Department of Physics and Astronomy
Ultrafast Lasers and Magnetodynamics Spectroscopies - IFIMUP

**Novel dual-colour
architecture for ultrafast
spin dynamics
measurements in sub-8 fs
regime**

PhD Thesis

Cledson Santana Lopes Gonçalves

Supervisors: Helder Crespo and David Schmool

A thesis submitted for the degree of *Philosophiae Doctor (PhD)*, in *Physics*.

Porto, October 2015

Dedication

I would like to dedicate this thesis to my loving parents ...

Acknowledgements

Agradeço a Deus por tudo o que tem feito em minha vida. Nada acontece por acaso... a minha família que tem me apoiado incondicionalmente em tudo. Aos meus orientadores Helder Crespo e David Schmool pela orientação neste trabalho e pela paciência. Ao professor D. Navas pelo apoio e ajuda em vários momentos. Aos meus amigos de laboratório que contribuíram em vários momentos no andamento do meu trabalho: Miguel Miranda (best friend), Ana Sofia (Sofi), Miguel Canhota (Macau), Francisco Silva (Chico), Tiago Pinto, Tiago Magalhães (the man) e Tania Ribeiro. Por fim, agradeço ao Capes e FCT pelo apoio financeiro.

Resumo

As técnicas de espectroscopia pump-probe são extremamente poderosas como ferramenta de visualização em escalas de tempo que outros métodos não podem atingir. Esse diferencial reside no fato de que tais técnicas usam como fonte pulsos de laser ultracurtos da ordem dos femtosegundos ($1 \text{ femtosegundo} = 10^{-15} \text{ segundos}$) para excitar e sondar a amostra. Assim é possível obter informações sob os fenômenos que ocorrem em escalas de femtosegundos. Efeitos nesta escala de tempo contêm informações importantes, por exemplo, em sistemas ferromagnéticos, sobre energias magnéticas, associadas a anisotropia magnética, interação spin-orbita e interação de troca (exchange). Além disso, também é possível usá-las para controlar diretamente (oticamente) a magnetização a partir da interação com a luz. Em geral, esses métodos têm mostrado grande sucesso na caracterização e observação de propriedades físicas fundamentais na dinâmica molecular e processos desmagnetização, tornando-se como um possível caminho para controlar magnetização em escalas de femtosegundos. Este trabalho tem como proposta a montagem e utilização de um aparato experimental de espectroscopia magneto-ótica do tipo pump-probe usando uma fonte com características únicas que irá proporcionar pulsos com duração da ordem de sub-8 fs no plano da amostra. Nesta escala de tempo, são necessárias técnicas avançadas de compensação de dispersão dos pulsos, uma vez que um pulso de luz ao propagar-se em um meio dispersivo (como o vidro ótico ou mesmo ar) alarga temporalmente. Ao garantirmos essa resolução temporal no plano da amostra, estaremos por volta de uma ordem de magnitude melhor do que o relatado na literatura recente (ver, por exemplo a referência [1]). Isso deverá permitir estudos detalhados da dinâmica magnética com uma precisão sem precedentes. Portanto, a escolha dos componentes apropriados, a compensação de dispersão, bem como as características do sistema de aquisição de dados foram fundamentais para atingirmos a resolução temporal desejada. Esse aparato experimental foi desenvolvido para estudar materiais magnéticos tais como em amostras de filmes ferromagnéticos de GdFeCo, Co etc. Pretende-se, com esse setup experimental, observar processos que ocorrem após um pulso de laser de femtosegundos interagir com a amostra. Entre esses processos podemos destacar: a interação dos fótons com os elétrons e spins do material; o relaxamento dos elétrons e spins para populações termalizadas, sendo que durante este regime temporal ocorrem mecanismos incoerentes que conduzem à desmagnetização. Outros processos relevantes são a precessão de magnetização ou a influência da anisotropia magnetocristalina na trajetória da amostra.

Palavras chaves: espectroscopia pump-probe, pulsos de femtosegundos, dinâmica magnética.

Abstract

The pump-probe spectroscopic techniques are extremely powerful as a visualisation tool in time scales that other methods can not reach. This difference lies in the fact that such techniques use as ultrashort laser pulse source with duration of the order of femtoseconds (1 femtosecond is 10^{-15} seconds) to excite and to probe the sample. So, it is possible to obtain information of phenomena that occurs in femtoseconds scales. Effects on this timescale contain important information, for example in ferromagnetic systems, about the energy associated with the magnetic anisotropy spin-orbit interaction and exchange interaction. Also, it is possible to use these pulses to control directly (optically) the magnetisation from the interaction with light. In general, these methods have shown great success in the characterisation and observation of fundamental physical properties of molecular and demagnetisation dynamic processes, being a possible way to control the magnetisation in femtosecond scales. This work proposed the development and use of an experimental apparatus for magneto-optical pump-probe spectroscopy using a source with unique features that provides pulses with sub-8 fs durations in the sample. On this time scale, advanced techniques are required for dispersion compensation of pulses, since when the light pulse propagates on a dispersive medium (such as optical glass or air) it broadens temporally. Therefore, the choice of suitable optical components, quality of the dispersion compensation, as well as the characteristics of the data acquisition system were essential to achieve the required temporal resolution. The experimental apparatus was developed to study magnetic materials such as ferromagnetic film samples GdCoFe, Co etc. The aim with this experimental setup, is to observe processes that occur after a few femtosecond laser pulse interaction with the sample. Among these processes we can highlight: the interaction of photons with electrons and spins of the material; the relaxation of electrons and spins for thermalise populations, where during this time regime incoherent mechanisms occur which lead to demagnetisation. Other significant phenomena are the precession of magnetisation or the influence of magnetocrystalline anisotropy.

Keywords: pump-probe spectroscopy, femtosecond pulses, magnetic dynamics.

Contents

Contents	ix
List of Figures	xi
List of Tables	xv
1 Introduction	1
1.1 Ultrafast Spectroscopy	1
1.2 Nanomagnetism: Static Equilibrium	2
1.2.1 Magnetic energies	2
1.2.2 Additional magnetic energies	7
1.3 Nanomagnetism: dynamic point of view	7
1.3.1 Larmor precession frequency	8
1.3.2 Landau-Lifshitz-Gilbert Equation	9
1.3.3 The Smit-Beljers equation	10
1.4 Ultrafast spectroscopy applied to Nanomagnetism	11
1.4.1 Direct Interaction between Photons and Spins	12
1.4.2 Electron-Phonon Spin-flip Scattering	13
1.4.3 Superdiffusive Spin Transport	14
1.5 Challenges in ultrafast magnetisation dynamics	14
1.6 About this thesis	15
2 Ultrafast Optical Pulses	17
2.1 Introduction	17
2.2 Mathematical background of ultrashort lasers pulses	18
2.2.1 Temporal domain	18
2.2.2 Frequency domain	19
2.2.3 Spectral phase	19
2.3 The Problem of Dispersion	21
2.3.1 Dispersive media	21
2.3.2 Dispersion compensation	22
2.4 Ultrafast lasers and Amplifiers: Generation of ultrashort pulses	24
2.4.1 Oscillator	24
2.4.2 Amplifier	24
2.4.3 Spectral Broadening in a Hollow Fiber	25
2.5 Characterization Ultrashort Pulses: Conventional method and the D-scan technique	26
2.5.1 Interferometric Autocorrelation	26
2.5.2 Intensity Autocorrelation	27
2.5.3 D-scan technique	28
2.6 Summary	30

3	Experimental technique I: Methods for investigating magnetisation dynamics	31
3.1	Methods for studying magnetisation dynamics	31
3.2	Pump-probe methods	31
3.2.1	Time-resolved Kerr effect (TR-MOKE)	32
3.2.2	Time-resolved Second-harmonic generation (TR-SHG)	32
3.2.3	Limitations in degenerate and non-degenerate systems	33
3.3	Magneto-optic effect Kerr (MOKE)	34
3.3.1	Theory	35
3.3.2	Experimental setup	36
3.3.3	Sample	37
3.3.4	Boxcar averager systems	37
3.4	Analysis of the MOKE signal	39
3.5	Summary	42
4	Experimental technique II: Femto-MOKE	43
4.1	Experimental Ultrafast Laser Setup in Porto	43
4.2	Stages of the experimental setup	44
4.2.1	Oscillator source	44
4.2.2	Amplifier source	45
4.3	Generation of the pump and probe pulses from broadband hollow fiber compressor	50
4.3.1	Characterisation of the pulses by autocorrelation and d-scan techniques . .	52
4.3.2	Zero delay between pump and probe by spectral interference method	54
4.3.3	Measurement of the pump beam spot size	54
4.4	Femto MOKE setup	60
4.5	Data acquisition	61
4.5.1	Lock-in amplifier	61
4.6	Summary	62
5	Results and Analysis	63
5.1	Introduction	63
5.2	Lase-induced precession dynamics	63
5.3	Ultrafast demagnetisation	70
5.4	Summary	73
6	Conclusion and future perspectives	75
	Bibliography	77
	Appendix	87
A	Nonlinear Index of Refraction	87
A.1	Self-focusing: Kerr Lens effect	88
A.2	Self-phase modulation	88
B	Second Harmonic Generation	91

List of Figures

1.1	Coordinate system for both the magnetisation and the external magnetic field . . .	3
1.2	Demagnetising factors of a sphere (a), an infinite rod (b) and an infinite thin film (c).	5
1.3	Directional cosines of the magnetisation in spherical coordinates where θ and ϕ are the polar and azimuthal angles, respectively	6
1.4	(a) In equilibrium, the magnetisation of a thin film should be parallel to the effective field of the system.(b) When the magnetisation is changed out from its equilibrium position by a laser pulse (c), it will show a precessional motion around the effective field.	8
1.5	Illustration of the precessional spin dynamics described by the Landau-Lifshitz-Gilbert equation. The magnetisation precesses around the effective field. A small damping torque gradually aligns the magnetisation with the effective field. Figure adapted from [2]	10
1.6	Time scales in magnetism as compared to magnetic field and laser pulse excitation. Figure obtained from Ref. [3]	12
1.7	Dependence of remanent magnetization (normalised to the signal without the presence of the pump beam) in a ferromagnetic <i>Ni</i> film with the delay between pump and probe beams	13
2.1	Electric field of a 4-fs Gaussian pulse with 800 nm center wavelength. The thin solid and the dashed line represent the electric field for different values of the carrier-envelope offset phase. Obviously, different maximum amplitudes are reached for the two cases. The envelope is shown as the thick solid curve	19
2.2	(a) Unchirped pulse; (b) chirped pulse showing the variation of instantaneous frequency. [4]	20
2.3	(a) Phase (solid line) and frequency-dependent delay (dashed line) vs. frequency for a cubic spectral phase; (b) calculated intensity profile. [5]	20
2.4	When a pulse of light is passed through a medium and subject to normal dispersion, the short-wavelength components, indicated in blue, travel slower than those at longer wavelengths. Adapted from [6].	21
2.5	Grating pairs used in the control of dispersion. The different wavelengths are dispersed in space and made to travel different paths.	22
2.6	Grating pairs used in the control of dispersion. The different wavelengths are dispersed in space and made to travel different paths. The relative time delay between the frequencies caused by the prism pair compensates for the time delay caused by other dispersive material.	23
2.7	Schematic drawing of a DCM. which is composed of four multilayer subsections. The position inside the mirror is determined by the variable m , where $m = 0$ defines the beginning of the theoretical DCM structure directly after the AR coating. Light, with wavenumber k , is reflected at the wavenumberdependent classical turning point $m_{t_l}(k)$. [7].	23

LIST OF FIGURES

2.8	DCMs characteristics. Each blue-green mirror pair provides a net GDD of $60fs^2$ per bounce (at 800 nm). This chirped mirror have bandwidth compatible with the spectral range of the beams used in our experimental setup.	24
2.9	Superposition of resonator modes. While a mode number of 5 results in a long pulse duration $\Delta\tau$ (blue), pulses with a spectral width $\Delta\nu$ of 50 modes are much shorter (red). The gain bandwidth determines the shortest duration obtainable for the pulses.	25
2.10	Conceptual schematic of a chirped-pulse amplification-based laser system. A dispersive element is used to make the pulse longer (sometimes, a glass element, or as shown some other dispersive element, such as a grating stretcher), typically to durations of a few picoseconds to hundreds of picoseconds. The pulse can then be safely amplified while keeping instantaneous intensities below to damage threshold. After amplification, the pulse generally has a smaller bandwidth due to gain-narrowing in the amplification process. Negative dispersion is then introduced to compress the pulse in time, typically to approximately $30fs$. Adapted from [8].	25
2.11	Illustration of our experimental setup for spectral broadening. The pulse is focused with a lens with appropriate focal distance and is inserted in a pressurized gas chamber, being then coupled into the hollow fiber. When exiting the hollow fiber and gas chamber the pulse has been spectrally broadened. The pulse then travels to the dispersion compensation stage and is then ready to be used in experiments. adapted from [9].	26
2.12	Michelson interferometer for collinear version. Adapted from [10].	27
2.13	Simulation of an interferometric autocorrelation shown the relation 8:1.	27
2.14	Interferometer for noncollinear Intensity autocorrelation. Adapted from [10]. . . .	28
2.15	Simplified schematic of the experimental setup of the d-scan.	29
2.16	Temporal characterisation of an ultrafast oscillator with the d-scan technique [11]. The fundamental spectrum (c) and the SHG spectra as a function of glass insertion (a) were measured. An iterative algorithm applies phases to the fundamental spectrum and simulates the SHG process to recreate (b) the measured trace. From this retrieved phase (c) the pulse can be reconstruct in the time domain (d).	30
3.1	Generic illustration of the pump-probe methods in reflection. (a) Degenerate system. (b) Non-degenerate system	32
3.2	(a) Schematics of a reflection-type pump-probe measurement and the generation of a transient grating in materials. (b) The shape of a coherent artifact signal with well-pronounced regular structure measured at a high resolution. From [12].	33
3.3	Illustration of the effect MOKE. The Kerr rotation occurs when the linearly polarised incident wave with components circularly polarised to right and left are reflected with different refractive indices for left and right, and ,therefore, different velocity of propagation. Two angles allow to characterise the elliptic polarisation of the light: Kerr rotation (θ_K) and the Kerr ellipticity (ϵ_K).	34
3.4	The three different types of MOKE effect: (a) Polar where the magnetisation is parallel to the plane of incidence and perpendicular to the magnetic film surface, (b) Longitudinal where the magnetisation is in the direction parallel to the plane of incidence and oriented in the plane of magnetic film (c)Transversal where the magnetisation is perpendicular to the plane of incidence and oriented in the plane of magnetic film.	35
3.5	Coordinate system used in the calculations of the Fresnel coefficients	36
3.6	Simplified experimental MOKE setup	37

