepwise modulations of the nonlinear component are in synchrony with the field squared.

The higher transmission for the strong incident field with respect to the weak one results in a negative nonlinear transferred energy. As previously mentioned, the strong NIR field reduces the extinction coefficient of nickel while propagating through the sample. As a result, Ni's ability to accumulate the nonlinear component of the energy decreases while interacting with the NIR pulse. This effect is irreversible, as it lasts even after the pulse.

When the weak NIR pulse interacts with the sample, the linear transferred energy increases over time and stays in nickel after the NIR excitation. This is not a surprising behaviour for a metal, as the presence of free electrons contribute to store the energy. Moreover, it is noticeable how the linear response sets in already before the pulse. Here, the intensity of the pre-pulse is sufficiently high to play a significant role in the transferred energy.



Figure 6.14: Linear, nonlinear and total work applied on nickel calculated from the measured fields. The curves are normalized over the total incident energy.

From Figure 6.15 it is clear how, by increasing the incident intensity, the total work decreases. The nonlinear component scales with the squared field, while the linear component scales linearly with the field. Accordingly, the total transferred energy gets smaller with growing intensity. However, as both the transmitted amplitude and the change in phase are involved, the scaling factor between work and intensity is not trivial.



Figure 6.15: Total transferred energy at $1.25 \cdot 10^{12}$ W/cm² (red curve), $1 \cdot 10^{12}$ W/cm² (green curve) and $7 \cdot 10^{11}$ W/cm² (blue curve) calculated from the measured fields. The curves are normalized over the total incident energy.

6.3.4 Comparison with the SALMON Calculations

The simulations for the polarisation sampling experiment in silicon as well as in nickel are performed by the group of K. Yabana with the *ab-initio* TD-DFT code "SALMON" [113,116]. The computational details can be found in Appendix A.

Transmitted Waveforms and Energy Transfer

Figure 6.16 depicts the calculated transmitted fields at $1 \cdot 10^{12}$ W/cm² (blue curve) and $5 \cdot 10^{11}$ W/cm² (red curve). The incident electric field (green curve) is chosen with a prepulse tail with a duration of **20** fs. The intensity ratio between the tail and the main pulse is **0.3**. These parameters are chosen to best reproduce the pulse used in the experiment. In fact, a sufficiently strong pre-pulse already excites carriers linearly and contributes to the increase of electron population inside the conduction band. It is explained later how the presence of the pre-pulse gives an essential contribution to the magnitude of saturable absorption and its intensity dependence.

From Figure 6.16 it is clear how the effect observed in the experiment is also wellpredicted by the simulated transmitted fields at similar intensities. Both the phase shift and the change in transmittance can be noticed. Moreover, by using the same formalism described in subsection 6.2.2, the amount of transferred energy is calculated from the transmitted fields and nicely reproduce the experimental data.



Figure 6.16: Fields simulated with SALMON. The green curve represent the incident electric field, while the blue and the red curve are the fields transmitted through nickel at $1 \cdot 10^{12}$ W/cm² and $5 \cdot 10^{11}$ W/cm², respectively.



Figure 6.17: Linear, nonlinear, and total work calculated from the fields plotted above. The simulations reproduce the qualitative behaviour of the experimental data.

Intensity Dependence of the Phase Shift and the Transmitted Amplitude

The calculations are performed in a wide intensity range to exhaustively investigate the intensity dependence of the phase difference between the incident and transmitted field,

as well as the scaling of the transmitted amplitude. The nonlinear response sets in at intensities greater than 10^{10} W/cm², which corresponds to a field strength of 0.027 V/Å. The values of the linear phase shift and the linear change of transmitted amplitude are not plotted in Figure 6.18 and Figure 6.19, as there is no experimental comparison at the considered field strength.

The phase shift $\Delta \Phi$ calculated from the fields simulated with TD-DFT is plotted in Figure 6.18, left. The theoretical $\Delta \Phi$ is directly compared with $\Delta \Phi$ from experiment. In both cases, the evaluation of the phase difference is taken at the strongest half-cycle of the transmitted field. The linear phase shift obtained from the theoretical predictions amounts to -0.338 rad. This value represents about 50% of the maximum phase shift measured with polarisation sampling spectroscopy, which includes both the linear and the nonlinear response of nickel.

The value of the phase from the experiment strongly depends on the temporal overlap of the pulses. The beamline, where the experiment takes place, has intrinsic drifts in the delay interferometer. Consequently, the time-axis of the measured pulses needs to be adjusted. This is done by making the traces overlap ~15 fs before the arrival of the main pulse. In view of this, the experimental error is estimated to be large.

Within the error bars, the experimental phase shift agrees well with theory, with exception of the last point above **0.35** V/Å. From the comparison it appears clear that the TD-DFT calculations underestimate the intensity dependence of nickel's nonlinearity. A plausible argument for this divergence is given by the shape of the pulse. In particular, a long main pulse or a short pulse with an intense (or long) tail significantly increase the magnitude and the intensity dependence of the observed effect. This phenomenon is justified by the fact that the pre-pulse already induces an increase in electron population in the conduction band due to linear absorption. A further aspect which could likely contribute to the underestimation of the change in phase is the oxidation of the sample. Although the experiment takes place in vacuum, the samples are prepared and transported to the sample and the nickel surface. The oxide layer is not contemplated in the simulations, as it is challenging to implement in the code.



Figure 6.18: Left: Phase difference between the incident field and the field transmitted through nickel. The phase is evaluated at the strongest half-cycle of the pulse. Right: Ratio between the squared field transmitted through nickel and the squared incident field. In both plots the red dots represent the experimental data, while the blue dots are the data obtained from the fields calculated with SALMON.

The dependence of the change in transmitted amplitude from the intensity is depicted in Figure 6.18, right. In the evaluation, the integral of the squared transmitted field is divided over the integral of the squared incident field. The plot shows good agreement between experiment and theory for field strengths below **0.3** V/Å. Above this value, the amplitude transmission ratio from the experimental data continues to grow with the same slope until **0.35** V/Å, where saturable absorption is reversed. The theoretical results depict the reversion already at **0.27** V/Å and on a smaller scale. The reasons for the divergence can be found also here in the shape of the pulse and in the presence of the oxide layer on top of nickel.

The intensity dependence of the phase shift between the total induced current J(t) and the incident field for the experimental and the theoretical data is studied and plotted in Figure 6.19. As the current is calculated from the incident and the transmitted fields, both their amplitude ratio and their phase relation are enclosed in J(t). Consequently, the theoretical underestimation of nickel's nonlinearity is observed as well in Figure 6.19. Furthermore, it appears clear how the phase shift between the incident field and the induced current reverses direction at higher field strength (0.35 V/Å) compared to what would be expected from the amplitude transmission ratio plotted in Figure 6.18 (0.31 V/Å). The origin of the difference remains unclear, but can probably be found in the wrong proportion between the amplitude ratio and the phase shift between the incident and transmitted fields at 0.31 V/Å.



Figure 6.19: Phase difference between the incident field and the induced current. The red dots represent the experimental data, while the blue dots are the data obtained from the fields calculated with SALMON.

Excited Carrier Density and Density of States

Pauli blocking induced by the high number of charges excited above the Fermi level is the origin of the saturable absorption effect observed in nickel. Therefore, it is clear how the excited carrier density constitutes an important physical quantity to describe the experimental results reported here. Figure 6.20 a) depicts the simulated number of excited charges n_{ex} normalised over the incident intensity *I*. Details about the evaluation of n_{ex} can be found in Appendix A.

It can be noticed how the carriers get excited already during the linear interaction of nickel with the pre-pulse (until ~ 20 fs). This is analogous to what is seen in the amount of energy deposited into the sample and proves the significance of linear carrier excitation in the electronic response of nickel.

By increasing the intensity by two orders of magnitude, n_{ex}/l considerably decreases. In particular, the excited carrier density at the highest intensity of $1 \cdot 10^{12}$ W/cm² exhibits an overshoot at ~30 fs, which is observed also in band-gap materials. As nickel becomes less conducting, n_{ex} shows the typical character of a dielectric material (see sections 5.1 and 5.2): the number of excited charges and the amount of transferred energy contain a reversible and an irreversible component. The overshoot represents the reversible component, as it lasts only for the duration of the pulse.



Figure 6.20: a) Time-dependent number of excited charges normalised over the incident intensity for $1 \cdot 10^{10}$ W/cm² (green curve), $1 \cdot 10^{11}$ W/cm² (blue curve) and $1 \cdot 10^{12}$

W/cm² (red curve) simulated with SALMON. b) Density of states as a function of $E - E_F$ at time t = 35 fs after the pulse for the same set of intensities (also simulated with SALMON).

Figure 6.20 b) depicts the density of states (DOS) at time t after the pulse. The DOS is plotted for the three different intensities considered in a). With increasing intensity, the density of occupied and unoccupied states increases. More specifically, at the time step t = 35 fs from the Fermi level to 1 eV, the density of the occupied states is 0.207% of the density of the total available states at $1 \cdot 10^{10} \text{ W/cm}^2$, 1.956% at $1 \cdot 10^{11} \text{ W/cm}^2$ and 7.318% at $1 \cdot 10^{12} \text{ W/cm}^2$. The highest occupation density is reached at $t \approx 30$ fs with 8.860% at $1 \cdot 10^{12} \text{ W/cm}^2$. These numbers reveal a significantly high level of optical doping in nickel. Standard doping values for silicon range from 10^{13} cm^{-3} to 10^{18} cm^{-3} [130]. Considering the total number of atoms in intrinsic crystalline silicon ($5 \cdot 10^{22} \text{ cm}^{-3}$), only one atom per $10^9 - 10^4$ atoms is doped.

At this intensity, the number of occupied states significantly increases not only near the Fermi level, but also at higher energies. This phenomenon shows that additional electron transitions occur from the already excited states to higher states in the conduction band. Furthermore, multi-photon absorption sets in at high intensities, exciting electrons from deeper states below the Fermi level. This additional excitation channel can be recognised in the increase of density of unoccupied states at energies below $E - E_F \approx -1.55$ eV: by increasing the intensity from $1 \cdot 10^{10}$ W/cm² to $1 \cdot 10^{12}$ W/cm², the density of the unoccupied states rises from 0.0025% to 0.4964% of the total density of states.

6.3.5 Calculation of the Conductivity

Due to its unsufficient temporal resolution, the LPPS detection technique has the disadvantage of not being sensitive at wavelengths below **600** nm. This restriction makes it challenging to retrieve characteristic quantities, such as the conductivity, in the frequency domain. In fact, in the polarisation sampling experiment on silicon, the lack of sensitivity prevents the determination of the refractive index of the material.

Here, the conductivity $\sigma(\omega)$ of nickel is calculated according to Eq.(6.15) from the reference and the field transmitted through the sample at low intensity. The real and the imaginary part of $\sigma(\omega)$ are plotted in Figure 6.21. The solid lines are calculated from the experimental data, while the dashed lines are the $Re(\sigma(\omega))$ and the $Im(\sigma(\omega))$ calculated with SALMON. Within the energy range supported by LPPS, experiment and theory satisfyingly agree for the real part of the conductivity. A further comparison can be done with the real part of $\sigma(\omega)$ from Wang and Callaway [131]. They compared the simulated data with the results of several experiments. For the central energy of **1.55** eV (800 nm), the calculated $Re(\sigma(\omega))$ is ~420 \cdot 10¹³ s⁻¹. The experimental values range from **360** \cdot 10¹³ s⁻¹ to **580** \cdot 10¹³ s⁻¹. In the results shown here, at **1.55** eV the $Re(\sigma(\omega))$ calculated with SALMON is **470** \cdot 10¹³ s⁻¹, whereas from the experiment **380** \cdot 10¹³ s⁻¹ is obtained.