3.7	(a) Typical structure of a GdFeCo sample, on either a float glass substrate or a SiN membrane. (b) Antiferromagnetic alignment of the magnetic moments of the constituent sub-lattices with respect to the external magnetic field of a generic ferromagnetic. (c) RE and TM sublattices show very different temperature dependencies which leads, in a certain concentration range, to the appearance of magnetisation compensation T_M . Adapted from [13].	38
3.8	Operation of a gate integrator boxcar in static mode, i.e, fixing the gate against the trigger signal.	38
4.1	Schematic representation of the laser system used in this work. OSC - oscillator; AOM - acousto-optic modulator; APD - avalanche photodiode; PD - photodiode; AOPDF - acousto-optic programmable dispersion filter; ISO - optical isolator (Faraday rotator); TOD CM - third-order dispersion chirped mirrors; SP - spectrometer; PC - personal computer [extracted from [9].	44
4.2	Experimental setup degenerate pump-probe technique using oscillator as source. .	45
4.3	Measurements of the static MOKE signal without the presence of the pump in cobalt samples with a thickness of $\sim 80nm$ for different intensities of the probe (different beam splitters with 5% and 0.7% reflecting,were used).	47
4.4	Experimental setup for the degenerate pump-probe technique using the amplifier as source.	48
4.5	Hysteresis loops for different pumpprobe delays, demonstrating the ultrafast demagnetisation. The chosen pump fluence is to $10 mJ/cm^2$. The black loop was recorded without the pump pulse and is the same in all figures.	49
4.6	Illustration of our experimental setup for spectral broadening through nonlinear propagation. Adapted from [14].	50
4.7	(a) Representative measured and (b) retrieved d-scans for the hollow fiber compressor. (c) Measured spectral intensity (black) and retrieved phase (thick red line, with the standard deviation indicated by thin red lines). (d) Retrieved electric field of the pulses for the BK7 wedge insertion that minimizes the intensity FWHM duration, corresponding to a sub-4 fs pulse	51
4.8	A glass window is used as beam splitter and colour filters are used to split the main beam into the pump (transmitted) and probe (reflected) pulses. The relevant measurements are shown for the main beam as well as those for the pump and probe after the beamsplitter.	52
4.9	(a) Simulation of the total dispersion of the pump, GDD vs λ . (b) Compensation of the total dispersion with 21 reflections in DCM9.	53
4.10	Picture of the double chirped mirrors used in the experimental setup with 21 reflections.	54
4.11	(a) Spectra for the pump and probe beams from the dichroic mirror, (b) measured intensity autocorrelation of probe beam and (c) measured interferometric autocorrelation of pump beam and corresponding (calculated) intensity autocorrelation. Retrieved pulse duration (assuming sech2 shapes) is 8 fs for both pulses.	55
4.12	(a) Measured and (b) retrieved d-scan traces for the probe pulse (central wavelength of approx. 600 nm); retrieved probe pulse in the spectral (c) and temporal (d) domains; probe pulse width is 7.2 fs (FWHM).	56
4.13	(a) Measured and (b) retrieved d-scan traces for the pump pulse (central wavelength of approx. 800 nm); retrieved pump pulse in the spectral (c) and temporal (d) domains; pump pulse width is 7.3 fs (FWHM).	57
4.14	Experimental scheme to find the zero delay between pump and probe.	57
4.15	Experimental results of spectral interferometry using pump and probe beams . . .	58
4.16	Experimental setup used to measure the spot of the pump.	59
4.17	Laser spotsize as viewed by the CCD camera and imported to a Python color map. Spot size measurements in X and Y axis. The data is fitted using a gaussian curve and the width is measure at $1/e^2$ of the maximum, since we are measuring an intensity	59

4.18	Schematic illustration of the pump-probe apparatus	61
4.19	(a) In the case where the delay is fixed, the amplitude of the measured signal is constant. (b) In the case of variable delay between pump and probe the amplitude of the measured signal varies with it. Dashed line represents an illustration of the TR-MOKE signal measured using the lock-in.	62
5.1	In-plane hysteresis loops of the GdFeCo thin film without (●) and with pump pulse (●) and using a pump fluence of 2.7 mJ/cm^2	64
5.2	Time-dependent MOKE demagnetisation and precessional curves for a GdFeCo ferromagnetic thin film as a function of the external applied field.	65
5.3	Precessional curves (○) and fittings (—) for a GdFeCo ferromagnetic thin film as a function of the external applied field: (a) 4150 Oe, (b) 3980 Oe, (c) 3680 Oe and (d) 3300.	67
5.4	Field dependence of the resonance frequency (○) and the theoretical fitting using the Kittel approximation (—).	68
5.5	(a) Field dependence of $(1/\tau)$: Experimental data (○) and theoretical fit ((—)) using Equation 5.3. (b) Field dependence of (eff) : Experimental data (○) and theoretical damping coefficient (—) ((—)) calculated from Equation 5.3.	69
5.6	(a) The experimental demagnetisation data of GdFeCo and (b) expected temporal evolution of the spin temperature using Equation 5.8 (open black symbols). Both curves were fitted within the 3T model (—).	70
5.7	(Calculated temperature profiles for a GdFeCo thin film excited by a 8 fs laser pulse and a fluence of 2.7 mJ/cm^2 , ((—) $T_e(t)$, (—) $T_l(t)$ and (—) $T_s(t)$).	71
5.8	TR-MOKE measurements in GdFeCo sample (a) with a waveplate and (b) without waveplate in the optical path of the pump.	72
5.9	Diagram illustrating of a linearly polarized plane wave incidence in a birefringent medium with the angle θ with relative to the optical axis of the medium (in the y direction), where the extraordinary (E) and ordinary (O) components are indicated.	73
A.1	The Kerr lens effect and self-focusing. The index of refraction varies with intensity along the beam diameter. Depending on the sign of the nonlinear term n_2 in the Equation A.7 the index of refraction increases or decreases towards the center of the laser beam. For positive n_2 the laser beam self-focuses.	88
A.2	Relation between (top) the time-dependent output intensity profile $ I(z, t) ^2$ and (middle) instantaneous frequency shift $\omega(z, t)$ in SPM, as well as (bottom) resultant power spectrum. A medium with $n_2 > 0$ is assumed, and $1 \text{ cm}^{-1} = 30 \text{ GHz}$. The left-hand side shows the case of pure (dispersionless) SPM with a peak nonlinear phase shift of about 6π . In this case the output intensity profile is identical to the input intensity profile. The right-hand column shows a calculation for SPM acting in concert with normal dispersion, with the peak intensity adjusted to yield the same spectral broadening [5].	90
B.1	When intense light is shone on materials that do not possess an inversion symmetry, the vibrating electric field of the incident beam results in the polarization of the medium, reemitting light at the original frequency ω_i but also at the frequency $2\omega_i$ that is twice the original one (with half of the wavelength). SHG involves only virtual energy transition. As a result, using ultrafast (femtosecond) pulsed lasers, the response time of SHG is at the femtosecond level allowing very fast and sensitive detection. Adapted form [15]	91

List of Tables

2.1	Values of K for various pulse shapes, in the inequality $\Delta\nu\Delta t\geq K$, when $\Delta\nu$ and Δt are half-maximum quantities [16]	18
4.1	Optical elements and their respective thickness. Each beam will pass through the specified thickness.	51

Abbreviations

LLG:	Landau-Lifshitz-Gilbert
XMCD:	X-ray Magnetic Circular Dichroism
TR-MOKE:	time-resolved magneto-optical Kerr effect
FWHM:	Full-Width at Half-Maximum
CEO:	Carrier-Envelope Offset
CEP:	Carrier-Envelope Phase
GDD:	Group Delay Dispersion
TOD:	Third Order Dispersion
DCM:	Double-Chirped Mirrors
KLM:	Kerr Lens Mode-Locking
CW:	Continuous Wave
CPA:	Chirped pulse amplification
SPM:	Self-Phase Modulation
SHG:	Second Harmonic Generation
OPA:	Optical Parametric Amplifier
MOKE:	Magneto-Optic Effect Kerr
CCD:	Charge-Coupled Device

List of Publications and Conferences

Parts of this thesis are published and presented in the following journal paper and conference proceedings:

C. S. Gonçalves, A. S. Silva, D. Navas, M. Miranda and F. Silva, H. Crespo and D. S. Schmool, “A Dual-Colour Architecture for Pump-Probe Spectroscopy of Ultrafast Magnetization Dynamics in the Sub-10-femtosecond Range,” submitted to Scientific Reports/Nature Publishing Group, 1st October, 2015.

C. S. Gonçalves, A. S. Silva, D. Navas, M. Miranda, F. Silva, H. Crespo and D. S. Schmool, “Ultrafast demagnetisation and precessional dynamics in GdFeCo thin films using a new pump-probe system in the sub-8 femtosecond range,” Recent Trends in Nanomagnetism, Spintronics and their Applications, 30 June - 3 July 2015, Ordizia, Spain.

C. S. Gonçalves, A. S. Silva, D. Navas, M. Miranda, F. Silva, H. Crespo, and D. S. Schmool, “Ultrafast demagnetisation and precessional dynamics in GdFeCo thin films using a new pump-probe system in the sub-8 femtosecond range,” The European Conference on Lasers and Electro-Optics, 2125 June 2015, Munich, Germany.

C. S. Gonçalves, Silva, A. S., Miranda, M., Silva, F., Oliveira, P., Crespo, H. and Schmool, D. S. “ dual-colour architecture for ultrafast spin dynamics measurements in the sub-10 fs regime,” Springer Proceedings in Physics. 1. ed. Switzerland: Springer International Publishing, vol. 1. pp. 53, 2015.

C. S. Gonçalves, A. S. Silva, M. Miranda, F. Silva, H. Crespo, and D. S. Schmool, “Ultrafast demagnetization and precessional dynamics in magnetic thin films using a new pump-probe system in the sub-10 femtosecond range,” II International Conference on Applications in Optics and Photonics (AOP), 26-30 May 2014, Aveiro, Porto.

C. S. Gonçalves, A. S. Silva, D. Navas, M. Miranda, F. Silva, H. Crespo, and D. S. Schmool, “Ultrafast demagnetization and precessional dynamics in GdFeCo thin films using a new pump-probe system in the sub-8 femtosecond range,” 23rd Congress of the International Commission for Optics (ICO), 2629 August 2014, Santiago de Compostela, Spain.

C. S. Gonçalves., Silva, Ana S., Crespo, Helder and Schmool, D. S. ”Dynamic demagnetization in magnetic thin films using a new pump-probe system in the 6 femtosecond range,” Proc. SPIE., vol. 8785, pp. 87854N-87854N-6, 2013.

Chapter 1

Introduction

In this chapter, we briefly summarise the importance of ultrafast spectroscopy in different research fields such as Chemistry, Optics, Biology, etc.

In particular, this thesis is focused on Nanomagnetism and the main theoretical concepts are described. Therefore, the related energy contributions, such as the Zeeman energy, the magneto-crystalline energy and the shape anisotropy energy have been considered for a ferromagnetic thin film. Furthermore, the dynamical behavior of this system is described using the Landau-Lifshitz-Gilbert (LLG) equation of motion.

The state of the art, regarding ultrafast spectroscopy in Nanomagnetism, has been summarised focusing on the ultrafast magnetisation dynamics from both experimental and theoretical points of view.

Finally, I describe the challenges in ultrafast magnetisation dynamics, i.e, questions which are still unresolved such as understanding the mechanisms which govern the dynamics of laser-induced demagnetisation processes on time-scales below 10 femtoseconds.

The aim of this chapter is to show the need for techniques with high temporal resolution for the study of magnetic properties. It is in this context that this thesis was developed.

1.1 Ultrafast Spectroscopy

In general, Ultrafast Spectroscopy is based on using ultrashort laser pulses with durations in picosecond or femtosecond time-regime [17]. These pulses are used to study the dynamics of the systems rather than the energy levels themselves. Elementary excitation in solids shows a complex nonequilibrium behavior. During the excitations, process thermalisation and relaxation, the electronic band structure, optical transition energies, carrier concentration, and phonon frequencies vary over a broad range, leading to a variety of ultrafast phenomena. Optical spectroscopy with ultrashort pulses provides direct measurement these processes occurring on a time scale between 10^{-10} and 10^{-14} s.

Ultrafast spectroscopies based on pump-probe methods are a general tool to study ultrafast physical phenomena in materials. The spectroscopic pump-probe technique is extremely powerful as a visualisation tool on time scales which cannot be achieved by other methods and has shown enormous success in the characterisation and observation of fundamental physical properties, such as molecular dynamics and magnetisation processes [18, 3].

In the pump-probe technique, an ultrafast laser pulse is split into two beams: a high-intensity pump pulse to excite the sample by the generation of a non-equilibrium state, and a weak probe pulse to monitor the photoinduced changes in the sample by either transmission or reflection and with a specific time-delay between pulses. The controlled variation of this delay, via the linear displacement of a delay line, permits the study of ultrafast process. Thus, it is possible to overcome electronic detection limitations and recover the dynamics of the material properties on ultrafast time scales (femtoseconds, picoseconds and nanoseconds depending on the processes and

mechanisms involved). This method has proven to be a powerful tool for dynamical studies of fundamental physical phenomena such as molecular spectroscopy [19, 20], chemical reactions [21], magnetisation dynamics [3, 1, 22, 23, 24, 25] and even biological processes [26].

The photoexcitation of a magnetic system with ultrashort laser pulses can strongly alter the thermodynamic equilibrium among the constituent degrees of freedom (charge electrons, spin, and lattice), triggering a variety of dynamical processes that opens up fascinating opportunities to control the magnetic state of materials on an extremely fast time scale and may create new transient spin states that are inaccessible via thermal equilibrium transitions. These effects could provide essential contributions to our understanding of the fundamental transient magnetic phenomena, and they have clear implications for future high-speed, multifunctional magneto-optical device technology [27]. The ways in which laser pulses can precisely change the collective spin ordering in the coherent regime, induce a complete spin reversal or a magnetic phase transition at ultrafast time domain are not completely understood.

1.2 Nanomagnetism: Static Equilibrium

From a microscopic point of view, the magnetisation of a material originates from the arrangement of its interacting atomic magnetic moments. These magnetic moments appear due to incomplete electronic shells. The mean value of the magnetisation per unit of volume of any system can be determined by:

$$\vec{M} = \frac{\sum_i \vec{m}}{V} \quad (1.1)$$

where $\vec{m}$ is the atomic (or ionic) magnetic moment and V is the volume of the magnetic material. From the above definition, we should note that the macroscopic magnetisation is non-zero when the sum of all $\vec{m}$ vectors is different from zero. In order to maximise the macroscopic magnetic moment of a sample, it is required that all microscopic magnetic moments be aligned in the same direction. This behaviour occurs when a magnetic field is applied to the system at a sufficiently low temperature. However, the spontaneous long-range magnetisation of a ferromagnetic material vanishes above an ordering temperature called the Curie temperature, T_c . In this situation the thermal energy is greater than the exchange energy. Examples of room temperature ferromagnetic materials are the 3d transition group elements *Fe*, *Co*, *Ni*, and their alloys. Have earth elements and compound also exhibit long range magnetic order, frequently with antiferromagnetic or ferromagnetic ground states

1.2.1 Magnetic energies

Generally, the domain structure of a ferromagnetic material and its responses to an applied external magnetic field are determined by the minimisation of the magnetic free energy [28, 29, 30]. The magnetic energy is composed of several contributions such as the exchange energy between the neighbouring magnetic moments, the magnetisation energy due to the external field or Zeeman energy, the magnetocrystalline anisotropy energy and the shape anisotropy energy. Therefore, the interactions between individual magnetic dipoles with the external magnetic field and the crystal lattice, among others factors, will determine the magnetic properties of the materials, and are key for understanding magnetic phenomena [1, 3].

We can consider the case where a sample with a magnetisation $\vec{M}$ is placed in an external magnetic field $\vec{H}$. The magnetic anisotropy energy of the system is defined as:

$$E_T = E_Z + E_{Ex} + E_{Cr} + E_{Sh} \quad (1.2)$$

where E_Z , E_{Ex} , E_{Cr} and E_{Sh} are the Zeeman, the exchange, the magnetocrystalline and the shape anisotropy energies, respectively.

Zeeman energy (E_Z)

The Zeeman energy holds information about the interaction of the atomic magnetic moment with a external magnetic field. When an external magnetic field $\vec{H}$ is applied, the magnetisation suffers a torque that makes all the magnetic moments align in the direction of such field. This kind of energy is always present when applying a magnetic field and can be used to overcome other forms of energy found in the sample. We define the magnitude of the Zeeman energy by the scalar product of the magnetisation with the external magnetic field:

$$E_Z = -\mu_0 \vec{H} \cdot \vec{M} = -\mu_0 H M \cos \psi \quad (1.3)$$

where ψ is the angle between $\vec{H}$ and $\vec{M}$, and μ_0 is the magnetic permeability in vacuum. We can express the Zeeman energy in terms of the $\vec{H}$ and $\vec{M}$ components, as follows:

$$E_Z = -\mu_0 (H_x M_x + H_y M_y + H_z M_z) \quad (1.4)$$

In order to evaluate the equilibrium orientation of the magnetisation vector, it is useful to choose a coordinate system where the angular dependence of the magnetisation can be evaluated. In this way, it will be easier to find those angles which minimise the free energy. Therefore, we use a system with spherical coordinates, as illustrated in Figure 1.1:

Figure 1.1: Coordinate system for both the magnetisation and the external magnetic field

We define the $\vec{H}$ and $\vec{M}$ components as:

$$\begin{cases} M_x = M \cos \phi \sin \theta \\ M_y = M \sin \phi \sin \theta \\ M_z = M \cos \theta \end{cases} \quad (1.5)$$

and

$$\begin{cases} H_x = H \cos \phi_H \sin \theta_H \\ H_y = H \sin \phi_H \sin \theta_H \\ H_z = H \cos \theta_H \end{cases} \quad (1.6)$$

After introducing these expressions in the Zeeman energy term (Eq. 1.4), we obtain:

$$E_Z = -\mu_0 H M [\sin \phi \sin \theta_H \cos(\phi - \phi_H) + \cos \theta \cos \theta_H] \quad (1.7)$$

This equation is isotropic and depends on the direction of both $\vec{H}$ and $\vec{M}$

Exchange energy (E_{Ex})

This term deals with the tendency for adjacent atomic magnetic moments to align parallel to each other and with the same direction in ferromagnetic materials. If two atoms i and j have spin angular momentum ($S_i\hbar$) and ($S_j\hbar$), respectively, the exchange energy between them is given by:

$$E_{Ex} = -2J_{Ex}\vec{S}_i \bullet \vec{S}_j = -2J_{Ex}S_iS_j \cos \varphi \quad (1.8)$$

where J_{Ex} is known as the exchange integral and $\cos \varphi$ is the angle between the spins. If J_{Ex} is positive, E_{Ex} reaches a minimum when the spin are parallel ($\cos \varphi = 1$) and a maximum when the spin are antiparallel ($\cos \varphi = -1$). If J_{Ex} is negative, the lowest energy state results from antiparallel spins. However, it is clear that a positive value of J_{Ex} is a necessary condition for ferromagnetism to occur.

Shape Anisotropy (E_{Sh})

This term is related with the demagnetising field ($\vec{H}_{Des}$) inside the ferromagnetic sample and it is associated with the samples macroscopic size. Then, the preference for the magnetisation to be oriented along a particular axis of the sample, so that the magnetostatic energy can be minimised, is called shape anisotropy.

If a sample is saturated by an applied field and the field is removed, the magnetisation will decrease to the remanence state under the action of the demagnetising field ($\vec{H}_{Des}$). Assuming that the sample is magnetised uniformly, the demagnetising field is proportional to its magnetisation [31]:

$$\vec{H}_{Des} = -N_d\vec{H}_{Sat} \quad (1.9)$$

where N_d is the demagnetising factor and depends on the sample shape. Determining the demagnetising factors is not a trivial question. However, we can consider an ellipsoid shaped sample since in this special case both the magnetisation and the demagnetising field will be uniform [32]. An ellipsoid shaped sample is formed by a major axis x and axis y and z . Then N_x , N_y and N_z are values of the demagnetising factor N_d for magnetisation along the x , y and z axis. Moreover, the condition, in the International System,

$$N_x + N_y + N_z = 1 \quad (1.10)$$

is fulfilled for any ellipsoid. As the demagnetising factors of an ellipsoid depends upon its dimensions

$$N_x \neq N_y \neq N_z \quad (1.11)$$

the demagnetising field is therefore different for different orientations of the magnetisation. As a result, the magnetostatic or shape anisotropy energy is only minimised when the magnetisation lies along the major axis of the ellipsoid. Therefore, the long axis of the ellipsoid is called the easy-axis of magnetisation and the uniaxial shape anisotropy is given by

$$E_{Sh} = \frac{\mu_0}{2}(N_y - N_z)M_{Sat}^2 \quad (1.12)$$

Magnetisation is easy along the x axis and for $N_y = N_z$ hard along any axis normal to x . However, the experimental samples are rarely ellipsoids and different demagnetising factors should be considered. Some examples are illustrated in this Figure 1.2. Although we have assumed that the magnetisation is uniform and constant, we should note that is not true for non-ellipsoidal samples.

For a sphere we have $N_x = N_y = N_z = \frac{1}{3}$, the shape anisotropy term is zero and there will be no well-defined easy-axis of magnetisation associated to the macroscopic sample shape. For an infinite thin film, we have $N_x = N_y = 0$ and $N_z = 1$, the xy -plane is an easy-plane of

Figure 1.2: Demagnetising factors of a sphere (a), an infinite rod (b) and an infinite thin film (c).

magnetisation, the z -axis is a hard magnetisation axis and the shape anisotropy contribution is given by

$$E_{Sh} = \frac{\mu_0}{2} M_{Sat}^2 \sin^2 \vartheta \quad (1.13)$$

For the case of a cylinder we obtain $N_y = N_z = \frac{1}{2}$ and $N_x = 0$.

Magnetocrystalline anisotropy (E_{Cr})

The magnetocrystalline anisotropy describes the preference for the magnetisation to lie in a particular direction along certain crystallographic directions of the sample [33]. For a single crystal the external magnetic field, required to saturate the material, depends on the orientation of the applied magnetic field with respect to the crystal axes. This dependency creates axes in which the energy, required to magnetise the sample is lower. The dependence of the magnetic anisotropy with the crystal lattice occurs because the spins of the electrons, responsible for magnetism, are coupled to the orientation of the crystalline orbitals, the so called spin-orbit interaction [34]. Thus, in the absence of external field, the electron spin interacts with the electric field, generated by the ions of the crystal, and this interaction makes it easier for the magnetisation of the material to aligned in certain directions.

Let us consider a single crystal of a magnetic material which is saturated, i.e., the system as a whole behaves as a single magnetic domain. It is common to express the energy associated with this anisotropy as a series of powers with respect to the principal axes and the magnetisation. These are referred to as the direction cosines. Thus, the magnetocrystalline anisotropy for a ferromagnetic crystal is given by:

$$E_A(\alpha_1, \alpha_2, \alpha_3) = \sum_i b_i \alpha_i + \sum_{i,j} b_{ij} \alpha_i \alpha_j + \sum_{i,j,k} b_{ijk} \alpha_i \alpha_j \alpha_k + \dots \quad (1.14)$$

where $\alpha_1, \alpha_2, \alpha_3$ are the directional cosines of $\vec{M}$ with respect to a coordinate system in the crystal and $b_i, b_{ij}, b_{ijk}, \dots$ are magneto-elastic constantes. We must remember that this expression

Figure 1.3: Directional cosines of the magnetisation in spherical coordinates where θ and ϕ are the polar and azimuthal angles, respectively

is completely general and does not take into account the symmetry of the crystal.

The most common types of magnetocrystalline anisotropies are uniaxial and cubic. The uniaxial anisotropy can arise in crystals which exhibit hexagonal or tetragonal symmetry. In the hexagonal case, such as *hcp* (cobalt), the easy magnetization axis is parallel to the *c* crystallographic axis and the hard axis lies in the basal plane of the *hcp* crystal. It will be described below that this behaviour can be also generated by mechanical stresses induced during film growth due to the mismatch between the lattice constants of the substrate and the material [35]. On the other hand, the cubic anisotropy arises from a cubic crystal structure, such as found in iron and nickel.

i) Uniaxial Anisotropy

The uniaxial anisotropy is related to the fact that there is a single easy magnetisation axis, where the energy, required to saturate the sample, is minimum. In the following sections, we will consider a ferromagnetic material like cobalt with hexagonal symmetry. In this case, as was already commented, while the easy axis magnetisation direction is the hexagonal *c-axis*, other any direction in the plane perpendicular to the *c-axis* should be a hard axis. Therefore, the magnetisation is almost isotropic in the basal and the anisotropy energy can be approximated as [33]:

$$E_U = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots \quad (1.15)$$

for a given angle, θ , between the direction of magnetisation and the axis of symmetry, and where K_1 and K_2 are the anisotropy constants.

ii) Cubic Anisotropy

Cubic systems are very important since many ferromagnetic metals crystallise with this symmetry. For example, *Fe* crystallises in *bcc* structure and *Ni* in *fcc* structure [36]. Since a cubic crystal shows several equivalent directions, the general equation defining the magnetocrystalline anisotropy energy is simplified. It can be expressed in terms of a series expansion of the directional cosines of $\vec{M}_{Sat}$ with respect to the crystal axes. If $\vec{M}_{Sat}$ make angles α_1 , α_2 and α_3 with the crystal axes, and considering α_1 , α_2 and α_3 as the cosines of these angles, the energy of cubic anisotropy can be given by

$$E_C = K_0 + K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2\alpha_1^2\alpha_2^2\alpha_3^2 \quad (1.16)$$

where K_0 , K_1 and K_2 are constants for a particular material at a particular temperature and they can be expressed in erg/cm^3 (cgs) or J/m^3 (SI). Usually higher powers are not required since K_2 is usually much smaller than the leading terms, and this term can be neglected. The first term, K_0 , is independent of the angle and is usually ignored since normally we are interested only in changes in the energy E when the $\vec{M}_s$ vector rotates from one direction to another. When K_2 is zero, depending on the material, K_1 can be positive or negative. For instance, in *Fe* we have $K_1 > 0$ and the easy magnetisation axis is parallel to the $\langle 100 \rangle$ direction. For *Ni*, $K_1 < 0$ and the easy magnetisation axis is the direction $\langle 111 \rangle$.

1.2.2 Additional magnetic energies

Although the free energy of a ferromagnetic material is mainly composed of these energy terms, additional contributions may also exist, such as the magnetoelastic and surface anisotropy terms. For example, when ferromagnetic thin films are studied, these terms can also play a significant role.

Magnetocrystalline surface anisotropy (E_S)

In 1954, Néel pointed out that the proportion of atoms on the surface of a thin film is much higher when compared to the bulk material [37]. Surface atoms present different properties, due to reduced symmetry, with respect to the interior or bulk atoms of the material. Thus, the atomic layers of the surface atoms have magnetic properties which differ from those that are in the volume atoms due to symmetry breaking [38, 37, 39]. The surface anisotropy in films is manifest as a uniaxial anisotropy term which depends on the angle between the magnetisation and the film normal. Therefore, this anisotropy is known as surface anisotropy introduced by Néel [37], and is given by the equation.

$$E_S = -K'_S \cos^2 \theta \quad (1.17)$$

where K'_S is a constant that depends on the sample anisotropy.

Magnetoelastic anisotropy ($E_{M_{elas}}$)

One of the consequences of the spin-orbit interaction is the phenomenon of magnetostriction. This effect, which is associated to changes of the sample size due to the change of the magnetisation direction (and vice versa), can produce a magnetic anisotropy contribution. Therefore, and as the spin moments are coupled to the lattice via the orbital electrons, if the lattice is changed by a strain the distances between the magnetic atoms are altered and hence the interaction energies are modified. This effect produces the magnetoelastic anisotropy [40].

Usually thin films show mechanical stresses, applied in a particular direction, which arise during the preparation process or by the different lattice mismatch between the film and the substrate. This situation can be described by Eq. 1.23, where the magnetoelastic energy is presented as a function of the isotropic magnetostriction coefficient, λ_m , the uniform tension, σ , and the angle between the magnetisation and stress directions, θ [36].

$$E_{elas} = -\frac{3}{2}\lambda_m\sigma \cos^2 \theta \quad (1.18)$$

1.3 Nanomagnetism: dynamic point of view

We know that the magnetic moment of a homogeneously magnetised system is given by Equation 1.1. The magnetisation direction is determined by the minimisation of the free energy. In an isotropic system, the magnetisation direction, $\vec{M}$, is parallel to an effective field, $\vec{H}^{\text{eff}}$, which is defined by the magnetic anisotropy energy (see (a) in Figure 1.4) [28]. When this alignment

is altered by any external excitation, such as a magnetic field, electrical current or a laser pulse, the magnetisation will react to recover an equilibrium direction (see (b) in Figure 1.4). In this recovery, the magnetisation describes a precession movement around the effective field direction (see (c) in Figure 1.4).

Figure 1.4: (a) In equilibrium, the magnetisation of a thin film should be parallel to the effective field of the system. (b) When the magnetisation is changed out from its equilibrium position by a laser pulse (c), it will show a precessional motion around the effective field.

1.3.1 Larmor precession frequency

The precessional motion of the magnetic moment in the absence of damping is described by the torque equation. According to quantum theory, the angular momentum is associated with the magnetic moment by:

$$\vec{L} = \frac{\vec{m}}{\gamma} \quad (1.19)$$

where γ is defined as the ratio of the magnetic moment to the angular momentum and it is called the gyromagnetic ratio. The existing torque on the magnetic moment exerted by the external magnetic field is given by:

$$\vec{\tau} = \vec{m} \times \vec{H}_{\text{ext}} \quad (1.20)$$

Usually, the time variation of the angular momentum is defined as the torque, or

$$\vec{\tau} = \frac{d\vec{L}}{dt} = \frac{1}{\gamma} \frac{d\vec{m}}{dt} \quad (1.21)$$

Manipulating the previous equations, we obtain:

$$\frac{d\vec{m}}{dt} = \gamma(\vec{m} \times \vec{H}_{\text{ext}}) \quad (1.22)$$

Recalling the relationship between a product and a vector dot product, we observe that:

$$\vec{m} \cdot \frac{d\vec{m}}{dt} = 0 \quad (1.23)$$

Equation 1.23 means that the magnitude of the magnetisation should be preserved. Therefore, the application of a magnetic field to a magnetised sample generates a magnetisation precession at a given frequency ω_L , called the Larmor frequency,

$$\omega_L = \gamma H \quad (1.24)$$

Let's consider that for each magnetic moment of spin ($\vec{\mu}_i$) within a volume element, we have:

$$\frac{d\vec{\mu}_i}{dt} = -\gamma \vec{\mu}_i \times \vec{H} \quad (1.25)$$

Considering that $\vec{H}$ is uniform, we can average within the volume ΔV :

$$\frac{1}{\Delta V} \frac{d(\sum_i \vec{\mu}_i)}{dt} = -\gamma \left(\frac{\sum_i \vec{\mu}_i}{\Delta V} \right) \times \vec{H} \quad (1.26)$$

Considering that the magnetisation vector in a volume ΔV is given by the average volume of several discrete magnetic moments in a continuous medium, we can write:

$$\frac{d\vec{M}}{dt} = -\gamma \vec{M} \times \vec{H} \quad (1.27)$$

where $\frac{\sum_i \vec{\mu}_i}{\Delta V} \equiv \vec{M}$. This equation describes the magnetisation precession in an applied magnetic field. It is a conservative equation and implies a constant precession frequency or the Larmor frequency. However, it is an incomplete equation since in this kind of processes, dissipative effects should be also considered.