While a good agreement can be found regarding the real part of the conductivity, the same does not happen for its imaginary part. In the experiment, it is underestimated for low energies and largely overestimated for high energies. The discrepancy can probably be found in the optically-induced nonlinearities. The applied incident intensity is $4.5 \cdot 10^{11}$ W/cm² and nonlinearities in nickel are already occurring from $\sim 1 \cdot 10^{11}$ W/cm². However, the experimental conditions do not allow one to measure in the intensity range where nickel responds only linearly to the optical excitation. In 6.3.1 it is mentioned how

the increase in the phase velocity of the pulse is caused by the decrease of the real part of the dielectric function $\varepsilon(\omega)$ of Ni. The two quantities are related through: $Re(\varepsilon(\omega)) = 1 - \frac{Im(\sigma(\omega))}{\omega\varepsilon_0}$. Accordingly, the NIR field induces an increase in $Im(\sigma(\omega))$.



Figure 6.21: The dashed lines are the real (red) and the imaginary (blue) part of the conductivity calculated with SALMON. The solid lines correspond to the real (red) and the imaginary (blue) part of the conductivity obtained from experiment at $4.5 \cdot 10^{11}$ W/cm².

6.4 Main Findings of the Field-Induced Electronic Motion in Nickel

In the present chapter, a manifold of results concerning the optical control of electronic motion in nickel are presented. First, the interband carrier motion is studied with transient absorption spectroscopy. From the time-integrated spectra, it is possible to recognise the shrinking of the valence band induced by the NIR pulse, as also observed by Stamm *et al.* [25].

The population redistribution within the bands of nickel, which is related to the change in XUV transmission, is studied on a long and on a short time-scale. On a duration of some hundreds of femtoseconds, Ni recovers from the NIR excitation with a characteristic time constant of **287 ± 33.14** fs (average value), which does not significantly depend on the intensity of the NIR pulse. During the few femtoseconds of interaction with the strong field, the electronic response of nickel oscillates with twice the frequency of the NIR pulse. This behaviour is observed in band-gap materials as well (Chapter 5) and suggests a universal response of matter to optical excitation. The oscillating behaviour of the XUV transmission change clearly demonstrates that the electronic system responds to the strong-field excitation within a half cycle of the exciting pulse.

The phase relation between the oscillations and the electric field reveals the nature of the induced modulations. This is investigated by comparing the change in XUV signal with the waveform of the pulse measured with streaking spectroscopy. Different than in band-

gap materials, the electronic response of Ni oscillates with the vector potential of the pulse. The result suggests that intraband electron currents are responsible for the $\pi/2$ phase shift of the modulated XUV signal with respect to the pulse electric field. This arises from the presence of a high number of delocalised electrons into the conduction band, which get accelerated by the strong NIR pulse.

The experimental results of transient absorption in nickel are confirmed by the *ab-initio* simulations performed with the Elk code [111]. The code permits the computation of the change of the dielectric function while the pulse propagates through the sample. This quantity is obtained from the number of charges excited by the NIR pulse and can be directly compared with the measured XUV absorption.

Future studies could be devoted to the further improvement of the spectral resolution. In this work, the XUV pulses probe the M-edges of nickel. However, both edges lie under the same absorption peak. As the transition probability from the M_2 edge is low, the major contribution to the XUV signal originates from the M_3 edge. By improving the spectral resolution, it would be possible to distinguish the two absorption edges and their role in nickel's electronic response.

A further interesting aspect which could be investigated more in detail, is the intensity dependence of the phase relation between the sub-cycle electronic response of Ni and the electric field. The question if a metal could start behaving as a dielectric for different intensities could be answered.

The second part is dedicated to the intraband transitions studied with polarisation sampling spectroscopy [1]. The technique allows the retrieval of the linear and the nonlinear response of nickel by comparing the incident and the transmitted field for low and high intensity. As in the silicon experiment, Linear Photo-Conductive Sampling (LPPS) in gas is applied for the detection of the electric field. The results show a captivating and non-trivial behaviour of the **8** nm thick Ni film while interacting with the NIR pulse. First, nickel becomes more transparent by increasing the intensity because of saturable absorption. Above the Fermi level, the high number of excited charges blocks further transitions and results in the increase of transmission. However, when the intensity is increased to $1.7 \cdot 10^{12}$ W/cm², approaching the damage threshold of the sample, saturable absorption is reversed: the electrons in the excited state are excited to higher states in the conduction band, causing an increase in absorption for optical frequencies.

A second effect, which can only be observed by directly measuring the transmitted electric field, is the increase in phase velocity of the pulse while it propagates through nickel. The phase difference between the incident and the transmitted field grows with the intensity until it reaches the value of $\pi/5$ at $1.7 \cdot 10^{12}$ W/cm². This value is considerably big considering the thickness of the Ni layer. It is known from theory that a small portion of the phase shift origins from the linear interaction with the pulse and is due to the complex refractive index of nickel. The remaining part is purely nonlinear and is a direct consequence of saturable absorption. The optically-induced transparency in Ni implies a transition from a conducting to an insulating behaviour. The phase relation between the induced current and the incident electric field differs by $\pi/2$ for a metal and a dielectric material. As a result, Nickel's de-metallisation results in a shift from a conducting to an insulating phase.

The upper limit of the incident intensity is given by the damage threshold of the material. The use of diamond instead of fused silica as a substrate could push the limit further, allowing the observation of a much stronger nonlinearity in nickel. The lower limit of the intensity is given by the sensitivity of the detection technique, i.e. of LPPS. Due to this experimental limitation, it is not possible to investigate the purely linear response of nickel. Therefore, all the measurements are performed in the nonlinear regime. Future experiments could focus on the optimization of the signal-to-noise ratio of LPPS for a better detection of weak fields, thus the linear component of the Ni's response could be properly determined.

The experimental results show for the first time how a thin metallic film can be used to modulate both the amplitude and the phase of an ultrashort optical pulse. Simulations performed with the *ab-initio* TD-DFT code "SALMON" [113] support the measurements. Both the change in amplitude and phase are observed in the calculations. However, the effects seem to be underestimated for intensities above $1.2 \cdot 10^{12}$ W/cm².

Two possible factors can be involved in the discrepancy: the shape of the pulse and the presence of the oxide layer on the nickel film. The simulations are performed by considering a pulse with a pre-pulse to better match the experiment. The length and the intensity of the tail strongly influence the intensity dependence of both the change in transmission and the phase shift. In fact, the pre-pulse induces linear absorption in nickel, causing an increase in electron population above the Fermi level. The second point is the oxidisation of the Ni surface which can't be straightforwardly reproduced in the simulations.

A critical issue which is already addressed in section 5.4 is the low sensitivity of the LPPS technique at high frequencies. The improvement or the development of new field-resolved detection techniques could open the door to a deeper understanding of the frequency dependence of the nonlinear effects observed in solids.

To conclude, the experimental results presented in the first part of this chapter demonstrate, for the first time, that the electronic motion in a transition metal can be controlled with a strong and ultrashort electric field within the duration of a half cycle of the optical pulse. Furthermore, the intraband electron dynamics is demonstrated to play a crucial role in the electronic response of the material. The time-resolved study of the nonlinearities in the thin nickel film, which is reported in the second part of the chapter, shows the transmutation of Ni from a conducting to a semiconducting material. This effect is observed in the intensity-dependent modulation of the amplitude and phase of the electric field transmitted through the thin Ni sample.

Both the experimental and the theoretical results reported here motivate future study of the subfemtosecond charge manipulation in thin films of metallic materials. Their investigation constitutes the first important step to realise future film-based optoelectronic and plasmonic devices operating above the actual limit of gigahertz frequencies.

Chapter 7

Experiments: Attosecond Spin Dynamics in

Nickel

The manipulation of spins on a sub-femtosecond time-scale is a captivating topic for pushing signal processing to Petahertz clock-rates. As mentioned previously in section 4.3, several experiments have shown the optical control of the material magnetic moment occurring with different channels of demagnetisation [24,25]. Typical processes, which lead to the decrease of the magnetic moment, are spin-orbit (S-O) coupling, thermalization of charges and spins, electron-phonon coupling and dissipation of angular momentum to the lattice. However, the time-scale on which the decrease in magnetic moment occurs is limited by the absence of first-order coupling between photons and spins in standard metallic films. In this kind of samples, the fastest demagnetisation can happen through S-O coupling, which takes place of a time-scale of few tens of femtoseconds.

A significant, coherent demagnetisation can take place in specific alloy compounds [27,118,119] or tailored systems [99,100]. In these peculiar samples, additional demagnetisation channels allow the change in magnetic moment on a time-scale which depends on the duration of the laser exciting pulse. In this chapter, we present the first experimental proof of the optically-induced reduction of the magnetic moment in nickel on a sub-femtosecond time scale. The shown results are published in [33,90].

The ultrafast spin dynamics is observed in a tailored Nickel/Platinum (Ni/Pt) system, where the Optically-Induced Spin Transfer (OISTR) is the main cause of demagnetisation of Ni during the time of interaction with the laser pulse [32]. The observation of the spin dynamics in Ni is achieved with the novel technique of atto-MCD. Based on the well-known transient absorption spectroscopy setup, it makes use of circularly polarised XUV pulses for the time-resolved detection of the MCD signal, which is a measure for the material magnetic moment. At the same time, the technique permits one to track the charge dynamics inside the material. Further details about the experimental setup are presented in 4.3.

7.1 Definition of Atto-MCD and Static Behaviour

The study of nickel's spin dynamics is conducted by probing the M_{2,3}-absorption edges at **68** eV and **66.2** eV, respectively. The conventional MCD signal is given by the difference between the XUV absorption μ_+ for one direction of the magnetic field + and

the XUV absorption μ_{-} for flipped magnetic field –. In the work of this thesis, the MCD signal is not evaluated in the standard way, but as the difference between the transmitted spectra $T^{+}(\omega)$ and $T^{-}(\omega)$ for the two directions of the magnetic field:

$$\Delta_{\text{MCD}}^{\text{Atto}}(\omega) = T^{+}(\omega) - T^{-}(\omega)$$
(7.1)

In Figure 7.1, right, the so-called atto-MCD is compared with the standard MCD signal. The first peak around **64** eV represents the absorption pre-edge, while the main peak at \sim **67** eV corresponds to the two M-absorption edges of nickel. As mentioned in 2.3.2, the absorption peaks at the M-edges energetically overlap and therefore the features lie under the same peak in the measured MCD signal.

According to the definition of absorption given by Eq.(4.3), the two ways of evaluating the magnetic dichroism do not show significant differences. However, due to the presence of the logarithm in the absorption expression, small distinctions in the shape of the signals are noticeable. The atto-MCD contrast shows a more pronounced pre-edge and a small shift to lower energies of the main peak. Nevertheless, both signals are equivalent in giving access to the magnetic moment of nickel.

For the study of nickel's spin dynamics, two different samples are analysed. The first one is the already-mentioned Pt(2 nm)/2x[Ni(4 nm)/Pt(2 nm)]/Ni(2 nm) multilayer system, while the second one is a **8** nm thick nickel film deposited on a **200** nm thick silicon substrate. The specially tailored samples are prepared by the group of M. Münzenberg from the university in Greifswald (Germany). Details about the sample preparation can be found in Appendix A. It is important to remark that platinum's O₂ absorption edge lies in the energy range probed by the XUV pulses (**65.3** eV). However, the edge extends over **10** eV and is considerably weaker compared to nickel's M-edges. As a result, the contribution of Pt is not observed in the MCD signal.



Figure 7.1: Left: atto-MCD signal for the pure nickel film (red curve) and for the Ni/Pt multilayer sample (blue curve). The two curves agree qualitatively. However, the Ni/Pt atto-MCD signal is smaller due to XUV absorption in the Pt layers. Right: comparison of the magnetic dichroism in the Ni film evaluated with the conventional MCD formalism (green curve) and with the atto-MCD formalism (red curve). Both signals give access to the magnetic moment of nickel.

It is shown in section 7.3 how the optically-induced demagnetisation in Ni occurs on different time-scales in the two samples. However, the static XMCD signal (in absence of the NIR pulse) of nickel is qualitatively the same in both samples. As shown on the left of Figure 7.1, the two curves representing the measured atto-MCD contrast agree well

qualitatively. On the other hand, the signal of the Ni/Pt sandwiched system is smaller than the signal of the Ni film, as platinum also absorbs the XUV radiation in the probed energy range.

7.2 Long Time-Scale Electronic Response

The electronic response of nickel to the optical excitation is given by the XUV transmission in the presence of the NIR pulse normalised over the XUV transmission in absence of the NIR pulse (Eq.(5.1)). Therefore, by taking the XUV transmission for one direction of the magnetic field, the electronic properties of Ni can be tracked in synchrony with its magnetic properties.

From the long-time scale measurement depicted in Figure 7.2, it can be observed how the XUV transmission resonant to the M_3 edge drops with the arrival of the NIR pulse, suggesting a decrease in electronic population density due to the NIR excitation of electrons above the Fermi level. The electronic response of nickel is introduced here with the aim of comparing its behaviour in the Ni film and in the multilayer sample. In section 7.3 it is additionally treated for determining time-zero of the arrival of the NIR pulse. However, further and more extensive investigations of Ni's electronic properties are presented in Chapter 6.



Figure 7.2: Bulk response of nickel in the nickel film (red curve) and in the Ni/Pt multilayer sample (blue curve) at $5 \cdot 10^{12}$ W/cm². The two curves are almost identical, suggesting for the same bulk response of nickel in the two samples.

Figure 7.2 shows the normalised XUV transmission change of nickel in the two samples under analysis for an incident intensity of $5 \cdot 10^{12}$ W/cm². The two curves are identical, suggesting that the same electronic behaviour of nickel in the two samples. The change in transmission recovers from the NIR excitation with a time constant of **321.65 ± 46.89**

fs for the Ni film and **348.10 \pm 41.97** fs for the NiPt multilayer. The two values are obtained with an exponential decay fit of the curves and agree within the errors.

7.3 Attosecond Magnetisation Dynamics

The results presented in 7.1 prove the validity of atto-MCD as a measure of magnetic circular dichroism and the consequent derivation of the magnetic moment. Moreover, it is shown how in the static MCD signal, as well as in the time-dependent electronic response, nickel does not show a different behaviour in the two analysed samples. In the following, the magnetisation status of Ni is modified by the presence of the NIR pulse. First, the atto-MCD contrast of the Ni/Pt multilayer system is measured at three different time steps, as depicted in Figure 7.3. At time t_1 before the arrival of the NIR pulse, the MCD signal is at its maximum, as the magnetisation has not being modified yet. Time t_2 corresponds to **20** fs after the interaction of the sample with the NIR pulse. Here, the MCD signal is already reduced by more than **20**%. At $t_3 = 200$ fs, the magnetisation amounts to **~40**% of its initial value. As a result, the demagnetisation of nickel is proven to occur by means of the NIR excitation.



Figure 7.3: The atto-MCD contrast is plotted for three different time steps while nickel interacts with the NIR electric field. The analysed sample is the Ni/Pt multilayer system. At time t_1 before the interaction, the signal is maximised. At time $t_2 = 20$ fs after the arrival of the NIR pulse, the magnetisation is reduced by more than 20%. At time $t_3 = 200$ fs after the pulse, the MCD-signal reaches 40% of its initial value (adapted from [90]).

As a next step, the atto-MCD signal is tracked as a function of time in the small time interval where the electric field interacts with the magnetic system. Figure 7.4 shows the measured MCD signals (red curves) together with the simple XUV transmission (blue curves) of the two samples under consideration: the **8** nm thick Ni film and the Ni(**2** nm)/Pt(**2** nm)/[Pt(**2** nm)/Ni(**4** nm)]x**2** multilayer system. The atto-MCD contrast is

evaluated at **66 ± 0.5** eV. The pulse duration is **< 4** fs, with an incident intensity that amounts to $4 \cdot 10^{12}$ W/cm².

As the electronic response to the NIR excitation is instantaneous, the drop of the XUV transmission at **66** eV is taken as time-zero for the arrival of the NIR pulse. The results for the Ni/Pt sandwiched system are shown in Figure 7.4, left. It is evident how the atto-MCD contrast, i.e. the magnetic response, is reduced by **40%** by the end of the pulse. This astonishingly fast and significant drop in magnetisation is not observed in the Ni film. From Figure 7.4, right, it can be noticed how the atto-MCD contrast stays constant in the Ni film during the propagation of the NIR pulse through the sample. By comparing the two measurements, it is clear that the presence of the platinum layers plays a crucial role in the process of optically-induced demagnetisation. The underlying physical phenomenon is called *optically-induced spin transfer* and is further discussed below.



Figure 7.4: Left: atto-MCD contrast (red curve), which is a measure for the magnetic response, and XUV transmission (blue curve), which corresponds to the electronic response, in the Ni/Pt multilayer system. The magnetisation of Ni drops of **40**% by the end of the NIR pulse. Right: atto-MCD contrast (red curve) and XUV transmission (blue curve) in the nickel film. The magnetisation of Ni stays constant within the error during the presence of the NIR pulse (adapted from [90]).

7.4 Long-Time Scale Spin Dynamics

A spontaneous question which arises from the results presented above, is how the magnetisation dynamics in Ni evolve on a long time-scale. In particular, it is of interest to inspect on which extent the dynamics are different in the two samples under analysis. Figure 7.5, depicts the atto-MCD contrast on a long time-scale at $2 \cdot 10^{12}$ W/cm² for the nickel film and the Ni/Pt multilayer system. The measurements are performed with 1 fs time-steps and without CEP stabilization, which allows an overall higher laser stability. In the first ~8 fs from the arrival of the NIR pulse (**Delay** \approx 0 fs), the magnetic response of the Ni/Pt sandwiched system shows a strong decrease, as also observed in the plot of Figure 7.4, left. On the other hand, the magnetic response of the Ni film exhibits a 5% reduction which is not observed in the short-time scale measurement shown in Figure 7.4,

right. As the observed change in the MCD-signal is small, the stability of the laser system plays a crucial role in its detection. Consequently, it is not visible in all results of the Ni film, but still confirmed by multiple measurements.

Between **8** and **30** fs the Ni/Pt multilayer system exhibits a plateau in the atto-MCD signal before further decreasing. In contrast, the curve of the Ni film starts reducing earlier. From about 40 fs both signals decrease with the same slope, as the process of demagnetisation becomes independent from the kind of sample.



Figure 7.5: atto-MCD signal for the Nickel film (red curve) and the Ni/Pt multilayer system (blue curve) on a long time-scale.

7.5 Comparison with the Elk Simulations

The investigation of the different demagnetisation channels occurring in nickel is conducted by comparing the experimental results with *ab-initio* TDDFT calculations. The simulations are performed by S. Sharma with the Elk code [111]. The code is able to determine the magneto-optical function β , whose imaginary part corresponds to half of the measured MCD signal [120]. The comparison between the two is shown in Figure 7.6 and proves very good qualitative and quantitative agreement.



Figure 7.6: The blue curve is the experimentally obtained MCD signal, while the red curve is 2x the imaginary part of the magneto-optical function β calculated with the Elk code. The two curves agree well (adapted from [90]).

Next, the time-evolution of the simulated $2 \cdot Im(\beta)$ is directly compared with the experimental results to identify the different demagnetisation processes taking place inside nickel. Figure 7.7 a) shows the measured atto-MCD signal for the Ni/Pt tailored system and the Ni film in blue and red, respectively. The dashed dark red curve represents the computed magnetisation of the nickel film. Here, Ni appears to demagnetise on a much slower time-scale compared to the experimental case. A possible explanation for the discrepancy is the thermalization of spins and phonon coupling already taking place in the early stage of nickel's demagnetisation. These effects can enhance the reduction of the magnetic moment, but can't be contemplated in the Elk code calculations.

For the NiPt multilayer sample, the calculation of the magnetic moment is performed by including the spin-orbit (S-O) coupling (orange curve) as well as without S-O (green curve). The two curves overlap for the first **10** fs from the arrival of the NIR pulse, demonstrating that the S-O coupling does not significantly contribute in this early time interval. On the other hand, after the first **10** fs until \sim **25** fs, the S-O coupling plays a role in the demagnetisation process of nickel. In fact, the green curve reaches a plateau, while the orange curve continues decreasing and shows perfect agreement with the experimental results.

The absence of dissimilarities between the two theoretical curves in the small time window of coherent interaction with the laser pulse suggests for a different process inducing the early-stage decrease of magnetic moment. Dewhurst *et al.* [99] have proposed the spin migration from the nickel to the platinum layer as the cause for the sub-femtosecond demagnetisation in Ni. The effect is known as Optically-Induced Spin Transfer (OISTR).

Panel b) of Figure 7.7 depicts the measured atto-MCD contrast for the Ni/Pt tailored system hundreds of femtoseconds after the interaction between the sample and the laser pulse. On this time-scale, stochastic processes dominate the reduction of nickel's magnetic moment.



Figure 7.7:The blue and the red curve depict the experimental atto-MCD signal for the Ni/Pt tailored system and the Ni film, respectively. The dashed dark red curve is the magnetic moment of the pure Ni film simulated with TD-DFT. The green and the orange curve represent the simulated magnetic moment of the Ni/Pt multilayer system with and without inclusion of the spin-orbit coupling inside nickel (adapted from [90]). b) Experimental atto-MCD signal for the Ni/Pt tailored system on the time-scale where stochastic processes set in.

7.6 Optically-Induced Spin Transfer (OISTR)

The optically-induced spin transfer is an optical effect which can take place in multilayer systems consisting, for example, of ferromagnetic/paramagnetic (FM/PM) layers. In the work of this thesis a FM/PM (Ni/Pt) tailored system is measured, but the effect can also be observed in a ferromagnetic/ferromagnetic or a ferromagnetic/antiferromagnetic stack of multilayers.

In OISTR, the excitation of the NIR pulse induces a transfer of spin-oriented electrons from the ferromagnet to the paramagnet. The created spin current from each FM to the adjacent PM layer causes the reduction of magnetic moment in the ferromagnetic layers, i.e. demagnetisation [99,100]. This charge migration process can be better understood in terms of the density of states (DOS). Figure 7.8 shows the calculated DOS for nickel (grey) and for platinum (yellow). Assuming an external magnetic field pointing in the down direction, the majority carriers have spin oriented up. Because of its ferromagnetic nature, nickel possesses an asymmetric density of states for spin-up \uparrow (majority carriers) and spin down \downarrow (minority carriers) electrons. On the other hand, platinum possesses a strong spin-orbit coupling which counteracts the alignment of spins. In other words, Pt is not affected by the presence of the external magnetic field, which implies that the states above the Fermi level are not spin-selective as in nickel. When the NIR pulse excites the Ni/Pt system, the majority carriers in Ni will migrate to the Pt layer because of a higher number of free states. The reduction of majority carriers induces the reduction of nickel's magnetic moment. On the other hand, the minority carriers will transfer from platinum to nickel. However, the electrons in the Pt layers do not have a particular spin orientation and hence do not compensate for the decrease in magnetisation of Ni. It is worthwhile to highlight that the total amount of charges in the sample stays constant. For this reason, the electronic response of the Ni film and the Ni/Pt tailored system is identical (see Figure 7.2).