1.3.2 Landau-Lifshitz-Gilbert Equation

When quantum and anisotropy effects are considered to describe the magnetisation precession in a continuous medium, the dynamical model of Landau and Lifshitz is attained. In this model, the spins experience the action of an external magnetic field. They are also affected by the magnetocrystalline anisotropy, the demagnetizing field associated with shape anisotropy, magnetic dipole interaction, etc [3, 41]. The sum of all these contributions gives rise to a thermodynamic potential that is associated with an effective magnetic field, i.e.:

$$\vec{H}^{\text{eff}} = -\frac{\partial \Phi}{\partial \vec{M}} \quad (1.28)$$

Thus the motion of the magnetisation vector may be described according to the Landau-Lifshitz equation given by:

$$\frac{d\vec{M}}{dt} = -\gamma \vec{M} \times \vec{H}^{\text{eff}} \quad (1.29)$$

which describes the magnetic precession around the effective field direction, see Figure 1.5. As mentioned, $\vec{H}^{\text{eff}}$ contains many contributions:

$$\vec{H}^{\text{eff}} = \vec{H}_{\text{ext}} + \vec{H}_{\text{ani}} + \vec{H}_{\text{dem}} + \dots \quad (1.30)$$

with the exception of $\vec{H}_{\text{ext}}$, all other contributions depend on the characteristics of the material.

At equilibrium, the variation of the angular momentum with time is zero showing that the torque is also zero. An extra contribution, the viscous damping term, can be added to describe the motion of precession. However, Equation 1.29 cannot describe the relaxation of $\vec{M}$ to $\vec{H}^{\text{eff}}$ after

being brought out of equilibrium and therefore we need to invoke a damping term. This dissipative term reduces the precessional motion the magnetic moment and consequently the magnetisation tends toward a position of equilibrium. Usually this relaxation proceeds slower than the precession and we can model it as a damping torque perpendicular to the precessional motion, with the precessional motion itself unperturbed by the damping. This leads to the famous Landau-Lifshitz-Gilbert equation:

$$\frac{d\vec{M}}{dt} = -\gamma\vec{M} \times \vec{H}^{\text{eff}} + \gamma \frac{\alpha}{|\vec{M}|} \vec{M} \times \frac{\partial \vec{M}}{\partial t} \quad (1.31)$$

where α is the Gilbert damping constant. Figure 1.5 shows the dynamics of the magnetisation precession around the effective field according to the Landau-Lifshitz-Gilbert equation (illustration both precessional and damping terms).

Figure 1.5: Illustration of the precessional spin dynamics described by the Landau-Lifshitz-Gilbert equation. The magnetisation precesses around the effective field. A small damping torque gradually aligns the magnetisation with the effective field. Figure adapted from [2]

1.3.3 The Smit-Beljers equation

To solve the Landau-Lifshitz-Gilbert equation, we must to use an appropriate system of coordinates. Recalling that the magnitude of the magnetisation is not changed, we can choose the spherical coordinate system. Thus, $\vec{H}^{\text{eff}}$ in spherical coordinates is given by:

$$\vec{H}^{\text{eff}} = -\frac{1}{\mu_0} \left(\frac{\partial F}{\partial r} \hat{e}_r + \frac{\partial F}{\partial \theta} \hat{e}_\theta + \frac{1}{M_s \sin \theta} \frac{\partial F}{\partial \phi} \hat{e}_\phi \right) \quad (1.32)$$

where F is the free energy per volume, and θ and ϕ are the polar and azimuthal angles, respectively (see Figure 1.3). In this coordinate system, the magnetisation is given by $\vec{M} = M_s \hat{e}_r$, where M_s is the saturation magnetisation. The infinitesimal change in the magnetisation vector can be expressed as $d\vec{M} = M_s(dr\hat{e}_r + d\theta\hat{e}_\theta + \sin\theta d\phi\hat{e}_\phi)$. Thus, the variation of magnetisation in relation to time can be written as:

$$\frac{d\vec{M}}{dt} = M_s \frac{d\theta}{dt} \hat{e}_\theta + M_s \sin \theta \frac{d\phi}{dt} \hat{e}_\phi \quad (1.33)$$

Performing the cross product $\vec{M} \times \vec{H}_{\text{ext}}$ and $\vec{M} \times \frac{d\vec{M}}{dt}$ and substituting in Landau-Lifshitz-Gilbert equation, we obtain:

$$\frac{d\theta}{dt} = -\frac{\gamma}{M_s \sin \theta} \frac{\partial F}{\partial \phi} + \alpha \sin \theta \frac{d\theta}{dt} \quad (1.34)$$

$$\frac{d\phi}{dt} = -\frac{\gamma}{M_s \sin \theta} \frac{\partial F}{\partial \theta} - \frac{\alpha}{\sin \theta} \frac{d\phi}{dt} \quad (1.35)$$

These are the nonlinear equations in spherical coordinates. As there is not an exact analytical solution, we must find perturbative solutions around the equilibrium configuration, assuming small deviations of both θ and ϕ around the equilibrium positions θ_0 and ϕ_0 . Therefore, the free energy F can be expanded in a Taylor series and considering only first-order terms, we obtain:

$$F(\theta, \phi) = F(\theta_0, \phi_0) + \frac{1}{2} \left(\frac{\partial^2 F}{\partial \theta^2} \theta^2 + \frac{\partial^2 F}{\partial \theta \partial \phi} \theta \phi + \frac{\partial^2 F}{\partial \phi^2} \phi^2 \right) \quad (1.36)$$

The solutions should be:

$$\begin{aligned} \delta\theta &\approx \theta - \theta_0 = A_\theta \exp(i\omega t) \\ \delta\phi &\approx \phi - \phi_0 = A_\phi \exp(i\omega t) \end{aligned} \quad (1.37)$$

where A_θ and A_ϕ are the amplitude of the precession. Inserting the calculated $d\theta/dt$ and $d\phi/dt$, from Eq. 1.37, and considering the Eq. 1.36, into the Landau-Lifshitz-Gilbert equation in spherical coordinates, the precession frequency of the magnetisation can be described by:

$$\omega^2 = \frac{\gamma^2(1 + \alpha^2)}{M_s^2 \sin^2 \theta} \left[\left(\frac{\partial^2 F}{\partial \theta^2} \right) \left(\frac{\partial^2 F}{\partial \phi^2} \right) + \left(\frac{\partial^2 F}{\partial \theta \partial \phi} \right)^2 \right] \quad (1.38)$$

This equation is known as the Smith-Belers equation. It is interesting to note that the frequency of precession is given by the partial derivatives of the magnetic free energy with respect to the polar and azimuthal angles of the magnetisation in their equilibrium values. This representation is therefore very practical since the resonance condition can be directly evaluated from the relevant free energy of a magnetic system, though it must be performed in conjunction with the equilibrium conditions:

$$\frac{\partial F}{\partial \theta} = 0 \quad \text{and} \quad \frac{\partial F}{\partial \phi} = 0 \quad (1.39)$$

1.4 Ultrafast spectroscopy applied to Nanomagnetism

In modern magnetism, one of the principal objective is to develop new high-performance magnetic structures beyond the current technologies of recording and processing of information that are of the order of $\text{Terabit}/\text{cm}^2$ with a switching time of a few nanoseconds and below [42]. Therefore, it is necessary to investigate the dynamic properties of magnetic materials and nanostructures that occur on a shorter timescale, compared with the switching time of magnetic devices, and for a length scale below a few hundred nanometers.

Standard ultrafast spectroscopy techniques are suitable methods for exploring the interaction mechanisms responsible for the modification of the magnetic order in nanostructures subjected to an external perturbation at temporal scales from a few femtoseconds to a few nanoseconds (see Figure 1.6) [1, 22, 24]. Such mechanisms include the spin-orbit interaction, the exchange interaction, the structural anisotropy of the materials and the spin-phonon interaction among the most relevant.

The first high-impact result in observing the magnetisation dynamics in magnetic films induced by femtosecond laser pulses using a pump-probe configuration was reported in 1996 by Beaurepaire et al. [22]. In this paper, it was shown that a Ni thin film can be demagnetised by a 60 fs laser pulse (see Figure 1.7) showing a magnetic response below 1ps. The three-temperature model for magnetisation dynamics has been invoked to help explain the sub-ps demagnetisation observed by Beaurepaire et al. The model assumes that the electron, the spins and lattice systems represent

Figure 1.6: Time scales in magnetism as compared to magnetic field and laser pulse excitation. Figure obtained from Ref. [3]

three mutually-interacting thermal reservoirs. The internal equilibration of the reservoirs occurs at the plasma frequency (electron), the spin-wave frequency and the phonon scattering rate (lattice).

After this first observation, much experimental effort was directed to confirm this finding in Nickel [43] as well as in a wide range of magnetic materials, such as other transition metals [44, 45], magnetic semiconductors [46], dielectrics [47] and half-metals [48]. Since then, manipulating and controlling magnetisation with ultrafast laser pulses have become a new field in modern magnetism and it is known as Femto- Magnetism [3, 1, 22, 42]. Studies in femto-Magnetism has attracted much research activity in order to understand the fundamental mechanisms and to control and manipulation of magnetisation on ultrafast timescale. Usually, changes in length and orientation of the magnetisation vector caused by an intense femtosecond laser pulse are probed using a lower intensity second pulse. This approach uses the magneto-optical pump-probe configuration [3, 42] based on the Kerr or Faraday effects. In order to attain information with femtosecond resolution, other techniques have also been employed such as the second harmonic generation [43], photo-emission [49] and more recently, the x-ray magnetic circular dichroism techniques [50].

Despite the huge effort, even in the study of the simplest materials such as ferromagnetic Ni , the underlying basic mechanisms that govern the demagnetisation process at the femtosecond timescale have not yet been fully identified. Then, the challenge lies in the complexity of a parallel, dynamic treatment of photons, electrons, phonons and the spins on various length and time scales. Currently, several groups are working on this topic and their results have generated an intense discussion about the physical interaction that allows the transfer of angular momentum between the reservoirs in the magnetisation and re-magnetisation processes. In fact, the mechanism responsible for the variation of angular momentum in this time scale, remains an open question. Next we show some microscopic models, found in the literature, that attempt to explain the issue of spin angular momentum transfer during ultrafast demagnetisation.

1.4.1 Direct Interaction between Photons and Spins

The direct interaction (at a microscopic level) between pump laser photons and spins for ul-

Figure 1.7: Dependence of remanent magnetization (normalised to the signal without the presence of the pump beam) in a ferromagnetic *Ni* film with the delay between pump and probe beams (Figure extracted from Ref. [22])

trafast demagnetisation was first proposed by Zhang and Hubner in 2000 [51]. According to these authors, ultrafast demagnetisation occurs in the presence of both the field of the external laser and the spin-orbit coupling, when spin-orbit coupling smears out singlet and triplet states allowing for optically induced spin flips. A discussion regarding the validity of this type of microscopic model should consider whether the number of photons, absorbed in the magnetic material due to laser irradiation, is large enough to explain the experimentally observed magnitude of magnetisation [52, 53]. Moreover, when the pump laser photons serve as the source for the angular momentum needed to flip a spin, the demagnetisation must proceed differently when the pump laser beam is linearly or circularly polarized. Moreover, when the pump laser photons serve as the source for the angular momentum needed to flip a spin, the demagnetisation must proceed differently when the pump laser beam is linearly or circularly polarized. However, Dalla Long et al. [54] found that changes in the polarisation of the laser in MOKE measurements are purely due to optical artifacts and magnetisation dynamics remain unchanged. Furthermore, Zhang and Hubner predicted a demagnetisation of around 50% of the magnetic moment in *Ni*. In contrast, magnetisation reductions in the order of 70 – 80% from the initial magnetic moment value have been observed experimentally [55]. Moreover, and according to Zhang and Hubner, ultrafast demagnetisation proceeds almost instantaneously and the observed time constant is given by the pump pulse length. However, the measurements of the demagnetisation time constant are typically larger than the laser pulse duration, for example in rare earths, such as *Tb* and *Gd*, the demagnetisation occurs on a time scale of 750 fs for a laser pulse of 50 fs [56]. Bigot et al. [1] proposed a similar microscopic mechanism, which additionally takes a laser field induced time-dependent modification of the spin-orbit interaction into account. However, this model is also susceptible to the same kind of criticisms as the Zhang and Hubner model.

1.4.2 Electron-Phonon Spin-flip Scattering

Koopmans et al. [57] proposed that during the ultrafast demagnetisation, the spin angular momentum is transferred to the lattice by way of phonon mediated spin-flip scattering. This spin-flip scattering is the Elliot-Yafet type [58, 59], which is found in paramagnetic metals. In

this case, each electron-phonon scattering event can lead to a spin flip with a probability α_{EY} , and depends on the material properties.

The Elliot-Yafet type relaxation mechanism of the electron spins occur because the spin-orbit interaction, induced by the ions of the lattice this means that the electron wave function would be a mixture of spin-up or spin-down states. Thus, the momentum scattered by phonons, impurities and defects can be coupled to the spin-up and spin-down states and leading the electron spin relaxation [59].

The modification of the Elliot-Yafet scattering in ferromagnetic metals [60] went through several stages. We can start by identifying α_{EY} , as being responsible for relaxation in sub-ps regime, and/or the Gilbert damping parameter that governs precessional dynamics on the time scale of hundreds of picoseconds [57, 61]. However, this behaviour was not confirmed when $Ni_{80}Fe_{20}$ doped with rare earth were studied [62]. In contrast to Koopmans et al. [57] predictions, and although the rare earth act as a doping agent that modifies the ferromagnet Gilbert damping parameter, changes in the demagnetisation time constants were not observed.

Koopmans et al adopted the model three temperature with an Elliot-Yafet-like spin-flip channel (microscopic three-temperature model) where the underlying spin-flip probability was calculated from ab-initio density functional theory [53]. The rate of demagnetisation, due to electron-phonon spin-flip scattering, and whether it is large enough to explain experimental observations is however contested. Carva et al. [63] found that the rate of demagnetisation distributions of thermalized electrons, assumed in the microscopic three-temperature model, was very small, and only a marginal increase for non-equilibrium distributions occurs in pump-probe experiments. Essert et al. [53] also concluded that the electron-phonon spin-flip scattering is not the dominant process behind the ultrafast demagnetisation and emphasized the importance of changes in the dynamics of the band structure which was not included in the microscopic three-temperature model.