Figure 7.8: Density of states of nickel (grey) and platinum (yellow) for an applied magnetic field in downward direction for spin-up (majority carriers) and spin-down electrons (minority carriers). When the NIR pulse excites the Ni/Pt multilayer system, the majority carriers migrate from the nickel to the platinum layer because of the higher number of empty states. In the same way, minority carriers transfer from the Pt to the Ni layer. These electrons are not spin-oriented and do not contribute significantly on the total magnetisation of nickel.

A further way to describe the OISTR effect is the semi-classical picture illustrated in Figure 7.9. The electrons in the nickel layer have the spins aligned parallel to the external magnetic field. The platinum layer is dominated by the spin-orbit coupling and hence the electrons possess only orbital momentum. When the NIR pulse excites the multilayer system, an electron wavepacket is created in the Ni layer. The wavepacket can cross the interface between the Ni and the Pt layer and occupy an empty state in Pt. In the same way, an electron wavepacket migrates from the Pt to the Ni layer but without positively affecting the magnetic moment of nickel, due to the arbitrary orientation of the electron spin in platinum.

In conclusion, the OISTR effect is an interface effect where the first three monolayers of nickel and platinum are involved. As experimentally proven, it induces a local change in the status of magnetisation of Ni which lasts for the duration of the pulse.



Figure 7.9: Semi-classical picture of the OISTR effect. The NIR pulse creates an electron wavepacket in the spin-oriented nickel layer. The wavepacket migrates to the Pt layer and occupies a free state. At the same time, an electron wavepacket created in the Pt layer crosses the interface with nickel. As the electrons in Pt possess mostly orbital momentum because of the strong spin-orbit coupling, their spin orientation is arbitrary. As a result, they do not compensate for the loss in magnetic moment of nickel.

7.7 Sum-Rules

In sub-section 2.3.2 it is explained how the magnetic moment of a material can be obtained from the measured MCD signal by applying the sum-rules. Using (2.93) and (2.94), the orbital L_z and the spin S_z component can be calculated. However, the applicability to the M-edges is limited by the fact that the spin-orbit coupling is smaller than the DOS bandwidth. The main obstacle comes from the fact that the absorption peaks of the M₂ and M₃ edges are not energetically separated as in the case of the L-edges, causing an underestimation of the value of S_z . However, even if the quantitative behaviour of S_z can't be exactly extrapolated, the qualitative time-evolution of L_z and S_z can be obtained from the above-mentioned formulas. The study of the magnetic moment from the measurements presented above can be found in [32].

7.8 Main Findings of Atto-MCD

In the present chapter it is shown for the first time how the electrons' spin and charge inside a ferromagnet can be manipulated simultaneously on the sub-femtosecond time-scale. This is achieved with a novel technique called "atto-MCD". The technique combines the capability of transient absorption spectroscopy to detect the electronic response of a material, with the ability of circularly polarised XUV pulses to give access to the magnetic response of a ferromagnet. The electronic response of nickel is used here to define time-zero of the arrival of the NIR pulse, but is further studied in the next chapter. A system of Ni/Pt multilayers was designed to be able to measure the demagnetisation in nickel with unprecedented speed. In such a tailored system consisting of alternating ferromagnetic (Ni) and paramagnetic (Pt) layers, optically induced spin transfer (OISTR) takes place. This effect consists in the migration of spin-oriented electrons from the nickel to the platinum layer during the interaction with an optical pulse. As a result, nickel demagnetises on a time-scale given by the length of the exciting pulse.

The first experimental evidence of the OISTR effect is given in the results reported here. Together with the Ni/Pt multilayer system, a pure nickel film is measured as a backup. The results show that the sub-femtosecond demagnetisation of Ni is observed only in the Ni/Pt tailored system, confirming the spin current from Ni to Pt as the main cause of Ni's demagnetisation in the time of coherent interaction with the laser pulse. The experimental finding is supported by *ab-initio* TD-DFT calculations which predicts the OISTR effect as the main cause of early-stage demagnetisation.

As the spin-orbit splitting is smaller than the bandwidth of the density of states, the Mabsorption edges energetically overlap. Consequently, the applicability of the sum rules for the determination of the magnetic moment is compromised, giving an underestimation of the value of the spin component S_z . On the other hand, the qualitative behaviour of both L_z and S_z can be retrieved from the measurements presented here [32].

The findings reported in this chapter represent the very first step for the future realisation of spintronic devices operating on petahertz clock-rates. Consequently, the presented results push for further experimental and theoretical investigation of sub-femtosecond demagnetisation dynamics.

An alternative approach to the study of the M-edges, and the consequent challenges of the applicability of the sum rules, is given by the analysis of the L-edges of ferromagnetic materials. For the generation of XUV radiation at the required photon energies, free-electron lasers (FEL) with attosecond time resolution can be operated.

A further interesting aspect which can be investigated in future works is the sub-cycle magnetisation of the paramagnet which happens in synchrony with the demagnetisation of the ferromagnet. As the absorption edges of both materials need to be probed by the XUV pulses, possible samples to analyse could be a multilayer system constituting of cobalt and platinum (Co/Pt), a permalloy [119] or a Heusler compound [118].

Chapter 8

Conclusions

The interest in the optical control of the electronic and magnetic properties of matter arises from the desire to realise future optoelectronic and spintronic devices, able to push the speed of information processing to petahertz clock-rates. The work of this thesis aimed to exhaustively investigate the fundamentals of charge and spin dynamics induced by a strong optical pulse inside solids of different nature.

In the study of the charge dynamics, the main question which was addressed is if there is a universal response of matter to optical excitation and if not, what makes solids behave differently. To solve this interrogative, different points were examined: a) how fast can the electrons be put in motion inside an indirect band-gap semiconductor and inside a metal b) what are the inter- and the intraband contributions to the nonlinear response of matter while interacting with an ultra-short laser pulse and c) what is the energy dissipation inside the material.

An extensive and versatile analysis of the optically-induced charge dynamics was performed by the combination of transient absorption and polarisation sampling spectroscopy with attosecond time resolution. It is shown for the first time how in both materials, nickel and silicon, the electronic population redistribution, given by the XUV transmission change, can be manipulated within a half cycle of the exciting NIR pulse. This was proven by the observation of distinct 2ω -oscillations in the XUV signal. However, the phase relation between the modulations and the NIR pulse was discovered to be different for nickel and for silicon. In the latter, they are measured to be in synchrony with the extrema of the electric field. For instance, the sub-half cycle response of the electronic system is mainly given by the polarisation induced by the strong oscillating field. On the other hand, nickel's electronic response oscillates with the vector potential of the NIR pulse, suggesting that the electron currents within the conduction band are the mainly responsible for the oscillations. This result can be easily explained by the presence of a high number of free electrons inside the metal, whose intraband motion plays a crucial role in the optically-induced change of carrier population distribution.

In addition to the interband dynamics, the intraband electronic motion in Ni and Si has been studied. The applied technique of polarisation sampling gave access to the different nonlinearities occurring in the sample under analysis. The investigation of the intensitydependent nonlinear response in nickel demonstrated for the first time how a thin metallic film can be used to modify both the amplitude and the phase of an optical pulse on the time scale of an optical cycle. The amplitude of the transmitted field shows a strong dependence on the incident intensity. More precisely, saturable absorption induced by Pauli blocking of the excited electrons causes an increase in Ni's transmissivity. This can be interpreted as the optically-induced de-metallization of nickel. The effect is reversed at intensities approaching the damage threshold of the material. At this point, NIR transitions of the excited charges to higher states in the conduction band take place, causing an increase in the NIR absorption.

The phase relation between the induced current and the incident field is different for metals and insulators. As a consequence, nickel's transition from a conducting to a semiconducting behaviour is observed also in the increase of the phase velocity of the incident field after propagating through the material. The measured phase shift between the incident and the transmitted field is significantly large for a **8** nm thick metallic film. Further, saturable absorption in nickel results in a negative nonlinear energy $W_{\rm NL}(t)$, deposited from the exciting pulse into the sample. $W_{\rm NL}(t)$ stays in nickel even after the pulse, as the process is irreversible.

In silicon, the main third-order nonlinear effects taking place are two-photon absorption and the Kerr effect. Both effects induce a change of the refractive index n of Si, but with opposite sign. More specifically, the Kerr effect produces an increase of the refractive index, while the free carriers generated through one- and two-photon absorption are responsible for a reduction of n. The absence of a phase shift between the transmitted pulses at different intensities suggests a balanced action of the two nonlinear effects. The amplitude of the transmitted field decreases with intensity, leading to a positive nonlinear energy deposited into the sample. As for nickel, the nonlinear energy transfer is an irreversible process. The study of the intensity dependence in the range of $1 \cdot 10^{12} - 4 \cdot$ 10^{12} W/cm² revealed a weaker scaling of the nonlinear polarisation compared to what is expected for third-order nonlinear effects. This can be explained by the fact that higher order nonlinearities are becoming of similar magnitude as the lowest order (third-order) nonlinearities. The observed behaviour is in agreement with the theoretical prediction of Schultze *et al.* [16], which indicates electron tunnelling through the direct band gap as the dominant nonlinear process in the considered range of intensities. Therefore, it has been shown how silicon can be turned from a linear into a nonlinear, direct band-gap absorber by making use of ultra-short and intense laser pulses.

Finally, the present work first proves the manipulation of spins inside a ferromagnetic material with sub-femtosecond time resolution. Tailored Nickel/Platinum layer stacks were specifically realised to conduct the novel attosecond magnetic circular dichroism (atto-MCD) experiment. Based on the setup of transient absorption spectroscopy, atto-MCD makes use of circularly polarised XUV pulses to track the change of the magnetic moment in nickel induced by the NIR pulse. At the same time, it is possible to measure the electronic response of Ni, which sets the time-zero for the arrival of the NIR pulse. It has been proven that the magnetic status of nickel can be changed on sub-femtosecond time scale while interacting with the NIR field. The ultrafast demagnetisation of Ni is observed in the Ni/Pt multilayer sample but not in a simple Ni membrane, proving the optically-induced spin transfer as the responsible channel of coherent demagnetisation. The effect consists in the transfer of spin-oriented electrons from the Ni to the Pt layer, causing the macroscopic demagnetisation of nickel on a sub-femtosecond time scale.

To conclude, the results reported in this work demonstrated the sub-cycle control of both the electronic and the magnetic state of matter with strong light fields. This could be achieved by combining multiple attosecond spectroscopic measurement techniques.

Appendix A

All the experiments reported in this work of this thesis are conducted at the Max-Planck Institute of Quantum Optics (MPQ) in the Laboratory of Attosecond Physics (LAP). The experiments were conducted by making use of the FP3 laser system in the AS2 beamline. A short description of the systems is reported here, further details can be found in [132,133].

A.1 FP3 Laser System and AS2 Beamline

The FP3 Lasersystem

The setup of the FP3 laser system is shown in Figure A.0.1. The front-end source of the FP3 laser system is a titanium-doped sapphire (Ti:Sa) oscillator, passively mode-locked with Kerr lensing. The oscillator is pumped with a frequency-doubled neodymium yttrium vanadate (Nd:YVO4) CW laser (Coherent Verdi V6), which is modulated at the output with an acousto-optical modulator (AOM). The pulses generated by the oscillator have a duration of **~8** fs, a pulse energy of **~ 2.5** nJ with a repetition rate of **78** MHz.