1.4.3 Superdiffusive Spin Transport

A Superdiffusive Spin Transport microscopic model to explain the origin of ultrafast demagnetisation was proposed by Battiato et al. [64]. In this model, there is no a channel for transferring spin angular momentum, i.e., spin flips, and the reduction of magnetization is explained by spin-dependent transport of charge carriers out of a ferromagnetic layer. Superdiffusive refers to carrier transport which has a ballistic character at the beginning but moves towards diffusive transport for longer times scales, and is thus not correctly described by either the ballistic or diffusive approximation for all timescales.

In the model of the Battiato et al. [64] the Superdiffusive Spin Transport leads to ultra-fast demagnetisation as follows: Due to the pump laser irradiation in a ferromagnetic layer, electrons are excited from quasi-localized d-bands to more mobile sp-bands. In this excitation, the spin angular momentum is assumed to be conserved. Subsequently, electrons are transported superdiffusively out of the excited sample volume into the substrate. Due to the fact the majority and minority electrons have different lifetimes, resulting in a higher mean free path for majority electrons, magnetisation is transported away from the probed volume on a sub-ps timescale. Since the modelling of superdiffusive spin transport involves the treatment of the electron scattering processes leading to their thermalisation explicitly, the non-equilibrium state after laser excitation is included by default as well as the usual assumption of instant thermalisation via the two temperature model. Also, the specific material band structure is included via the energy- and spin-dependent electron lifetimes. The amount and timescale of demagnetisation, resulting from superdiffusive spin transport, were calculated for a 15nm thick Ni film on an Al substrate, and these results were found to coincide with time-resolved XMCD measurements performed by Stamm et al. [65].

1.5 Challenges in ultrafast magnetisation dynamics

How fast can the magnetisation of a magnetic medium or element be changed or what are

the fundamental and practical speed limitations in the magnetic writing and reading processes? These questions are connected with a lot of exciting research that addresses very fundamental issues of spin and magnetisation dynamics as well as very practical points such as how to generate and detect them. Finding ultimate limits for the preparation and handling of physical systems is one of the most challenging objectives of fundamental science. In the context of magnetic materials such limits will affect future information storage technologies regarding storage density and time scales for accessing and writing information. Currently, the fastest pulses that have been used to manipulate magnetic structures are laser pulses in the range of 40 femtoseconds [3, 1]. The fundamental theory, which describes the ultrafast magnetisation dynamics, is far from being understood, even 19 years after the first experimental demonstration.

Magnetic information storage technology is rapidly approaching the nanometer scale as storage densities are projected to increase to a terabit per square inch. This necessity represents new challenges and opportunities in nanometer scale materials engineering and in understanding their related magnetic properties. Among the critical issues, is the understanding of how and how fast the magnetisation direction could be switched from one stable configuration to another. There are currently several fundamental issues which remain poorly understood, including the role of thermal fluctuations, the basic mechanism of damping in magnetisation motion, and the ultimate speed with which magnetisation can be reversed.

Although experimental results begin to converge, they still fail to answer a fundamental question to what does TRMOKE really probe, a simple optical excitation artefact (charge origin) or a genuine magnetic excitation (spin origin)? [66]. Answering this question means having confidence in the TR-MOKE tool to probe the ultrafast dynamics of magnetisation. Zhang, et al [66], attempted to answer this question through simulations using laser pulses of 12 fs. In these simulations it was possible to verify that the pulse duration has a substantial effect on the correlation between the magnetic and optical responses. By constructing a phase-sensitive polarisation versus magnetisation plot, Zhang, et al found that for short pulses the magnetic signals are delayed by 10 fs with respect to the optical signals. For longer pulses, the delay shortens and the behaviour approaches the continuous-wave response.

Therefore, in the context discussed so far, it is fundamental that a short duration of the pulse is used to excite and probe the magnetisation dynamics, thus allowing to observation of the interactions between the electrons, spin and lattice. Considering this requirement, we propose to develop a pump-probe system with high temporal resolution (sub-8 fs). The development of the system will be addressed in this thesis in the following chapters.

1.6 About this thesis

This thesis was divided as follows:

Chapter 2

We will show important concepts for the understanding of femtosecond laser pulses, in particular we will make a mathematical review of the time and frequency domain. Next we will discuss the sources for the generation of these pulses. Finally we will show the methods used for making the temporal characterisation of ultrashort laser pulses.

Chapter 3

In this chapter we will discuss the main all-optical pump-probe techniques and also their limitations. Next we will describe the phenomenology of the magneto-optical effect and the experimental setup used to measure this effect. This stage is fundamental for the development of a TR-MOKE system with high temporal resolution.

Chapter 4

In this chapter we will make a detailed description of all the stages of our system including optical components, the characterisation of pulses and the data acquisition system.

Chapter 5

In chapter 5 we will use this system to measure magnetic precession and ultrafast demagnetisation in ferromagnetic films of GdFeCo and then compare with existing results in the literature to show the reliability of our system.

Chapter 6

Finally, in Chapter 6 will summarise the conclusions and indicate some future perspectives of this work.

Chapter 2

Ultrafast Optical Pulses

This chapter gives a brief introduction into the world of femtosecond laser pulse and the most frequently used techniques to measure such ultrashort pulses, i.e., the first part the aim is to give a concise introduction to provide basic information about the most-widely used femtosecond laser sources, in particular Ti:sapphire oscillators, Ti:sapphire amplifiers, etc. The second part, is devoted to the diagnostic techniques used in the present work which allow the measurement of these ultrafast events. The aim of this chapter is to present the tools used, of the point of view of ultrafast optical, in the development of pump-probe experimental apparatuses in the femtosecond range.

2.1 Introduction

The term ultrafast lasers is often used for mode-locked lasers emitting ultrashort pulses, i.e. pulses with durations less than a few picoseconds ($10^{-12}s$). A more precise term is actually ultrashort pulse lasers. For example, in the reference [14] is reported the generation of pulses comparable to the duration of the electric field cycle. In the optical domain, this corresponds to around 2 fs ($1fs = 10^{15}s$). In addition to ultrashort durations, ultrashort pulses have a broad spectrum, a high peak intensity and can form pulse trains at a high repetition rate. Therefore, it is important to acknowledge the relationship between spectral width and pulse duration when considering the generation of ultrashort pulses.

The general time and frequency Fourier transforms of a pulse can be expressed in terms of the electric field as [16]:

$$E(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} E(\omega) e^{-i\omega t} d\omega \quad (2.1)$$

$$E(\omega) = \int_{-\infty}^{+\infty} E(t) e^{i\omega t} dt \quad (2.2)$$

where $E(\omega)$ and $E(t)$ represent the frequency and time evolution of the electric field of the pulse, respectively. The duration and spectral bandwidth of a pulse can then be calculated with standard statistical definitions [16],

$$\langle \Delta\omega^2 \rangle = \frac{\int_{-\infty}^{+\infty} \omega^2 |E(\omega)|^2 d\omega}{\int_{-\infty}^{+\infty} |E(\omega)|^2 d\omega} \quad (2.3)$$

$$\langle \Delta t \rangle = \frac{\int_{-\infty}^{+\infty} t |E(t)|^2 dt}{\int_{-\infty}^{+\infty} |E(t)|^2 dt} \quad (2.4)$$

It can be shown that the relationship between the duration and spectral bandwidth of the laser pulse are related by the following inequality (relation to uncertainty principle):

$$\langle \Delta t \rangle \langle \Delta \omega \rangle \geq \frac{1}{2} \quad (2.5)$$

This relationship is the product of pulse duration and spectral bandwidth and is known as the time-bandwidth product. In principle this means that in order to produce a light pulse with a given duration it is necessary to use a broad enough spectral bandwidth. For example, a Gaussian pulse lasting for one picosecond (10^{-12} s) has a minimum spectral bandwidth of $\Delta\omega = 4.41 \times 10^{11}$ Hz. If the central frequency ν_0 of the pulse lies in the visible part of the electromagnetic spectrum, say $\nu_0 = 4.84 \times 10^{14}$ Hz (wavelength $\lambda_0 = 620$ nm), then the relative frequency bandwidth is $\Delta\nu/\nu_0 \approx 10^3$. But for a 100 times shorter pulse ($\Delta t = 10$ fs), $\Delta/\nu_0 \approx 0.1$. As $|\Delta\lambda/\lambda_0| = \Delta\nu/\nu_0$, the wavelength extension of this pulse is 62 nm, covering 15% of the visible window of the electromagnetic spectrum. Taking into account the wings of the spectrum, a 10 fs pulse actually covers most of the visible window. If the equality is reached in one speaks about a Fourier-transform-limited pulse or simply a transform-limited pulse. From the experimental point of view, half-maximum quantities are easier to measure; the Fourier inequality is then usually written as:

$$\Delta\nu\Delta t \geq K \quad (2.6)$$

where $\Delta\nu$ is the frequency bandwidth measured at full-width at half-maximum (FWHM) with $\omega = 2\pi\nu$ and Δt is the FWHM in time of the pulse and K is a number which depends only on the pulse shape (see Table 2.1). One can also calculate the minimum time duration of a pulse giving a spectrum with $\Delta\lambda$ (nm) at FWHM, central wavelength λ_0 (nm) and the speed of light c (m/s):

$$\Delta t \geq K \frac{\lambda_0^2}{\Delta\lambda \cdot c} \quad (2.7)$$

Shape	E(t)	K
Gaussian function	$\exp[-(t/t_0)^2/2]$	0.441
Exponential function	$\exp[-(t/t_0)/2]$	0.140
Hyperbolic secante	$1/\cosh(t/t_0)$	0.315
Rectangle	—	0.892
Cardinal sine	$\sin^2(t/t_0)/(t/t_0)^2$	0.336
Lorentzian function	$[1 + (t/t_0)^2]^{-1}$	0.142

Table 2.1: Values of K for various pulse shapes, in the inequality $\Delta\nu\Delta t \geq K$, when $\Delta\nu$ and Δt are half-maximum quantities [16]

2.2 Mathematical background of ultrashort lasers pulses

2.2.1 Temporal domain

An ultrashort optical pulse consists of a real-valued oscillating electric field (see Figure 2.1), but the mathematical description can be simplified if a complex representation is used (at the origin ($x = 0$)):

$$E(t) = A(t)e^{-i\omega_0 t} \quad (2.8)$$

where $A(t)$ is the complex amplitude envelope, and ω_0 is the carrier frequency, usually chosen to be close to the center of gravity of the spectrum. In this representation the rapidly oscillating part of the electric field can be separated from the slowly varying envelope $A(t)$. The complex electric field can be further decomposed:

$$E(t) = |E(t)|e^{-i\phi_0}e^{-i(\phi(t)+\omega_0 t)} \quad (2.9)$$

Figure 2.1: Electric field of a 4-fs Gaussian pulse with 800 nm center wavelength. The thin solid and the dashed line represent the electric field for different values of the carrier-envelope offset phase. Obviously, different maximum amplitudes are reached for the two cases. The envelope is shown as the thick solid curve

Here $|E(t)|$ is referred to as the electric field envelope, $\phi(t)$ is the temporal phase and ϕ_0 is the absolute phase, which relates the position of the carrier wave to the temporal pulse envelope (see Figure 2.1). For this reason ϕ_0 is also called the carrier-envelope phase (CEP) [67]. It is particularly relevant for few-cycle pulses and its measurement and control [68, 14] are crucial pre-requisites for optical metrology [69] and single attosecond pulse generation [70].

If the temporal phase $\phi(t)$ changes with time, the oscillation period of the electric field also becomes a function of time. In this case the instantaneous frequency is varying in time and the pulse is called "chirped" (see Figure 2.2) and is described by the instantaneous frequency $\omega(t)$ given by

$$\omega(t) = \omega_0 + \frac{d\phi(t)}{dt} \quad (2.10)$$

2.2.2 Frequency domain

For many purposes it is more convenient to represent a pulse in the frequency domain rather than in the time domain. Similar to the time domain, we can write:

$$E(\omega) = |E(\omega)|e^{i\phi(\omega)} \quad (2.11)$$

where $\phi(\omega)$ is called the spectral phase. We should note that the temporal electric field $E(t)$ can be regarded as a superposition of monochromatic waves with frequency ω , spectral amplitude $|E(\omega)|$ and phase $\phi(\omega)$.

2.2.3 Spectral phase

For ultrashort pulse the spectral phase is generally assumed to be a smooth function which can be written using Taylor series expansion around ω_0 , the central frequency, as:

Figure 2.2: (a) Unchirped pulse; (b) chirped pulse showing the variation of instantaneous frequency. [4]

$$\phi(\omega) = \phi_0 + \phi'(\omega - \omega_0) + \frac{1}{2!}\phi''(\omega - \omega_0)^2 + \frac{1}{3!}\phi'''(\omega - \omega_0)^3 + \dots \quad (2.12)$$

where the first ϕ_0 term corresponds the absolute phase. This term is extremely important in highly nonlinear effects and few-cycle pulses [67, 68, 14]. The second term ϕ' represents the group delay, i.e. the arrival time of the pulse. The effect of this term in the spectral domain is a translation in time. The term ϕ'' , called group delay dispersion (GDD), leads to a linear variation in delay with frequency (see Figure 2.2 (b)). This imparts a linear chirp to the output pulse. The term ϕ''' , usually named third order dispersion (TOD), leads to a quadratic variation in delay with frequency. This results in an asymmetric pulse distortion with an oscillatory structure (see Figure 2.3). The higher order terms induce additional phase shifts resulting in further pulse chirping and distortion.

Figure 2.3: (a) Phase (solid line) and frequency-dependent delay (dashed line) vs. frequency for a cubic spectral phase; (b) calculated intensity profile. [5]

2.3 The Problem of Dispersion

2.3.1 Dispersive media

When a short pulse travels through a dispersive medium, its component frequencies are separated in time and space. Figure 2.4 shows the effect of dispersion on an arbitrary ultrashort pulse travelling through a piece of glass. There are two points to note. First, the center of the pulse is delayed with respect to a pulse travelling in air. This is usually called the group delay, which is not a broadening effect. Second, normally dispersive media such as glass impose a chirp on the pulse, meaning that the blue components are delayed with respect to the red. In summary, the propagation of a short optical pulse through a transparent medium results in an increase in temporal pulse duration. The pulse broadens with time but, from energy conservation, its time-integrated intensity remains constant [16]. The effects of propagation on a pulse can be studied particularly well in the frequency domain. We consider the propagation of a rightward-traveling light pulse through a linear dispersive medium of length L . The dispersive character of the medium is described by a refractive index $n(\omega)$ where ω is the angular frequency. Furthermore, we assume that the pulse is transform-limited, when it enters the medium. Each spectral component experiences a phase shift

$$\phi(\omega) = k(\omega)n(\omega)L = \frac{\omega}{c}n(\omega)L \quad (2.13)$$

by passing through the linear medium. In Equation 2.13 $k = \omega/c$ denotes the vacuum wavenumber, where c is the light velocity in vacuum. The refractive index dependence on wavelength (or frequency) is very similar in many transparent and non-transparent media in the visible and near infrared ranges. This can be described by the well-known Sellmeier formula [71]:

$$n(\lambda) = \sqrt{1 + \sum_{i=1}^m A_i \frac{\lambda^2}{\lambda^2 - C_i^2}} \quad (2.14)$$

In this thesis the Sellmeier formula was used to calculate the total dispersion of the components of our experimental setup (lenses, prisms, air, etc.). In this way, it was possible to quantify the amount of dispersion we should compensate (see Chapter 4).

Figure 2.4: When a pulse of light is passed through a medium and subject to normal dispersion, the short-wavelength components, indicated in blue, travel slower than those at longer wavelengths. Adapted from [6].