The carrier-envelope-offset (CEO) phase of the output pulses is stabilised by making use of a fast loop, which is based on a f-to-0 interferometer. The beam is focussed into a periodically-poled lithium-niobate crystal (PPLN), where difference frequency generation (DFG) takes place [134]. The fundamental (f) and the DFG signal (0) create a beat signal by interfering with each other. This is detected by a fast photodiode. The CEO phase, which is retrieved from the interference signal, is stabilised by modulating the power through the AOM. The f-to-0 is a particular configuration of the f-to-2f system where the zero-frequency signal (0) is generated instead of the second harmonic (2f).

The phase-stabilised output of the oscillator is stretched in a 13.5 cm long SF57 glass to ~ 1 ps. After, the pulse seeds a chirped pulse amplification (CPA) system [135]. Here, the pulse gets amplified in a Ti:Sapphire crystal used as a medium, which is pumped by a frequency doubled Nd:YLF laser (Photonics Industries DM30). After four passes through the crystal, the repetition rate is reduced to 4 kHz by sending the beam through a Pockels cell (PC). After the PC, a Dazzler (FASTLITE) corrects for higher-order dispersion effects. Next, the pulses undergoes five more passes through the crystal until they reach an energy of 1 mJ. The beam is then collimated and directed to a grating compressor, where the pulses get compressed to ~ 20 fs, close to the Fourier limit.

Gain narrowing inside the CPA induces a drastic reduction of the bandwidth of the pulse. Therefore, the beam is focussed into a **1.5** m long hallow-core fibre (HCF) filled with neon at a pressure of **1.6** mbar. Inside the fibre, self-phase modulation takes place and new frequencies are generated. The coupling to the fibre is kept by stabilizing the position

of the beam in front of the fibre. This is achieved with a beam stabilization consisting of two photodiodes. At the output of the fibre, the pulses extend from **350** nm to **1100** nm. After the HCF, the dispersion is further adjusted by two wedges. Slow drifts of the CEO are compensated by a f-to-2f system (slow loop). A reflection of the wedges is sent into a BBO crystal where second harmonic generation (SHG) takes place. In analogy to the f-to-0, the fundamental and the second harmonic spectrally overlap and create an interferometric signal which carries information about the phase. The phase is therefore read out and corrected through a glass wedge positioned into the oscillator. At the end, the pulses are compressed by a set of chirped mirrors with a bandwidth of **450** – **900** nm. The achieved pulse duration is ~**4** fs with a central wavelength of **780** nm.



Figure A.0.1: Setup of the FP3 laser system. It provides pulses centred at **780** nm with **0.5** μ J energy, a duration below **4** fs and a repetition rate of **4** kHz. Adapted from [82].

The AS2 Beamline

Figure A.0.2 depicts the setup of the AS2 beamline where the experiments are performed. The NIR beam coming from the FP3 laser system reaches the HHG chamber, where the XUV radiation is generated through high harmonic generation (HHG). For this purpose, the NIR beam is focussed into a **300** μ m large hole into a ceramics target. The target is filled with noble gas, usually argon for generating XUV with energies below **80** eV or neon for XUV pulses centred at **100** eV or higher energies.Both the NIR and the

XUV beam propagate collinearly until they get spatially separeted by a perforeted mirror. With a hole diameter of **1.5** mm. Compared to the NIR radiation, the XUV radiation has smaller divergence due to its smaller wavelength. Therefore, the XUV radiation passes through the hole of the mirror, while most of the near-infrared gets reflected. In the Transient Absorption (TA) and the Attosecond Magnetic Circular Dichroism (Atto-MCD) experiment, the remaining NIR light in the XUV arm is filtered out with a metallic filter. In the Polarisation Sampling (PS) experiment, no filter is used. In the XUV arm, a stage with two mirrors allows to send the beam to the diagnostics. Both the beam profile (mirror + CCD camera) and the spectrum (grating + CCD camera) of the XUV can be monitored.

After, the XUV pulses get reflected by a mirror (XUV corner mirror in Figure A.0.2) which is different for each kind of experiment reported in the work of this thesis. For the TA and the Atto-MCD measurements of nickel, a multilayer mirror with **45°** angle of incidence is used to reflect the XUV pulses centred at **66** eV. For probing the L-edges of silicon at ~**100** eV, the multilayer mirror is replaced by a set of three rodium mirrors with **16°** angle of incidence. In the PS experiment of silicon and nickel, the XUV radiation needs to be centred at 20 eV. Therefore, an unprotected gold mirror, placed at **45°** with respect to the infalling beam, is used.

In the NIR arm, an intermadiate focus is created. Here, the sample is placed for performing the PS experiment. The focussing mirror is placed on a piezo stage which allows to introduce a delay between the NIR and the XUV pulses. After, the two beams are recombined with a second perforated mirror and focussed with a toroidal mirror into the experimental chamber. When the transient absorption and the Atto-MCD experiments are performed, the sample to analyse is positioned in focus and the transmitted XUV radiation is collected by an XUV spectrometer consisting of a grating and a CCD camera. A Time-Of-Flight (TOF) spectrometer is placed above the focus to conduct attosecond streaking spectroscopy. For this purpose, a gas nozzle filled with neon is placed below the TOF. In the polarisation sampling experiment, the electric field is measured with Linear Photo-Conductive Sampling (LPPS) applied in gas by using a sample with two electrodes placed in focus. The gas nozzle is then positioned in between the two electrodes. Both the sample and the nozzle are placed on the same stage which permits to move them in x-, y-, and z-direction.

For the diagnostics of the NIR beam, a CCD camera and a spectrometer are placed outside the experimental chamber. A stage with a mirror can be driven in the beam path to send the near-infrared to the diagnostics.



Figure A.0.2: Setup of the AS2 beamline. It consists of three chambers: the HHG chamber where the XUV radiation is generated, the delay chamber where a delay is introduced between the NIR and the XUV pulses, and the experimental chamber, where the TOF, the XUV spectrometer and the sample for LPPS are placed. Adapted from [33].

A.2 Sample Preparation for Atto-MCD Measurements

The 8 nm thick nickel film and the Pt(2 nm)/2x[Ni(4 nm)/Pt(2 nm)]/Ni(2 nm) multilayer system are grown on polycrystalline silicon with fcc structure. The Si substrate is 200 nm thick and commercially available (Norcada). The Ni membrane and the Ni/Pt multilayers are deposited on the substrate with electron beam evaporation at room temperature and ultra-high vacuum conditions ($< 1 \cdot 10^{-9}$ mbar). The used materials have a purity of 99.95%. The number and the thickness of the layers in the multilayer system are chosen to maximise the atto-MCD contrast induced by the OISTR effect, still have sufficient XUV transmission and ensure a homogeneous in-plane magnetisation.

An inert 2 nm thick Pt capping is deposited on the top of the Ni/Pt system, while between the Ni/Pt system and the substrate a non-magnetic, 2 nm thick Ni seed layer is grown. The purpose is to provide a uniform deposition of the layer stack and identical surroundings to all the Pt layers.

The in-plane magnetic properties of the samples are characterised with a longitudinal magneto-optical Kerr effect (MOKE) setup based on a **3** mW HeNe continuous wave laser, a photoelastic modulator and Glan-laser prisms in longitudinal geometry. Both samples show similar ferromagnetic properties. The measured coercive fields are of a few mT and the remanence is about 60 - 70% of the saturation magnetisation. The absence of ferromagnetism in the Ni seed layer is also confirmed by the MOKE measurements. The preparation of the samples as well as the shipping and the experiment are performed in vacuum. Nevertheless, it is proven with MOKE that after **48** hours of exposure to air, the magnetic properties of the samples are not changed by the presence of an oxide layer.

A.3 Sample Preparation for Polarisation Sampling in Nickel

The sample used for performing polarisation sampling in nickel consists in a 8 nm thick nickel film coated on a 10 μ m thick SiO₂ substrate (size: 1 × 1 cm). The purity of Ni amounts to 99.99% and the layer thickness has a relative standard deviation of 0.35%. The samples are prepared with an ion-beam deposition machine (NEXUS IBD-0, Veeco Instruments, USA) by applying a beam voltage of 600 eV for krypton ions (neutralized by a plasma bridge neutralizer). The background pressure of $10^{-7} - 10^{-8}$ mbar is maintained by a cryogenic and a turbo pump to minimize contaminations of the layer material. The layer thickness is controlled via the sputtering time, where the sputter rate for nickel is 0.0555 nm/s and it was previously calibrated by using a surface pro-filer (Dektak 150, Veeco Instruments, USA). The sputter time calculations are based on a numerical model [136], to compensate both diffusion losses and systematic deposition variations due to, e.g., shutter response times and rate dependence on the sample height. The substrate holder is rotated during deposition with a spinning frequency of 40 rpm. To insure a high lateral homogeneity of the film growth, a shaper is used for shaping the ion flux laterally.

A.4 Computational Details of the Elk Code

The Elk code is used to simulate both the magneto-optical function of nickel for the Atto-MCD experiment and the dielectric function of Ni and Si to compare with the transient absorption experiments.

The computations are based on the Runge-Gross theorem, which affirms that the timedependent external potential is a unique functional of the time dependent density, given the initial state [137]. The theorem establishes that a system of non-interacting particles can be chosen in a way that its density is equal to that of the interacting system for all times. The wave function is represented as a Slater determinant of single-particle Kohn-Sham (KS) orbitals. A fully non-collinear spin-dependent version of this theorem entails that these KS orbitals are two-component Pauli spinors determined by the equations:

$$i\hbar \frac{\partial \psi_j(\vec{r},t)}{\partial t} = \left[\frac{1}{2} \left(-i\nabla + \frac{1}{c} \vec{A}_{ext}(t) \right)^2 + v_s(\vec{r},t) + \frac{1}{2c} \sigma \vec{B}_s(\vec{r},t) + \frac{1}{2c} \sigma \vec{B}_s(\vec{r},t) + \frac{1}{2c} \sigma \vec{D}_s(\vec{r},t) + \frac{1}{2c} \sigma \vec{D}_s(\vec{r}$$

Where \hbar is the Planck constant and c is the speed of light. The first term on the right is the kinetic term and is responsible for the flow of current across the interface [138]. $\vec{A}_{ext}(t)$ represents the vector potential of the applied laser pulse, and σ are the Pauli matrices.

The KS effective potential $v_s(\vec{r}, t)$ is decomposed into the external potential $v_{ext}(\vec{r}, t)$, the classical electrostatic Hartree potential $v_H(\vec{r}, t)$ and the exchange-correlation potential $v_{XC}(\vec{r}, t)$:

$$v_{s}(\vec{r},t) = v_{\text{ext}}(\vec{r},t) + v_{H}(\vec{r},t) + v_{XC}(\vec{r},t)$$
(A.2)

Similarly, the KS magnetic field can be written as:

$$B_{s}(\vec{r},t) = B_{\text{ext}}(\vec{r},t) + B_{H}(\vec{r},t) + B_{XC}(\vec{r},t)$$
(A.3)

where $B_{\text{ext}}(\vec{r}, t)$ is the magnetic field of the applied laser pulse, plus a possible additional magnetic field and $B_{XC}(\vec{r}, t)$ is the exchange correlation magnetic field. The term $B_H(\vec{r}, t)$ is the spin-orbit coupling term.

The calculations of the magneto-optical function for the Ni/Pt layer are performed by a process consisting in three steps: (i) The ground-state of Ni/Pt multilayers is determined using DFT, (ii) a fully spin-polarised GW calculation is performed to determine the correct position and width of Ni's **3***p* states and (iii) the response function is calculated on top of the GW-corrected Kohn-Sham ground-state. In step (iii), the response function is calculated within the linear response TD-DFT, in which the excitonic effects [139] and the local field effects can be easily included. This allows to determine the magneto-optical function without any experimental parameter. This is given by the two components ε_{xy} and ε_{xx} of the dielectric response function [140].

For a periodic sequence of **3** monolayers of nickel on **7** monolayers of platinum, a fully non-collinear version of TD-DFT, as implemented within the Elk code [111], is used for all calculations presented in the work of this thesis. The computational cost prohibits the inclusion of more mono-layers in the calculation. The results presented for the Ni/Pt multilayer system require **240** Xeon processors constantly running for **47** days. A regular mesh in k-space of **8** × **8** × **1** is used and a time step of $\Delta t = 2$ as is employed for the time-propagation algorithm. To mimic the experimental resolution, a Gaussian energy broadening with spectral width of **0.027** eV is applied. The laser pulse used in the present work is linearly polarised (out of plane polarisation), it has a central frequency of **1.55** eV, a full-width-at-half-maximum duration **8** fs and a fluence of **5.4** mJ/cm².

For the determination of the dielectric function describing the transient XUV absorption in nickel and silicon, the simulations were performed with the same conditions. In this case, only the ε_{xx} component needs to be considered.

A.5 Computational Details of the Salmon Code

The results of the polarisation sampling experiment are supported by the theory developed with the SALMON code. The calculations are performed in a couple scheme, analogous to [1]. The propagation of the laser pulse in vacuum is expressed by the one-dimensional wave equation. The interaction of the pulse with the silicon and the nickel sample are described by the time-dependent density function theory (TD-DFT). The theory is able to describe the optically-induced electron dynamics [116].

The propagation of the pulse along the z-direction is described by the wave-equation:

$$\frac{1}{c^2} \frac{\partial^2 A(z,t)}{\partial t^2} - \frac{\partial^2 A(z,t)}{\partial z^2} = \frac{4\pi}{c} J(z,t)$$
(A.4)

Where A(z, t) is the vector potential of the optical pulse and J(z, t) is the induced current obtained from the TD-DFT calculation. The electron dynamics in silicon and nickel, after interacting with a strong field, is described by the Kohn-Sham equation where the
solutions $u_{nk}(z, t)$ are Bloch orbitals of the band with index n and the crystalline wave number k [112]:

$$i\hbar \frac{\partial u_{nk}(z,t)}{\partial t} = \left[\frac{1}{2m} \left(\vec{p} + \hbar \vec{k} + \frac{e}{c} \vec{A}(t) \right)^2 + V_{KS}(\vec{r},t) V_{ion}(\vec{r},t) + V_H(\vec{r},t) + V_{KS}(\vec{r},t) V_{ion}(\vec{r},t) + V_H(\vec{r},t) + V_{KS}(\vec{r},t) V_{ion}(\vec{r},t) + V_H(\vec{r},t) \right]$$

Where *e* and *m* are the electron charge and mass, respectively. The Kohn-Sham potential $V_{KS}(\vec{r}, t)$ can be written as the sum:

$$V_{KS}(\vec{r},t) = V_{ion}(\vec{r},t) + V_H(\vec{r},t) + V_{XC}(\vec{r},t)$$
(A.6)

Where $V_{ion}(\vec{r}, t)$, $V_H(\vec{r}, t)$ and $V_{XC}(\vec{r}, t)$ are the ionic potential, the Hartree potential and the exchange-correlation potential, respectively. The choice of the exchange-correlation interaction plays a crucial role in the correct reproduction of the material band-gap. For simulating the electron dynamics in silicon, the MetaGGA is used [141]. For describing nickel's response, the FHI potential is used.

The induced electron current J(z, t) is calculated from the Bloch orbitals according to [142]. The polarisation of a band-gap material can hence be obtained from:

$$\vec{P}(t) = \int_{t} dt' \vec{J}(t')$$
(A.7)

The input electric field used in simulating silicon's electronic response is the waveform retrieved from the experimental streaking trace. The calculations are performed on the Oakforest PACS supercomputer using **50** nodes. The real space grid consists of **16** × **16** × **16** points and the k-space grid has $8 \times 8 \times 8$ points. The time steps are **1.92** as.

For the calculation of nickel's electron dynamics, a **15** fs long pulse centred at **1.55** eV is used. The pulse presents a pre-pulse which is 20 fs long. The intensity ratio between the pre- and the main pulse is **0.30**. The excited carrier density in Ni is evaluated according to [112]:

$$n_{\text{ex}} = \frac{1}{N_k} \sum_{k,n} \left| \int dr u^*_{n,k+\frac{A(t)}{c}}(\vec{r}) u_{n,k}(\vec{r},t) \right|^2$$
(A.8)

Where N_k is the volume of the Brillouin zone, A(t) is the vector potential of the pulse and $u_{n,k}$ are the Bloch orbitals with band index n and wavenumber k.

The calculations of nickel are performed on the Fugaku supercomputer. The cell calculation consists in a primitive unite cell of FCC lattice with $24 \times 24 \times 24$ points in the real space grid and $16 \times 16 \times 16$ points in the k-space grid. The time steps are 0.12 as, which results in **300000** steps for the considered time interval of **36** fs. The typical calculation time with the mentioned parameters is **2.35** hours (**1024** nodes).

Appendix B

B.1 Data Preservation

All the figures, the data and the evaluation codes which are analysed and presented in this thesis are stored in the data archive computer of the Max-Planck Institute of Quantum Optics. They are organised in chapters; every chapter is organised in part differently. In all chapters, each figure has an own folder. The figures which are not obtained from experimental data are given only in PNG format.

Chapter 2: The figures do not present experimental data. Every figure is saved in PNG format.

Chapter 3: The folder contains the Origin document with all the data shown in this chapter. Each figure has a folder with the following information: the figure itself in PNG format, the evaluated data "Data_...txt", a TXT file "Info_...txt" with the necessary information for evaluating the data and obtain the plot.

Chapter 4: Except Fig.4.9, no other figure contains experimental data. The folder "Fig.4.9" contains the data and the code for plotting it. All the other figures are saved in PNG format in the corresponding folder.

Chapter 5: The folder contains the two Matlab codes and the functions used for evaluating the raw data, an Origin document where some of the data were analysed and plotted. Each figure has its own folder with the figure itself in PNG format, the raw data (in the folder "Raw Data"), the evaluated data "Data_...txt", a TXT file "Info_...txt" with the necessary information for evaluating the raw data and obtain the plot. Some figures also contain a screenshot with the settings to insert in the Matlab evaluation code.

Chapter 6: The folder contains the Matlab code and the functions used for evaluating the raw data, two Origin documents where some of the data were analysed and plotted. Each figure has its own folder with the figure itself in PNG format, the raw data (in the folder "Raw Data"), the evaluated data "Data_...txt", a TXT file "Info_...txt" with the necessary information for evaluating the raw data and obtain the plot. Some figures also contain a screenshot with the settings to insert in the Matlab evaluation code.

Chapter 7: The folder contains the Matlab code and the functions used for evaluating the raw data until Figure No.7.7, one Origin document where some of the data were analysed and plotted. Each figure has its own folder with the figure itself in PNG format, the raw data (in the folder "Raw Data"), the evaluated data "Data_...txt", a TXT file "Info_...txt" with the necessary information for evaluating the raw data and obtain the plot., the Matlab code to obtain the specific figure. Some figures also contain a screenshot with the settings to insert in the Matlab evaluation code.

References

- [1] A. Sommer et al., Attosecond nonlinear polarization and light–matter energy transfer in solids, 86, Nature, Vol. 534, 2 June (2016).
- [2] R. C. JOHNSON, IBM Leapfrogs Intel to 7nm. In: EETimes 7(9) (2015).
- [3] Robert W. Keyes, High performance cooling and Large scale integration: Methods and Materials in Microelectronic Technology (Paper collection), edited by Joachim Bargon, Springer (1984).
- [4] Otto G. Folberth, Limitations of digital electronics: Methods and Materials in Microelectronic Technology (Paper collection), edited by Joachim Bargon, Springer (1984).
- [5] G. E. Moore, Cramming more components onto integrated circuits, Electronics 38, 114–117 (1965).
- [6] M. Mitchell Waldrop, The chips are down for Moore's law, Nature 530, 144–147 (2016).
- [7] IBM, IBM News room 2017-06-05 IBM Research Alliance Builds New Transistor for 5nm Technology, [21.06.21], https://www-03.ibm.com/press/us/en/pressrelease/52531.wss.
- [8] Samsung, Samsung Electronics' Leadership in Advanced Foundry Technology Showcased with Latest Silicon Innovations and Ecosystem Platform, [21.06.21], https://news.samsung.com/global/samsung-electronics-leadership-in-advancedfoundry-technology-showcased-with-latest-silicon-innovations-and-ecosystemplatform.
- [9] S. B. Desai et al., MoS2 transistors with 1-nanometer gate lengths, Science 354, 6308, 99–102 (2016).
- [10] D. Mamaluy and X. Gao, The fundamental downscaling limit of field effect transistors, Appl. Phys. Lett. 106, 193503 (2015).
- [11] S. S. Verma, Electronics at the speed of light, https://electronicsmaker.com/electronics-at-the-speed-of-light.
- [12] F. Krausz & M. I. Stockman, Attosecond metrology: from electron capture to future signal processing, Nature Photonics volume 8, pages205–213 (2014).
- [13] M. Hentschel, R. Kienberger, Ch. Spielmann, G. A. Reider, N. Milosevic, T. Brabec, P. Corkum, U. Heinzmann, M. Drescher & F. Krausz, Attosecond metrology, Nature volume 414, 509–513 (2001).