2.3.2 Dispersion compensation

The pulse broadening effects of GDD can be reversed and recompressed by using pairs of prisms [72], gratings [73] or chirped mirrors [74].

Gratings

Figure 2.5: Grating pairs used in the control of dispersion. The different wavelengths are dispersed in space and made to travel different paths.

In the method of compressing pulses by pairs of gratings (Figure 2.5) the pulses are spectrally separated by the first grating, the second grating compensates the spatial dispersion, the mirrors shift up and reflect back the beam. In between the gratings the optical way of each spectral component is different, so that the arrival time at the output is the same for all spectral components (induces/compensates a linear "chirp" leading to an increase/decrease of the pulse length). In case of compression, the desired pulse length can be set by the distance in between the gratings. This technique leads to compression of pulses down to 30 fs and is still extensively used due to the high amount of negative dispersion obtainable in this way.

Prisms

In this method, the chirped pulse enters prism 1 and the beam spreads as it is then diverted towards prism 2. As Figure 2.6 shows, a prism disperses the different wavelengths of light into different angles, due to the wavelength dependence on refractive index in the prism. The system introduces a negative GDD and the magnitude of this created GDD can be controlled by the amount of glass in the prism. The total system GDD is compensated by orienting the prisms so the light travels through either more or less of the glass. The prisms are almost less dispersive than gratings, so that larger distances between prisms are needed to provide enough spatial separation between the different spectral components. Furthermore, because the light has to traverse glass, there is intrinsic material dispersion that limits the amount of total negative dispersion achievable.

Double-Chirped Mirrors (DCM)

According to Figure 2.7, a DCM is an optical interference coating that in general consists of four multilayer subsections deposited on a substrate [7, 75]. For dispersion-compensating broadband high reflectors dielectric materials, such as SiO_2 is used. The first section of a DCM is a broadband AR coating, which typically consists of 8 to 14 layers. The double-chirp section is necessary for the avoidance of Gires-Tournois interferometer (GTI)-like oscillations in the group delay [76, 7]. Double-chirping means that the local Bragg wavelength of the index grating and the local coupling

Figure 2.6: Grating pairs used in the control of dispersion. The different wavelengths are dispersed in space and made to travel different paths. The relative time delay between the frequencies caused by the prism pair compensates for the time delay caused by other dispersive material.

of the incident wave to the reflected wave are chirped simultaneously. The chirp of the duty cycle (coupling coefficient) leads to an adiabatic matching of the impedance of the grating to the low-index layer at the front. In the subsequent simple-chirp section only the Bragg wavelength is chirped. This means that the high- and low-index layers are quarter-wave layers for maximum reflection of waves with a wavelength close to the local Bragg wavelength. The fourth section is a quarterwave Bragg mirror with fixed Bragg wavelength. The third and fourth sections are optional and depend on the special design problem considered. However, they are required to obtain ultimate broadband reflectance.

Figure 2.7: Schematic drawing of a DCM. which is composed of four multilayer subsections. The position inside the mirror is determined by the variable m , where $m = 0$ defines the beginning of the theoretical DCM structure directly after the AR coating. Light, with wavenumber k , is reflected at the wavenumberdependent classical turning point $m_{t_l}(k)$. [7].

The advantage of such approach is that a mirror can be specifically designed to have a phase curve that matches a given target, e.g., a glass (see Figure 2.8), and the reflectivity is usually very high (typically over 97%). Also they are quite compact, which is important in the development of our experimental setup. In this thesis we use this method to compensate the dispersion of our experimental apparatus (for details see Chapter 4).

Figure 2.8: DCMs characteristics. Each blue-green mirror pair provides a net GDD of 60 fs^2 per bounce (at 800 nm). This chirped mirror has bandwidth compatible with the spectral range of the beams used in our experimental setup.

2.4 Ultrafast lasers and Amplifiers: Generation of ultrashort pulses

2.4.1 Oscillator

Ultrashort pulses are generated by a mode-locked laser. By constructive interference, a short pulse is formed when many longitudinal modes are held in phase in a laser resonator (see Figure 2.9). In other words, in a laser cavity, many longitudinal modes oscillate on different frequencies within the range supported by the gain medium. If these modes oscillate with random relative phase, the laser oscillator generates continuous wave light (CW operation). However, if the modes are phase-locked to each other, they will interfere constructively at certain times, resulting in a train of potentially short pulses. This mode of operation is called mode-locking. There are several techniques to achieve mode-locking, of which the most commonly used for ultrashort Ti:Sapphire lasers is Kerr lens mode-locking (KLM). It employs the optical Kerr effect to establish a phase relation between adjacent laser modes without the need for external modulation (passive mode-locking). Since the Kerr effect (Appendix A) depends non-linearly on the intensity, the Kerr lens, due to self-focusing [77] in the laser crystal, only occurs for short pulses in the cavity. If a mechanism is introduced into the cavity which favors the mode-locked light over the continuous light, eventually only modes which are phase-locked will survive in the cavity. With Kerr lens mode-locked Ti:Sapphire lasers, sub-10-fs pulses can routinely be generated and even sub-5-fs pulses have been produced directly. A detailed description can be found in many standard texts [78, 79] and review articles [80, 81].

2.4.2 Amplifier

Chirped pulse amplification (CPA) has enabled the creation of ultrafast lasers with high pulse energies and very short pulse lengths [82]. In CPA, a short seed pulse (laser Ti:Sapphire, for example) is dispersed using a diffraction gratings, greatly stretching the pulse so that it can be amplified without harming the gain medium and the pulse itself. After amplification, a second set of gratings or prism recompresses the pulse (see Figure 2.10). The output pulse duration is longer than the seed pulse duration, because the spectral bandwidth of the pulse is reduced during amplification through the gain-narrowing effect [83]. In other words, CPA is only able to amplify the pulse in wavelengths inside the gain curve of Ti:Sapphire. As such, it can only produce spectra up to 50 nm wide (FWHM), which limits the output duration to $\sim 20 \text{ fs}$.

Figure 2.9: Superposition of resonator modes. While a mode number of 5 results in a long pulse duration $\Delta\tau$ (blue), pulses with a spectral width $\Delta\nu$ of 50 modes are much shorter (red). The gain bandwidth determines the shortest duration obtainable for the pulses.

Figure 2.10: Conceptual schematic of a chirped-pulse amplification-based laser system. A dispersive element is used to make the pulse longer (sometimes, a glass element, or as shown some other dispersive element, such as a grating stretcher), typically to durations of a few picoseconds to hundreds of picoseconds. The pulse can then be safely amplified while keeping instantaneous intensities below to damage threshold. After amplification, the pulse generally has a smaller bandwidth due to gain-narrowing in the amplification process. Negative dispersion is then introduced to compress the pulse in time, typically to approximately 30 fs . Adapted from [8].

2.4.3 Spectral Broadening in a Hollow Fiber

The generation of ultrashort high energy pulses has been achieved by CPA combined with Ti:sapphire laser technology. By using this technique, it is possible to obtain pulses in the order of $20\text{--}100\text{ fs}$. However, this method has shown some limitations such as the gain-narrowing effect. In order to generate radiation in the sub-5fs regime, a high energy pulse compression technique with pulses created by CPA can be employed. This technique consists in two stages: nonlinear spectral broadening and dispersion compensation [84, 85] (see Figure 2.11). The nonlinear nature of the spectral broadening process, originating mainly from self-phase modulation (SPM) (Appendix A), provides a broader spectrum in the center space of the beam where the intensity of the pulse is higher. The spectral broadening stage and subsequent propagation after this stage induces dispersion in the setup - to obtain the pulse with the shortest duration (i.e. flattest spectral phase) one needs to compensate for this dispersion. For this purpose one employs a dispersion compensation stage, normally composed of chirped mirrors capable of inducing negative dispersion [14].

Figure 2.11: Illustration of our experimental setup for spectral broadening. The pulse is focused with a lens with appropriate focal distance and is inserted in a pressurized gas chamber, being then coupled into the hollow fiber. When exiting the hollow fiber and gas chamber the pulse has been spectrally broadened. The pulse then travels to the dispersion compensation stage and is then ready to be used in experiments. adapted from [9].

2.5 Characterization Ultrashort Pulses: Conventional method and the D-scan technique

There are several techniques for ultrashort pulse characterization autocorrelation (AC) [86], frequency-resolved optical gating (FROG) [86, 87] and spectral phase interferometry for direct electric-field reconstruction (SPIDER) [86, 88] are most commonly used. Autocorrelation is simple and convenient, but can give only the autocorrelation width; the waveform and phase is difficult to obtain. FROG is a two dimensional measurement technique, where pulse waveform and phase can be retrieved from the FROG trace, but an iterative procedure is needed. SPIDER can directly extract spectral phase and reconstruct the pulse waveform. Recently a new method has been developed to characterize ultrashort laser pulses called d-scan (or dispersion scan) [89]. With this method, it is possible to obtain the duration and phase of the pulses. In this section two methods used for the characterization of our pulses will be described namely: the autocorrelation (Interferometric and Intensity) and d-scan techniques.

2.5.1 Interferometric Autocorrelation

The Setup for an interferometric autocorrelator is showed in Figure 2.12). A nonlinear crystal is used to generate the second harmonic (appendix B) at the output of a Michelson interferometer in a collinear geometry.

In this case, the signal recorded by a "slow" detector is $I(\tau)$ is called the interferometric autocorrelation and can be expressed using the equation below. This Equation 2.15 contains some information about the phase of the pulse: the fringes in the autocorrelation trace wash out as the spectral phase becomes more complex.

$$I(\tau) = \int_{-\infty}^{+\infty} |[E(t) + E(t - \tau)]|^2 dt \quad (2.15)$$

The duration of the input pulse is calculated from the FWHM. In the graph we can see that there is a contrast ratio of 8:1 (see Figure 2.13). This is due to two reasons: 1) When the pulses are

Figure 2.12: Michelson interferometer for collinear version. Adapted from [10].

not completely overlapping, the autocorrelation signal is constant and equal to twice the integral of intensity on the time; 2) When the pulses are overlapped (zero delay) the total electric field is twice the pulse's field. The theoretical contrast between the peak value of an Interferometric Autocorrelation and its background is a good check for the quality of a measurement.

Figure 2.13: Simulation of an interferometric autocorrelation shown the relation 8:1.

2.5.2 Intensity Autocorrelation

In an Intensity autocorrelation setup, first an incoming pulse is split into two parts. A path length difference is introduced between the parts, resulting in a delay, τ , between them. Finally both beams are recombined in a nonlinear optical medium like a SHG crystal and the output is measured, as shown in Figure 2.14.

An intensity autocorrelation trace $I(\tau)$ depends on the intensity I of the two incoming pulses as

$$I(\tau) = \int_{-\infty}^{+\infty} I(t)I(t - \tau)dt \quad (2.16)$$

It can be shown that the intensity autocorrelation width of a pulse is related to the intensity width by a numerical factor [10]. For example, for a hyperbolic secant squared (sech^2) profile,

Figure 2.14: Interferometer for noncollinear Intensity autocorrelation. Adapted from [10].

the numerical factor is 1.54. This numerical factor, which depends on the shape of the pulse, is sometimes called the deconvolution factor. If this factor is known, or assumed, the time duration (intensity width) of a pulse can be measured using an intensity autocorrelation. It is obvious from Equation 2.16 that the intensity autocorrelation does not contain full information about the electric field of the pulse, since the phase of the pulse in the time domain is completely lost.

2.5.3 D-scan technique

An ultrashort laser pulse can be described by its complex spectral amplitude:

$$U(\omega) = |U(\omega)|e^{i\phi(\omega)} \quad (2.17)$$

In Section 2.3 we saw that when a pulse goes through a dispersive medium, the electric field acquires a additional phase. Then, we can write:

$$U(\omega) = |U(\omega)|e^{i\phi(\omega)}e^{i\frac{\omega}{c}n(\omega)z} \quad (2.18)$$

When the pulse goes through a SHG crystal, a second harmonic $U_{2\omega}(\omega)$ will be generated. We can use a simple model to write down the second harmonic electric field $U_{2\omega}(\omega)$ using the following steps [11]:

$$U(\omega) \xrightarrow{F^{-1}} U(t) \xrightarrow{\wedge^2} U(t)^2 \xrightarrow{F} U_{2\omega}(\omega) \quad (2.19)$$

So, we can write the spectral intensity of the second harmonic as:

$$S(\omega) = |U_{2\omega}(\omega)|^2 = A \left| \int \left(\int |U(\Omega)|e^{i\Omega t} d\Omega \right)^2 e^{-i\omega t} dt \right|^2 \quad (2.20)$$

where A is a constant, which contains all the omitted constants, and Ω represents the frequency of the second Fourier transform. So, applying Equation 2.20, the SHG spectrum as a function of the glass thickness z is then:

$$S(\omega, z) = A \left| \int \left(\int |U(\Omega)|e^{i\phi(\Omega)}e^{i\frac{\Omega}{c}n(\Omega)z} d\Omega \right)^2 e^{-i\omega t} dt \right|^2 \quad (2.21)$$

where $S(\omega, z)$ is the spectral intensity of the SHG measured by the spectrometer as a function of z , $n(\Omega)$ is given either by the manufacturer of the glass wedges, $|U(\Omega)|$ is the fundamental spectrum, is also measured by a spectrometer.

This simple SHG model assumes that the nonlinearity has infinite bandwidth, or at least that the spectral response is flat in the region of interest, which is seldom the case for pulses in the few-cycle regime and under normal experimental conditions. Therefore, this method consists in measuring the fundamental power spectrum and guessing the spectral phase that reproduces the measured SHG trace, $S(\omega, z)$. Furthermore, this technique can be implemented using chirped

Figure 2.15: Simplified schematic of the experimental setup of the d-scan.

mirrors that introduce negative dispersion in the pulse, a pair of wedges which introduces glass in the propagation of the pulse after the chirped mirrors, a crystal for the SHG and a spectrometer to measure the SHG signal (see Figure 2.15).

In order to find the phase from the 2D scans, which consist of SHG spectra as a function of glass insertion is used an iterative algorithm that uses the measured fundamental spectrum, and tries to find which spectral phase best recreates the measured scan. So using this algorithm it is possible to reconstruct the phase and width of the pulse (see Figure 2.16). This approach has some advantages from a bandwidth point of view: since all the generated wavelength components depend, to some degree, on the generating wavelength components, the phase can be retrieved even when some wavelengths are not phase-matched, or are purely absent.

Figure 2.16: Temporal characterisation of an ultrafast oscillator with the d-scan technique [11]. The fundamental spectrum (c) and the SHG spectra as a function of glass insertion (a) were measured. An iterative algorithm applies phases to the fundamental spectrum and simulates the SHG process to recreate (b) the measured trace. From this retrieved phase (c) the pulse can be reconstruct in the time domain (d).

2.6 Summary

In this chapter, the mathematical concepts to describe ultrashort optical pulses are briefly reviewed. Two equivalent physical pictures are introduced: the time-domain representation and the frequency-domain description, which are connected by a Fourier transform. The effect of propagation of a pulse through a dispersive medium in which the refractive index n depends on frequency has as a consequence the increase of temporal pulse width. This effect and possible solutions are discussed in this chapter. The generation of ultrashort, intense infrared pulses is discussed here, starting with the generation of short pulses by Ti:Sapphire oscillators followed by their amplification using the chirped-pulse amplification. The amplified pulses can subsequently be compressed down to sub-4 fs through spectral broadening, which is achieved with the hollow fiber method. The final part in this chapter, is devoted to the diagnostic techniques used in the present work which allow the measurement of these ultrafast events namely, d-scan and autocorrelation techniques.