- [14] E. Gent, Could Photonic Chips Outpace the Fastest Supercomputers?,
 [23.06.21], https://singularityhub.com/2020/02/03/could-photonic-chips-outpacethe-fastest-supercomputers/.
- [15] D. H. Auston, Picosecond optoelectronic switching and gating in silicon, Applied Physics Letters, Vol. 26, No.3 (1975).
- [16] M. Schultze et al., Attosecond band-gap dynamics in silicon: Science, Vol. 346, Issue 6215, 12 December (2014).
- [17] F. Schlaepfer et al., Attosecond optical-field-enhanced carrier injection into the GaAs conduction band: Nature Phys., Vol. 14, 560-564, June (2018).
- [18] R. Atanasov, A. Haché, J. L. P. Hughes, H. M. van Driel, and J. E. Sipe, Coherent Control of Photocurrent Generation in Bulk Semiconductors, Phys. Rev. Lett. 76, 1703 (1995).
- [19] M. Schultze et al., Controlling dielectrics with the electric field of light: Nature, Vol. 493, 75, 3 January (2013).
- [20] F. Bonaccorso, Z. Sun, T. Hasan & A. C. Ferrari, Graphene photonics and optoelectronics, Nature Photonics volume 4, pages611–622 (2010).
- [21] C. Chang et al., Highly Plasmonic Titanium Nitride by Room-Temperature Sputtering, Scientific Reports 9, 15287 (2019).
- [22] R. Malureanu and A. Lavrinenko, Ultra-thin films for plasmonics: a technology overview, [24.06.21], https://www.degruyter.com/document/doi/10.1515/ntrev-2015-0021/html.
- [23] S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. A. G. Requicha, H. A. Atwater, Plasmonics—A Route to Nanoscale Optical Devices, Adv. Mater. 13, No. 19 (2001).
- [24] E. Beaurepaire, J.-C. Merle, A. Daunois, and J.-Y. Bigot, Ultrafast Spin Dynamics in Ferromagnetic Nickel, Phys. Rev. Lett. 76, 4250 (1996).
- [25] C. Stamm et al., Femtosecond modification of electron localization and transfer of angular momentum in nickel: Nature Materials 6, 740–743 (2007).
- [26] J. Wu et al., Ultrafast optically induced spin dynamics in single-crystal Fe ultrathin films and patterned dot arrays, Central Laser Facility Annual Report (2006/2007).
- [27] Chan La-O-Vorakiat, Mark Siemens, Margaret M. Murnane, Henry C. Kapteyn, Stefan Mathias, Martin Aeschlimann, Patrik Grychtol, Roman Adam, Claus M. Schneider, Justin M. Shaw, Hans Nembach, and T. J. Silva, Ultrafast Demagnetization Dynamics at the M Edges of Magnetic Elements Observed Using a Tabletop High-Harmonic Soft X-Ray Source, Phys. Rev. Lett. 103, 257402 (2009).
- [28] F. Hellman, Interface-induced phenomena in magnetism, Rev. Mod. Phys. 89, 025006 (2017).
- [29] K. Bühlmann et al., Ultrafast demagnetization in iron: Separating effects by their nonlinearity, Structural Dynamics 5, 044502 (2018).
- [30] Th. Gerrits, H. A. M. van den Berg, J. Hohlfeld, L. Bär & Th. Rasing, Ultrafast precessional magnetization reversal by picosecond magnetic field pulse shaping, Nature 418, 509–512 (2002).

- [31] C. D. Stanciu, F. Hansteen, A. V. Kimel, A. Kirilyuk, A. Tsukamoto, A. Itoh, and Th. Rasing, All-Optical Magnetic Recording with Circularly Polarized Light, Phys. Rev. Lett. 99, 047601 (2007).
- [32] F. A. Siegrist, Light-Field Driven Charge and Spin Transfer, Ludwig-Maximilians-Universität (2019).
- [33] F. Siegrist, Attosecond Dynamics Based on Electron Correlation and Excitation, Master's thesis, Technische Universität München (2016).
- [34] J. C. Maxwell, A dynamical theory of the electromagnetic field: Philosophical Transactions of the Royal Society of London, 136, 1-20 (1846).
- [35] E. Hecht, Optik: De Gruyter, Berlin, Boston, 2018.
- [36] R. Boyd, Nonlinear Optics, 3rd edition, Burlington: Academic Press (2008).
- [37] T. Brabec & F. Krausz, Nonlinear Optical Pulse Propagation in the Single-Cycle Regime, Phys. Rev. Lett. 78 (1997).
- [38] B. E. A. Saleh & M. C. Teich, Grundlagen der Photonik, 2d edition, WILEY-VCH (2008).
- [39] F. DeMartini, C. H. Townes, T. K. Gustafson, and P. L. Kelley, Self-Steepening of Light Pulses, Phys. Rev. Vol. 164, No. 2 (1967).
- [40] J. R. De Oliveira et al., Self-steepening of optical pulses in dispersive media, Vol. 9, No. 11/November 1992/J. Opt. Soc. Am. B 2025 (1992).
- [41] A. J. Sabbah & D. M. Riffe, Femtosecond pump-probe reflectivity study of silicon carrier dynamics, Physical Review B - Condensed Matter and Materials Physics 66, 1–11 (2002).
- [42] Y. Li, Plasmonic Optics: Theory and Applications, Chapter 1, Spie.Digital Library (2017).
- [43] P. Drude, Zur Elektronentheorie der Metalle, Annalen der Physik 306, 566–613 (1900).
- [44] J. Stöhr, NEXAFS Spectroscpy: Springer Series in Surface Sciences 25 (1992).
- [45] J. Stöhr, H. C. Siegmann, Magnetism, From Fundamentals to Nanoscale Dynamics: Springer (2006).
- [46] C. Sorg, Magnetic Properties of 3d and 4f Ferromagnets Studied by X-Ray Absorption Spectroscopy: PhD Thesis, Freie Universität Berlin (2005).
- [47] R. Menzel, Photonics, Linear and Nonlinear Interactions of Laser Light and Matter: Springer (2001).
- [48] J. Stöhr & Y. Wu (Ed.), X-Ray Magnetic Circular Dichroism: Basic Concepts and Theory for 3D Transition Metal Atoms: In New Directions in Research with Third-Generation Soft X-Ray Synchrotron Radiation Sources, 221–250 Springer Netherlands, Dordrecht, (1994).
- [49] E. C. Stoner, Collective electron ferronmagnetism: Royal Society Publishing (1937).
- [50] C. KITTEL, Einführung in die Festkörperphysik, 13. korrigierte Aufl., WALTER DE GRUYTER (2002).
- [51] L. Nèel, Antiferromagnetism and Ferrimagnetism: The proceedings of the physical society, Section A, Vol.65, Part II, No. 395 A, 1 November (1952).

- [52] N. F. Mott, A discussion of the transition metals on the basis of quantum mechanics: Proc. Phys. Soc. 47, 571–588 (1935).
- [53] J. C. Slater, The Ferromagnetism of Nickel: Phys. Rev., Vol.49, 537-545, 1 April (1936).
- [54] F. Bloch, Bemerkung zur Elektronentheorie des Ferromagnetismus und der elektrischen Leitfhigkeit, ZS. für Phys. 57, 545–555, (1929).
- [55] F. Bloch, Über die Quantenmechanik der Elektronen in Kristallgittern, ZS. f. Phys. 52, 555–600, (1929).
- [56] P. Weiss, L'hypothèse du champ moléculaire et la propriété ferromagnétique, J. Phys. Theor. Appl., Vol. 6, No. 1, 661–690 (1907).
- [57] H. von Helmholtz, Physical Memoirs Selected and Translated from Foreign Sources, Taylor & Francis, (1888).
- [58] M. Faraday, Experimental researches in electricity: Philosophical Transactions, Royal Siciety Publishing Vol.136 (1846).
- [59] J. L. Erskine and E. A. Stern, Calculation of the M2,3 magneto-optical absorption spectrum of ferromagnetic nickel: Phys. Rev. B12, 5016, 1 December (1975).
- [60] G. Schütz, W. Wagner, W. Wilhelm, and P. Kienle, Absorption of Circularly Polarized X Rays in Iron: Phys. Rev. Let., Vol.58, No.7, 16 February (1987).
- [61] B. D. Cullity, C. D. Graham, Introduction to magnetic materials, 2nd ed., Wiley-IEEE, Hoboken, New Jersey, (2008).
- [62] H. A. Bethe, E. E. Salpeter (Ed.), Quantum Mechanics of One- and Two-Electron Atoms: Springer US, Boston, (1977).
- [63] G. Schütz et al., Spin-dependent photoabsorption at the L-edges of ferromagnetic Gd and Tb metal, Z. Phys. B - Condensed Matter 73, 67–75 (1988).
- [64] B. T. Thole, P. Carra, F. Sette, and G. van der Laan, X-ray circular dichroism as a probe of orbital magnetization, Phys. Rev. Lett. 68, 1943, 23 March (1992).
- [65] P. Carra, B. T. Thole, M. Altarelli, and X. Wang, X-ray circular dichroism and local magnetic fields, Phys. Rev. Lett. 70, 694, 1 February (1993).
- [66] R. Wu, D. Wang, A. J. Freeman, First principles investigation of the validity and range of applicability of the x-ray magnetic circular dichroism sum rule, Phys. Rev. Let., Vol. 71, No. 21, 3581–3584 (1993).
- [67] R. Wu and A. J. Freeman, Limitation of the Magnetic-Circular-Dichroism Spin Sum Rule for Transition Metals and Importance of the Magnetic Dipole Term, Phys. Rev. Lett., Vol. 73, No.14, 1994–1997 (1994).
- [68] J. Stöhr and H. König, Determination of Spin- and Orbital-Moment Anisotropies in Transition Metals by Angle-Dependent X-Ray Magnetic Circular Dichroism, Phys. Rev. Lett., Vol. 75, No. 20, 3748-3751 (1995).
- [69] J. Stöhr, X-ray magnetic circular dichroism spectroscopy of transition metal thin films, Journal of Electron Spectroscopy and Related Phenomena 75, (1995) 253– 272.
- [70] C. Sorg, Magnetic Properties of 3d and 4f Ferromagnets Studied by X-Ray Absorption Spectroscopy: PhD Thesis, Freie Universät Berlin (2005).

- [71] C. T. Chen et al., Experimental Confirmation of the X-Ray Magnetic Circular Dichroism Sum Rules for Iron and Cobalt, Phys. Rev. Lett., Vol. 75, No. 1, 152–155 (1995).
- [72] C. Stamm, N. Pontius, T. Kachel, M. Wietstruk & H. A. Dürr, Femtosecond xray absorption spectroscopy of spin and orbital angular momentum in photoexcited Ni films during ultrafast demagnetization, Phys. Rev. B 81, 104425 (2010).
- [73] C. Boeglin et al., Distinguishing the ultrafast dynamics of spin and orbital moments in solids: Nature, Vol. 465, 458-461, 27 May (2010).
- [74] Y. Teramura, A. Tanaka & T. Jo, Effect of Coulomb Interaction on the X-Ray Magnetic Circular Dichroism Spin Sum Rule in 3d Transition Elements, Journal of the Physical Society of Japan 65, 1053–1055 (1996).
- [75] A. Scherz et al., Limitations of Integral XMCD SumRules for the Early 3d Elements, Physica Scripta 2005, 586 (2005).
- [76] X. Wang, T. C. Leung, B. N. Harmon & P. Carra, Circular magnetic x-ray dichroism in the heavy rare-earth metals, Phys. Rev. B 47, 9087–9090 (1993).
- [77] A. L. Ankudinov, J. J. Rehr, H. Wende, A. Scherz & K. Baberschke, Spindependent sum rules for X-ray absorption spectra, Europhysics Letters (EPL) 66 (2004).
- [78] A. Scherz, Spin-dependent X-ray Absorption Spectroscopy of 3d Transition Metals: Systematics and Applications: Phd thesis, Freie Universität Berlin (2003).
- [79] S. Shin, S. Suga, H. Kanzaki, S. Shibuya & T. Yanaguchi, Multiplet structures of the inner core absorption spectra of KMnF3 and KCoF3 measured by synchrotron radiation, Solid State Communications 38, 1281–1284 (1981).
- [80] A. Sommer, Ultrafast Strong Field Dynamics in Dielectrics, PhD Thesis, Ludwig-Maximilians-Universität (2015).
- [81] M. Sheik-Bahae, A. Said, T. Wei, D. J. Hagan, E. W. Van Stryland, Sensitive Measurement of Optical Nonlinearities Using a Single Beam, IEEE Journal of Quantum Electronics 26 (1990).
- [82] M. C. Schröder, Ultrafast Electron Dynamics in Semiconductor and Ferromagnetic Materials, Master thesis, Ludwig-Maximilians-Universität (2018).
- [83] A. Dragomir, J. G. McInerney & D. N. Nikogosyan, Femtosecond measurements of two-photon absorption coefficients at $\lambda = 264$ nm in glasses, crystals, and liquids, Applied Optics, Vol. 41, Issue 21, pp. 4365-4376 (2002).
- [84] P. Liu, W. L. Smith, H. Lotem, J. H. Bechtel and N. Bloembergen, Absolute two-photon absorption coefficients at 355 and 266 nm, Phys. Rev. B 17, 4620–4632 (1978).
- [85] C. Schinke et al., Uncertainty analysis for the coefficient of band-to-band absorption of crystalline silicon, AIP Advances 5, 067168 (2015).
- [86] G. Vuye et al., Temperature dependence of the dielectric function of silicon using in situ spectroscopic ellipsometry, Elsevier, Thin Solid Films, Volume 233, Issues 1–2, 12 October 1993, Pages 166-170 (1993).
- [87] A. D. Bristow, N. Rotenberg and H. M. van Driel, Two-photon absorption and Kerr coefficients of silicon for 850–2200nm, Applied Physics Letters 90, 191104 (2007).

- [88] Q. Lin et al., Dispersion of silicon nonlinearities in the near infrared region, Applied Physics Letters 91, 021111 (2007).
- [89] E. L. Buckland & R. W. Boyd, Electrostrictive contribution to the intensitydependent refractive index of optical fibers, Opt. Lett. 21 (1996).
- [90] F. Siegrist et al., Light-wave dynamic control of magnetism: Nature, 571, 240-244 (2019).
- [91] M. Lucchini et al., Attosecond dynamical Franz-Keldysh effect in polycrystalline diamond: Science, Vol. 353, Issue 6302, 26 August (2016).
- [92] M. Volkov et al., Attosecond screening dynamics mediated by electron localization in transition metals: Nature Phys., Vol. 15, 1145-1149 (2019).
- [93] J. Itatani et al., Attosecond Streak Camera: Phys. Rev., Vol. 88, Num. 17, 29 April (2002).
- [94] E. Goulielmakis et al., Direct Measurement of Light Waves: Science, Vol. 305, 1267-1269, 27 August (2004).
- [95] M. Ossiander, K. Golyari, K. Scharl, L. Lehnert, F. Siegrist, J. P. Bürger, D. Zimin, J.A. Gessner, M. Weidman, I. Floss, V. Smejkal, C. Lemell, F. Libisch, N. Karpowicz, J. Burgdörfer, F. Krausz and M. Schultze, Exploring the speed limit of optielectronics, submitted to Nature Photonics.
- [96] V. Lopez-Flores, Time-resolved x-ray magnetic circular dichroism study of ultrafast demagnetization in a CoPd ferromagnetic film excited by circularly polarized laser pulse: Phys. Rev., B 86, 014424 (2012).
- [97] J. Bigot, M. Vomir and E. Beaurepaire, Coherent ultrafast magnetism induced by femtosecond laser pulses: Nature Phys., Vol. 5, 515-520, July (2009).
- [98] I. Radu et al., Transient ferromagnetic-like state mediating ultrafast reversal of antiferromagnetically coupled spins: Nature, Vol. 472, 205-208, 14 April (2011).
- [99] J. K. Dewhurst, P. Elliott, S. Shallcross, E. K. Gross U. & S. Sharma, Laser-Induced Intersite Spin Transfer, Nano Letters 18, 1842–1848 (2018).
- [100] J. K. Dewhurst, S. Shallcross, E. K. Gross & S. Sharma, Substrate-Controlled Ultrafast Spin Injection and Demagnetization, Physical Review Applied 10, 044065 (2018).
- [101] T. Koide and T. Shidara, Production and direct measurement of circularly polarized vacuum-ultraviolet light with multireflection optics: Appl. Phys. Lett. 58, 2592 (1991).
- [102] Hartmut Höchst, Rajesh Patel, Fred Middleton, Multiple-reflection $\lambda/4$ phase shifter: A viable alternative to generate circular-polarized synchrotron radiation: Volume 347, Issues 1–3, 107-114, 11 August (1994).
- [103] Hartmut Höchst, Dai Zhao, David L. Huber, M2,3 magnetic circular dichroism (MCD) measurements of Fe, Co and Ni using a newly developed quadruple reflection phase shifter: Surface Science, 353-354, 998-1002 (1996).
- [104] B. Vodungbo et al., Polarization control of high order harmonics in the EUV photon energy range: Vol. 19, No. 5/ OPTICS EXPRESS 4346-4356, 28 February (2011).
- [105] Yi-Ping Chang, Circularly Polarized Attosecond Pulses for Time-Resolved XUV Spectroscopy: Master Thesis, Ludwid-Maximilians-Universität (2017).

- [106] K. Rabinovitch, L. R. Canfield, and R. P. Madden, A Method for Measuring Polarization in the Vacuum Ultraviolet: APPLIED OPTICS, Vol. 4, No. 8, 1005-1010, August (1965).
- [107] M. Zürch et al., Direct and simultaneous observation of ultrafast electron and hole dynamics in germanium, Nat. Commun. 8, 15734 (2017).
- [108] Y. Shinohara et al., Coherent phonon generation in time-dependent density functional theory, Phys. Rev. B 82, 155110 (2010).
- [109] M Hase et al., Frequency comb generation at terahertz frequencies by coherent phonon excitation in silicon, Nature Photon. 6, 243-247 (2012).
- [110] S. K. Sundaram and E. Mazur, Inducing and probing non-thermal transitions in semiconductors using femtosecond laser pulses, Nature Mater. 1, 217-224 (2002).
- [111] J. K. Dewhurst, S. Sharma & E. Gross, The Elk Code, https://elk.sourceforge.io/.
- [112] M. Uemoto, S. Kurata, N. Kawaguchi, and K. Yabana, First-principles study of ultrafast and nonlinear optical properties of graphite thin films, Phys. Rev. B 103, 085433 (2021).
- [113] K. Yabana et al., SALMON, https://salmon-tddft.jp/.
- [114] B. El-Kareh, Fundamentals of Semiconductor Processing Technologies, Norwell: Kluwer Academic Publishers (1995).
- [115] M. A. Green & M. J. Keevers, Optical properties of intrinsic silicon at 300 K, Progress in Photovoltaics: Research and Applications 3, 189–192 (1995).
- [116] M. Noda, S. A. Sato, Y. Hirokawa, M. Uemoto, T. Takeuchi, S. Yamada, A. Yamada, Y. Shinohara, M. Yamaguchi, K. Iida, I. Floss, T. Otobe, K.-M. Lee, K. Ishimura, T. Boku, G. F. Bertsch, K. Nobusada, and K. Yabana, Salmon: scalable ab-initio light-matter simulator for optics and nanoscience, Comp. Phys. Comm., 235, 356-365 (2019).
- [117] K. Yabana, T. Sugiyama, Y. Shinohara, T. Otobe, and G. F. Bertsch, Timedependent density functional theory for strong electromagnetic fields in crystalline solids, Phys. Rev. B 85, 045134 (2012).
- [118] P. Elliott, T. Müller, J. K. Dewhurst, S. Sharma & E. K. U. Gross, Ultrafast laser induced local magnetization dynamics in Heusler compounds, Scientific Reports, Vol. 6, No. 38911 (2016).
- [119] M. Hofherr et al., Ultrafast optically induced spin transfer in ferromagnetic alloys, Science Advances, Vol.6, No.3, eaay 8717 (2020).
- [120] F. Willems et al., Magneto-Optical Functions at the 3p Resonances of Fe, Co, and Ni: Ab initio Description and Experiment, Physical Review Letters 122, 217202 (2019).
- [121] H. T. Chang et al., Electron thermalization and relaxation in laser-heated nickel by few-femtosecond core-level transient absorption spectroscopy, Phys. Rev. B 103, 064305 (2021).
- [122] M. van Kampen, J. T. Kohlhepp, W. J. M. de Jonge, B. Koopmans and R. Coehoorn, Sub-picosecond electron and phonon dynamics in nickel, J. Phys.: Condens. Matter 17 6823–6834 (2005).
- [123] B. Johansson and N. Mårtensson, Core-level binding-energy shifts for the metallic elements, Phys. Rev. B 21, 4427 (1980).

- [124] S. Yamada, Time-dependent density functional theory for interaction of ultrashort light pulse with thin materials, Phys. Rev. B 98, 245147 (2018).
- [125] A. Delan, M. Rennau, S.E. Schulz, T. Gessner, Thermal Conductivity of Ultra Low-k Dielectrics, Microelectronics Engineering 70, pp. 280-284 (2003).
- [126] M. Burzo, P. Komarov, P. Raad, Thermal Transport Properties of Gold-Covered Thin-Film Silicon Dioxide, IEEE CPMT 26, pp. 80-88 (2003).
- [127] Y. Gao et al., Saturable absorption and reverse saturable absorptionin platinum nanoparticles, Optics Communications 251 429–433 (2005).
- [128] C. Quan et al., Transition from saturable absorption to reverse saturable absorption in MoTe2 nano-films with thickness and pump intensity, Applied Surface Science, Vol. 457, 115-120 (2018).
- [129] Y. Unutulmazsoy, R. Merkle, D. Fischer, J. Mannhart and J. Maier, The oxidation kinetics of thin nickel films between 250 and 500 °C, Phys. Chem. Chem. Phys., 19, 9045-9052 (2017).
- [130] Wikipedia, Doping (Semiconductor), [22.06.21], https://en.wikipedia.org/wiki/Doping_(semiconductor).
- [131] C. S. Wang and J. Callaway, Band structure of nickel: Spin-orbit coupling, the Fermi surface, and the optical conductivity*, Phys. Rev. B 9, 4897 (1974).
- [132] W. Schweinberger et al., Waveform-controlled near-single-cycle milli-joule laser pulses generate sub-10 nm extreme ultraviolet continua, Optics Letters 37, 3573 (2012).
- [133] M. Fiess et al., Versatile apparatus for attosecond metrology and spectroscopy, Review of Scientific Instruments 81, 093103 (2010).
- [134] T. Fuji et al., Monolithic carrier-envelope phase-stabilization scheme, Optics Letters 30, 332 (2005).
- [135] D. Strickland & G. Mourou, Compression of amplified chirped optical pulses, Optics Communications 56, 219–221 (1985).
- [136] A. Guggenmos, R. Rauhut, M. Hofstetter, S. Hertrich, B. Nickel, J. Schmidt, E. M. Gullikson, M. Seibald, W. Schnick and U. Kleineberg, A periodic CrSc multilayer mirrors for attosecond water window pulses, Opt. Express, 21, 21728–21740 (2013).
- [137] E. Runge & E. K. U. Gross, Density-Functional Theory for Time-Dependent Systems, Physical Review Letters 52, 997–1000 (1984).
- [138] K. Krieger et al., Ultrafast demagnetization in bulk versus thin films: an ab initio study, J. Phys. Condens. Matter 29, 224001 (2017).
- [139] S. Sharma, J. K. Dewhurst, A. Sanna & E. K. U. Gross, Bootstrap approximation for the exchange-correlation kernel of time-dependent density-functional theory, Phys. Rev. Lett. 107, 186401 (2011).
- [140] J. K. Dewhurst, F. Willems, P. Elliott, Q. Z. Li, C. von Korff, Schmising, C. Strüber, D. W. Engel, S. Eisebitt, and S. Sharma, Element specificity of transient extreme ultra-violet magnetic dichroism, Phys. Rev. Lett. 124, 077203 (2020).
- [141] F. Tran & P. Blaha, Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential, Physical Review Letters 102, 226401 (2009).

[142] M. Uemoto, Y. Kuwabara, S. A. Sato & K. Yabana, Nonlinear polarization evolution using time-dependent density functional theory, Journal of Chemical Physics 150, 094101 (2019).

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