Chapter 3

Experimental technique I: Methods for investigating magnetisation dynamics

This chapter presents a brief summary of the all-optical pump-probe approach that allows access to the magnetisation dynamics. We show the important techniques that are used to investigate ultrafast magnetisation dynamics. Next, we present the origin of the magneto-optical Kerr effect. This effect is the basis of most of the techniques that investigate magnetisation dynamics in optical systems. There is then a detailed description of the experimental MOKE system developed in this thesis. This is the starting point for the femto-MOKE system that will be presented in the next chapter.

3.1 Methods for studying magnetisation dynamics

Generally, in the study of magnetic processes in pump-probe methodology the magnetisation is first taken out of equilibrium and its relaxation such to its equilibrium position is recorded. Due to the timescale of these processes, it is possible to separate the near-adiabatic processes, which occur on a timescale from several picoseconds up to nanoseconds, and the strongly non-adiabatic processes, which occur on a timescale from femtosecond up to picoseconds after the excitation. The near-adiabatic processes include long wavelength spin waves [90], dynamics of the domain walls [91], and field- and current induced magnetisation switching [92]. In the case of strongly non-adiabatic processes we consider the mechanism of ultrafast demagnetisation (see Sections 1.4 and 1.5). Therefore, to measure processes that occur on a timescale from several picoseconds up to nanoseconds the following techniques can be used Kerr microscopy [93], spin-polarised photoemission electron microscopy [94], ferromagnetic resonance [95, 96], Brillouin light scattering [97], etc. While processes that occur on an even shorter timescale can be investigated by the time-resolved Kerr effect [3, 1, 22, 98], Time-resolved second harmonic generation [3], etc. The techniques presented here for the study of ultrafast demagnetisation dynamics on a femtosecond time scale ($< 100\text{fs}$) are based on pump-probe methods, described in the following section.

3.2 Pump-probe methods

Usually, studies of ultrafast laser-induced magnetisation dynamics are performed using the pump-probe method, where the magnetisation dynamics is triggered by an ultrashort laser pulse in the optical range, while detection of the laser-induced magnetic changes is made with the help of a second laser pulse. In other words, this method consists of using two beams which reach the sample with a precisely controlled temporal delay between them. While a first is used to excite

the sample (pump), the second (probe) measures the dynamical response of the material to the excitation. As the pump is more intense than the probe, changes in the equilibrium condition of the sample should be induced. Then, the measurements are made by monitoring changes in the intensity and/ or polarisation state of the probe (reflected or transmitted by the sample) as a function of the temporal delay with the pump (see Figure 3.1).

Figure 3.1: Generic illustration of the pump-probe methods in reflection. (a) Degenerate system. (b) Non-degenerate system

Pump-probe systems have been classified into two types: degenerate systems where both pump and probe beams have the same spectral bandwidth or frequency (Figure 3.1a). Or the non-degenerate systems where the pump and probe have different spectral bandwidths (Figure 3.1b). The non-degenerate setups are frequently referred to the literature as dual-colour pump-probe systems [98]. The temporal resolution or the sensitivity of these techniques is related with the characteristics of both the pump and the probe pulses. For example, the choice of the probe spectrum in the infrared [1, 99], ultraviolet [100] or x-ray [101] spectral regimes should define the study of specific elements or electronic transitions which are responsible for the interaction of the probe with medium. As a result, all spectroscopic methods are characterised by different sensitivity to spin and orbital degrees of freedom. In the following section most important all optical techniques for the study of ultrafast magnetisation are presented.

3.2.1 Time-resolved Kerr effect (TR-MOKE)

TR-MOKE investigations are based on repeated excitation of magnetisation dynamics, usually by magnetic field pulses or by intense light pulses [3, 98]. The resulting excitations are then stroboscopically detected making use of the magneto-optical Kerr effect (see section 3.3). Therefore, this technique provides an insight into the magnetisation dynamics in the time domain. The temporal resolution of this technique is directly related to the optical pulse duration used in the experiment. It is common process to use a FFT of the temporal trace of the MOKE signal to transfer to the frequency domain. Here the excitation frequencies can then be obtained.

3.2.2 Time-resolved Second-harmonic generation (TR-SHG)

In this case TR-SHG is also based on the all-optical approach. It differs from TR-MOKE in that the magnetic contrast originates by magnetic second-harmonic generation, i.e., from the nonlinear response of the ferromagnetic sample in an intense laser field. The polarisation, $P(2\omega)$, (see appendices A and B), results in the phenomenon of second-harmonic generation when the medium excited by the optical field $E(\omega)$ with a high intensity generates light at the double frequency 2ω . The intensity of the second harmonic light in ferromagnets can be found to be [3]:

$$I(2\omega) \sim |P(2\omega)_i|^2 = [\chi_{ijk}^{nl} E_j(\omega) E_k(\omega) + \alpha_{ijk}^{nl} E_j(\omega) E_k(\omega) M(0)_l]^2 \quad (3.1)$$

where χ_{ijk}^{nl} and α_{ijk}^{nl} are tensors that define the optical properties of the medium, and the superscripts l (nl) indicate the linear (nonlinear) response, respectively. From this equation we can see that the second-harmonic generation can also be used as a measure of the magnetisation $M(0)$. However, in contrast to linear magneto-optical effects, the second harmonic in the electric dipole approximation is generated only in media in which the crystallographic symmetry does not contain a center of inversion. In centrosymmetric media second-harmonic generation is thus only allowed at surfaces and interfaces where the bulk symmetry is broken. Consequently, the magnetic second-harmonic generation technique can serve as a unique tool for probing surface and interface magnetism [3].

3.2.3 Limitations in degenerate and non-degenerate systems

As mentioned in the previous sections, the techniques based on probe-pump methodology can be degenerate, non-degenerate and the temporal resolution is associated with the duration of the pulses. There are some limitations in both cases these are discussed below.

Coherent signal problem

Let's consider the case of a degenerate system. An important problem in these systems lies in the fact that the pump can contaminate the signal from the probe, i.e., close to zero delay, an interference between pump and probe can give rise to temporal oscillation of the probe and can be transmitted to the measured signal (this problem was observed in our experiment). This effect is so called coherent signal problem also referred to as coherent artifact" (see Figure 3.2b) [12, 102]. There are two possibilities of interfering pump pulses [102]. One is due to the scattering from the surface of samples. The other is due to the diffraction from the transient grating in materials (see Figure 3.2a). From more details in Reference [102]. As a consequence of this diffraction grating, part of the pump beam is reflected in the same direction as the probe beam and both contributions are sent to the data acquisition system.

Figure 3.2: (a) Schematics of a reflection-type pump-probe measurement and the generation of a transient grating in materials. (b) The shape of a coherent artifact signal with well-pronounced regular structure measured at a high resolution. From [12].

In order to overcome this problem, several methods have been suggested. For example, using cross polarisation between the both pulses for removing or reducing the contributions of the reflected pump beam [102], have been explored. Another problem that could limit the interpretation of experimental measurements in degenerate systems is the physical mechanism known as state blocking [100]. State blocking, or dichroic bleaching, is the transient saturation of an optical transition by the pump pulse. When both pump and probe pulses are applied to a magnetic material using the same spectral range and polarisation, the pump can saturate the same transition accessed by the probe. This effect can generate a nonmagnetic contribution to the measured signal. State-blocking artifacts can be suppressed by using different spectral ranges for pump and probe pulses.

Temporal pulse width

In the literature, most all-optical TR-MOKE experiments developed for study of ultrafast magnetic phenomena are based on optical parametric amplifiers (OPAs). The temporal resolution of these technique is determined by the available laser pulse width. OPAs, generally, are commercially available in the temporal regime of picoseconds and femtoseconds. OPAs in the femtosecond are pumped by Ti:sapphire lasers with central wavelength at 800 nm , energy between 0.5 and 1 mJ with pulse duration ranging from 50 to 150 fs . So, one of the major limitations in all-optical TR-MOKE is related to temporal resolution, typically on the limit of 40 fs [3, 1].

Therefore, in Chapter 4 we present a detailed explanation of a new experimental TR-MOKE dual-colour setup based on the Magneto-optic effect Kerr. The our methodology proposed eliminates contamination of the pump in addition to providing sample pulses with a large spectral width, which gives pump and probe lengths of the order of sub-8fs in the sample.

3.3 Magneto-optic effect Kerr (MOKE)

Figure 3.3: Illustration of the effect MOKE. The Kerr rotation occurs when the linearly polarised incident wave with components circularly polarised to right and left are reflected with different refractive indices for left and right, and, therefore, different velocity of propagation. Two angles allow to characterise the elliptic polarisation of the light: Kerr rotation (θ_K) and the Kerr ellipticity (ε_K).

In general, we can separate two distinct classes of materials which exhibit magneto-optical phenomena. First, the magneto-optical effect results from the direct action of the magnetic field external on the orbital motion of the electrons, such as the Faraday effect [103] or magneto-circular dichroism (different absorption frequencies due to different polarisations) [104]. Second, the effect

results from the direct spin-orbit coupling, known as the Kerr effect (polarisation change, i.e., rotation and elliptical effects on the reflected light) in ferromagnetic materials [103]. As shown in Figure 3.3, the MOKE signal results from changes in the polarisation state of the incident light when it is reflected by a magnetised sample. From the microscopic point of view, the MOKE effect is based on the spin-orbit interaction and the coupling between the electron spin of the medium and the movement of its orbits perturbed by magnetic fields [103]. From a macroscopic point of view, one can describe the phenomenology of the MOKE through a dielectric permittivity tensor. This tensor can be calculated using the Maxwell's equations [105].

Three different experimental Kerr configurations are distinguished: polar, longitudinal and transversal (see Figure 3.4):

Figure 3.4: The three different types of MOKE effect: (a) Polar where the magnetisation is parallel to the plane of incidence and perpendicular to the magnetic film surface, (b) Longitudinal where the magnetisation is in the direction parallel to the plane of incidence and oriented in the plane of magnetic film (c) Transversal where the magnetisation is perpendicular to the plane of incidence and oriented in the plane of magnetic film.

3.3.1 Theory

In general, the dielectric tensor, $\tilde{\varepsilon}_{ij}$, which characterises the electrical property of a medium, can be decomposed into symmetric and anti-symmetric parts [106, 107], where the symmetric part can be diagonalised. The symmetric part does not contribute to the magneto-optical effect and it is assumed that it is isotropic with the dielectric constant ε [107]. The following expression represents the coupling of the anti-symmetric terms in the dielectric tensor to the magnetisation of a sample:

$$\tilde{\varepsilon} = \varepsilon \begin{vmatrix} 1 & -iQ_z & iQ_y \\ 1 & 0 & -iQ_x \\ -iQ_y & iQ_x & 0 \end{vmatrix} \quad (3.2)$$

Two normal modes can be derived from Maxwell's equations for an electromagnetic wave in a medium with a dielectric tensor of the form Equation 3.2. These modes are left-handed and right-handed circularly polarised light with refractive index, respectively;

$$n_L = n \left(1 - \frac{1}{2} \vec{Q} \cdot \vec{k} \right) \quad (3.3)$$

$$n_R = n \left(1 + \frac{1}{2} \vec{Q} \cdot \vec{k} \right) \quad (3.4)$$

where $\vec{Q} = Q_x, Q_y, Q_z$ contains magnetic information of the material and is known as the Voigt vector [108, 109], $\vec{k}$ is the unit vector along the direction of the light propagation. The complex Kerr rotation is proportional to the difference between n_R and n_L , which leads to the expression $\Phi_k = \theta_k + i\epsilon_k$, where θ_k is the Kerr rotation and ϵ_k is the Kerr ellipticity [106, 107]. Therefore the

magneto-optic effect can be equivalently described by two different complex indices of refraction for light of right- and left-handed circular polarisation. The two circular modes travel in the medium with different velocities and are attenuated differently resulting in rotation and elliptical effects on the reflected light.

In the case where the light is reflected at a nonzero incidence angle, it is convenient to decompose the incident and reflected light into p- and s-polarised plane waves, for which the polarization vector is in the plane of incidence and perpendicular to it, respectively. In order to make the link between the reflected field $\vec{E}^r$, and the incident field $\vec{E}^i$ using the unit vectors $\hat{e}_p$ and $\hat{e}_s$, we have considered that $\vec{E}^i$, linearly polarised, propagating in a dielectric medium of refractive index n_1 , forming an angle θ_1 with the incidence plane, and is reflected with an angle θ_2 from a magnetic medium with refractive index n_2 (see Figure 3.5). Thus, the reflection event is described by the following complex matrix relation [110, 111]:

$$\begin{bmatrix} E_p^r \\ E_s^r \end{bmatrix} = \begin{bmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{bmatrix} \begin{bmatrix} E_p^i \\ E_s^i \end{bmatrix} \quad (3.5)$$

where r_{ij} are the Fresnel coefficients. These coefficients are complex numbers which depend on the optical properties of the sample such as the complex refractive index n , the complex Voigt constant Q , and the polar, longitudinal and transversal magnetisation components. We need to find the Fresnel coefficients. However, this work has been done in the references [110, 111]. In Figure 3.5 θ_1 and θ_2 are the incidence and refraction angles, respectively, and they are related through the Snell's law [112].

Figure 3.5: Coordinate system used in the calculations of the Fresnel coefficients

3.3.2 Experimental setup

The experimental L-MOKE setup used in our experiment is presented in Figure 3.6. A laser pulse, generated in the amplifier system + hollow fiber, is used as the light source (more details in chapter 4). The generated probe beam has a spectral bandwidth between $550 - 650 \text{ nm}$ with a temporal duration of $7,4 \text{ fs}$ (see chapter 4). A polariser is used to guarantee that the incident

light is linearly polarised and it is focused on the sample using lens. After the reflection from the magnetic sample, the divergent beam is focused by a second lens onto a half-wave plate and the analyser. In our analysis, the reflected beam signal is separated into the s and p components and they are balanced by the half wave plate. The signal difference is measured using balanced amplified photodetector that acts as a balanced receiver by subtracting the two optical input signals from each other, resulting in the cancellation of common mode noise. This protocol allows us to observe small changes in the signal path extracted from the interfering noise floor.

Figure 3.6: Simplified experimental MOKE setup

3.3.3 Sample

In this work we have samples which consist of a 20-nm thick film of the ferrimagnetic rare earth-transition metal (RE-TM) amorphous alloy $Gd_{23}Fe_{68}Co_9$ with out-of-plane anisotropy. These were provided by the Kimel Group at Radboud University Nijmegen, Netherlands. The sample was grown by magnetron sputtering with the following multilayer structure: glass—AlTi (10 nm)—SiN(5nm)—GdFeCo(20 nm)—SiN(60 nm) (see Figure 3.7a). The AlTi layer serves as a heat sink and the SiN as buffer and capping layers. The latter also serves as an antireflection coating. This sample $Gd_{23}Fe_{68}Co_9$ alloys is ferromagnetic, where the Fe and Gd sublattices are coupled antiferromagnetically (see Figure 3.7b), while the Co magnetic moments are parallel to those of iron. These alloys are widely used in magneto-optical recording and known for their strong magneto-optical effects [113]. Depending on the RE ion concentration, RE-TM alloys can exhibit magnetisation and angular momentum compensation temperatures, T_M and T_A respectively, where the magnetisation (angular momentum) of the RE and TM sublattices are equivalent and, therefore, the net magnetisation (angular momentum) is zero (see Figure 3.7c) [13].

3.3.4 Boxcar averager systems

In order to acquire the signal from each component separately, we have used balanced amplified

Figure 3.7: (a) Typical structure of a GdFeCo sample, on either a float glass substrate or a SiN membrane. (b) Antiferromagnetic alignment of the magnetic moments of the constituent sublattices with respect to the external magnetic field of a generic ferromagnetic. (c) RE and TM sublattices show very different temperature dependencies which leads, in a certain concentration range, to the appearance of magnetisation compensation T_M . Adapted from [13].

photodetectors, model PDB210A, which have two acquisition channels. However, the response time of this kind of detector is on the order of 400 ns. Comparing the detection time with the laser repetition rate, 1 KHz, we verify that the signal is not continuous, but it is a pulse train. This fact happens because the time between two consecutive pulses ($1ms$) is larger than the detector time response. In other words, the detection time of our system should be improved. A way to solve this problem, allowing the observation of a continuous signal in our acquisition system, has been achieved by using a gated integrator and boxcar averager system [114]. Moreover, this method increases the signal/noise ratio because the signal is integrated over a chosen time-window.

The working principle of a gated integrator boxcar is illustrated in Figure 3.8. It is shown how the laser trigger signal synchronizes the gate and the laser pulse. During a controlled time, the gate is opened and the signal is measured. Then, the gate closes until a new trigger signal is received and new data are acquired. The measured signal for each gate is proportional to the selected time-window. The signal/noise ratio is controlled by changing the size and position of the gate.

Figure 3.8: Operation of a gate integrator boxcar in static mode, i.e., fixing the gate against the trigger signal.

We can improve the signal/noise ratio through of the averaging function in the device. Let us assume that the input signal is given by V_{signal} and the signal to noise ratio by V_{noise} , when V_{noise} is the standard deviation of the noise signal. As the noise signals, measured at different times, are uncorrelated, the resulting noise is given by the root of the sum of squares of the standard deviations of the stochastic signals, i.e. $(V_{noise})^2 = (V_{noise1})^2 + (V_{noise2})^2$ (in statistics this quantity is known as the cross-correlation of two independents events). Thus the averaged signal after N measurements is given by:

$$V = \frac{1}{N} \sum_{i=1}^N V_{signal,i} + \frac{1}{N} \sqrt{\sum_{i=1}^N (V_{noise})^2} = V_{signal} + \frac{1}{\sqrt{N}} \sqrt{(V_{noise})^2} \quad (3.6)$$

Thus the signal/noise ratio after N measurements is given by:

$$\frac{V_{signal}}{V_{noise}} = \frac{V_{signal}}{\frac{1}{\sqrt{N}} \sqrt{(V_{noise})^2}} \propto \sqrt{N} \quad (3.7)$$

3.4 Analysis of the MOKE signal

The calculation of the electric field vector after the interaction of the light with the optical components (the polariser, the lenses, the magnetic sample, the analyser and eventually the half-wave plate) has been realized using the Jones matrix formalism [115]. Thus, the electric field vector, $\vec{E}^t$, corresponding to the light after its interaction with the system, is expressed as a function of the electric field vector of the incident ligth, $\vec{E}^i$, using the equation:

$$\vec{E}^t = \mathbf{J}_{system} \vec{E}^i \quad (3.8)$$

where the $\mathbf{J}_{system}$ represents the Jones matrix associated to the optical system. Thus the polarisation of the electric field after a sequence of n optical devices can be easily determined if the respective Jones matrices are known. Therefore, we can write the Jones matrix of the system as the product of the Jones matrix of each element. In our system:

$$\mathbf{J}_{system} = \mathbf{J}_{analyser} \cdot \mathbf{J}_{waveplate} \cdot \mathbf{J}_{sample} \cdot \mathbf{J}_{polariser} \quad (3.9)$$

Obviously, the elements of the Jones matrix depend on the chosen coordinate system. Thus, if $\mathbf{J}$ and $\mathbf{J}'$ are representations of a Jones matrix in the bases $\{\hat{e}_x, \hat{e}_y\}$ and $\{\hat{e}'_x, \hat{e}'_y\}$, respectively, both matrices must be transformed according to the relationship:

$$\mathbf{J}' = \mathbf{T}(\beta) \cdot \mathbf{J} \cdot \mathbf{T}(-\beta) \quad (3.10)$$

$$\mathbf{J} = \mathbf{T}(-\beta) \cdot \mathbf{J}' \cdot \mathbf{T}(\beta) \quad (3.11)$$

where

$$\mathbf{T}(\beta) = \begin{bmatrix} \cos \beta & \sin \beta \\ -\sin \beta & \cos \beta \end{bmatrix} \quad (3.12)$$

If the axis $\hat{e}'_x$ is rotated by an angle β in relation to the vector $\hat{e}_x$. The Jones matrices for the analyser, half-wave plate and magnetic sample is described separately.

Polariser (analyser)

The polariser component consists of a birefringent medium, that is used to separate a beam of light into its orthogonal polarisation states for isolation or routing. When this component is used to analyse the light polarisation after its reflection from the magnetic sample, it is called an analyser.

The field transmitted by a polariser in direction $\hat{e}_x$ is given by:

$$\vec{E}^t = \vec{E}_x^i \hat{e}_x \quad (3.13)$$

where $\vec{E}_x^i$ is the component in direction $\hat{e}_x$ of the field incident on the polariser. Then, if $\hat{e}_x$ makes an angle θ_p with the axis $\hat{e}_p$, the Jones matrix of the Glan-Thompson polariser can be expressed [115]:

$$\mathbf{J}_p = \begin{bmatrix} \cos^2 \theta_p & \sin \theta_p \cos \theta_p \\ \sin \theta_p \cos \theta_p & \sin^2 \theta_p \end{bmatrix} \quad (3.14)$$

However, it is known that it is convenient to use the relationship $\hat{e}_x = \sin \theta_p \hat{e}_p + \cos \theta_p \hat{e}_s$, which allows us to express the polarisation of the field after the polariser, in the form of the Jones vector:

$$\vec{E}^t = \begin{bmatrix} \cos \theta_p \\ \sin \theta_p \end{bmatrix} \vec{E}_x^i \quad (3.15)$$

Half-wave plate

This optical component aims to introduce a phase ϑ in the component of the electric field parallel to slow axis relative to the component parallel to the fast axis. Thus, the transmitted field by a half-wave plate can be written as:

$$\vec{E}^t = e^{-i\vartheta} \vec{E}_{fast}^i \hat{e}_{slow} + \vec{E}_{fast}^i \hat{e}_{slow} \quad (3.16)$$

We consider that the slow axis is rotated an angle θ_r relative to the axis $\hat{e}_p$. Representing $\vec{E}^t$ in the $\{\hat{e}_p, \hat{e}_s\}$ base, we obtain:

$$\mathbf{J} = \mathbf{T}(-\theta_r) \cdot \begin{bmatrix} e^{-i\vartheta} & 0 \\ 0 & 1 \end{bmatrix} \cdot \mathbf{T}(-\theta_r) \quad (3.17)$$

From which, we obtain the Jones matrix for the general case of a wave plate:

$$\mathbf{J}_{wp} = \mathbf{T}(-\theta_r) \cdot \begin{bmatrix} \sin^2 \theta_r + \cos^2 \theta_r e^{-i\vartheta} & \sin \theta_r \cos \theta_r (e^{-i\vartheta} - 1) \\ \sin \theta_r \cos \theta_r (e^{-i\vartheta} - 1) & \cos^2 \theta_r + \sin^2 \theta_r e^{-i\vartheta} \end{bmatrix} \cdot \mathbf{T}(-\theta_r) \quad (3.18)$$

We are interested in special case where $\vartheta = \pi$. The Jones matrix for this particular case is known as half-wave plate, i.e.

$$\mathbf{J}_{\lambda/2} = \begin{bmatrix} \cos(2\theta_r) & \sin(2\theta_r) \\ \sin(2\theta_r) & -\cos(2\theta_r) \end{bmatrix} \quad (3.19)$$

The half-wave plate rotates the polarisation plane by an angle $2\theta_r$ relative to the $\hat{e}_p$ axis.

Signal detection

As already mentioned, the reflected light exhibits elliptical polarisation and may be described with the aid of a complex angle $\varphi = \varphi' + i\varphi''$ [116], i.e.

$$\vec{E}^r = \begin{bmatrix} \cos \varphi \\ \sin \varphi \end{bmatrix} |\vec{E}| \quad (3.20)$$

where the intensity $|\vec{E}|$ is given by:

$$|\vec{E}|^2 = |r_{pp} \cos \theta_0 + r_{ps} \sin \theta_0|^2 + |r_{sp} \cos \theta_0 + r_{ss} \sin \theta_0|^2 \quad (3.21)$$

So far, the described system is sensitive to changes in the polarisation of the incident beam. Thus, the polarisation of the incident beam on the analyser is given by the equation

$$\begin{bmatrix} E_p \\ E_s \end{bmatrix} = \begin{bmatrix} \cos(2\theta_r) & \sin(2\theta_r) \\ \sin(2\theta_r) & -\cos(2\theta_r) \end{bmatrix} \begin{bmatrix} \cos \varphi \\ \sin \varphi \end{bmatrix} |\vec{E}| \quad (3.22)$$

When the reflected beam passes through the analyzer is divided into two polarisation components (s and p). These two components are focused on a detector with two channels allowing the analysis of each signal separately and also the difference between them.

In general, magneto-optical effects are small, being of fundamental interest to optimize the MOKE magnetometer to obtain maximum sensitivity [117]. For the polar and longitudinal Kerr effects we achieve a good sensitivity on the Kerr rotation (θ_k) of the polarisation plane by performing a differential measurement of the two components (s and p) of the reflected light. If Δ is the difference between the intensity of these two signals and $|\vec{E}^r|$ is the amplitude of the reflected light, we obtain

$$\Delta = |\vec{E}^r|^2 (\cos^2 \theta_k - \sin^2 \theta_k) = |\vec{E}^r|^2 \cos^2(2\theta_k) \quad (3.23)$$

and the sensitivity is therefore given by

$$\frac{d\Delta}{d\theta_k} = -2|\vec{E}^r|^2 \sin^2(2\theta_k) \quad (3.24)$$

being maximum for $\theta_k = 45^\circ$. Upon hitting the sample, the reflected light has a high electric field component in the plane of incidence (small θ_k) because the incident wave was initially linearly polarised in that plane (E_p). To maximize the sensitivity of the setup, we place (after the sample) a $\lambda/2$ wave plate with its optical axis rotated $22,5^\circ$ relative to the p-plane. The beam will then emerge from the plate with its polarisation plane rotated $\sim 45^\circ$ ($2 \times 22,5^\circ$) relative to the p-plane, since the reflected. Therefore, considering the case where $2\theta = 45^\circ$ the intensities of p-polarised and s-polarised beam are given by:

$$I_s = \frac{|\vec{E}|^2}{2} |\cos \varphi + \sin \varphi|^2 \quad (3.25)$$

$$I_p = \frac{|\vec{E}|^2}{2} |\cos \varphi - \sin \varphi|^2 \quad (3.26)$$

Using some trigonometric relations, we can rewrite the above equations as:

$$I_s = \frac{|\vec{E}|^2}{2} (\cosh 2\varphi'' + \sin 2\varphi') \quad (3.27)$$

$$I_p = \frac{|\vec{E}|^2}{2} (\cosh 2\varphi'' - \sin \varphi') \quad (3.28)$$

To characterize a linearly polarised beam,

To characterise an elliptical polarisation we need to know two parameters: the angle between the polarisation and the fast axis (for exemple) and the ellipticity (ϵ). These two parameters were incorporated in the definition of the complex angle φ . It is particularly useful if the polarisation is almost linear $\epsilon \approx 0$ and $\theta \approx 0$, which corresponds to a polarisation field parallel to $\hat{e}_p$. Assuming that $\theta = \theta_0 + \eta$ with $\eta \ll 1$, we can write

$$\varphi = \theta_0 + \eta + i\epsilon \quad (3.29)$$

Using this result to express the relation of the magnetisation with the polarisation after the reflection and considering $\epsilon, \eta \ll 1$, only the terms of zero order in Q in the module $|\vec{E}|$ are relevant. Then,

$$I_s = R(1 + 2\eta) \quad (3.30)$$

$$I_p = R(1 - 2\eta) \quad (3.31)$$

where $\frac{|r_{pp}|^2}{2} = R$ and the difference between these two intensities ($I_s - I_p$) are:

$$I_{\text{dif}} = 4R\eta \quad (3.32)$$

The magnetisation measurements using the MOKE technique require the application of an external magnetic field. As was already commented, the rotation η undergone by polarisation is the sum of the optical and magnetic effects:

$$\eta = \theta_{\text{opt}} + \theta_{\text{mag}} \quad (3.33)$$

where θ_{opt} is a rotation whose origin electronic, being linear with the field, and θ_{mag} is the rotation produced by the Kerr effect. However, as we are only interested in the latter contribution or the magnetisation produced by the Kerr effect, we can consider that

$$I_{\text{dif}} = 4R\theta_{\text{mag}} \quad (3.34)$$

is analysed MOKE signal. To measure this signal, a glantaylor prism + half wave-plate is used to separate the resulting beam into its two orthogonal components (E_p and E_s), which are then measured with differential detector. The Kerr signal is sent to a gated integrator and boxcar averager and then displayed on a computer connected to a DAQ. The automatisation of the MOKE setup is performed through a home-made LABVIEW program. Thus, to demonstrate the capabilities of our apparatus we have studied a thin film sample of the ferrimagnetic alloy GdFeCo. In Figure 5.1 we show hysteresis loops for the sample with and without the pump beam. In the latter case we obtain a normal static MOKE loop for the sample. The loop obtained in the presence of the pump beam, of fluence 2.7 mJ/cm^2 , pulse width sub -8 fs and at a time zero delay, shows a strong demagnetisation with respect to the normal state of the sample. The increased sample temperature causes the loss of the ferromagnetic order (more details in Chapter 5).

3.5 Summary

In this chapter, which is divided into two parts, we summarised the main techniques the all-optical pump-probe approach that allows access to magnetisation dynamics, namely Time-resolved Kerr effect and Time-resolved second harmonic generation. We have shown that pump-probe methods may be degenerate (pump and probe to the same spectral band) and non-degenerate (beams with different spectral band). It was shown that each configuration has its limitations, for example, the contamination of the pump in the measurements or temporal resolution. In the second part of this chapter, We described the phenomenology of Magneto-optic Kerr effect, which is the basis of the TR-MOKE techniques. In addition, the experimental apparatus used to measure the Kerr signal was presented, and a description of each optical component and the data acquisition system used in the experimental setup. Finally, an analysis of the signal MOKE was made using the formalism of the Jones Matrix.

Chapter 4

Experimental technique II: Femto-MOKE

Our system has been carefully designed for the various sources of femtosecond pulses existing in an laboratory (oscillator, amplifier and pulses of the combination amplifier + hollow fiber compressor). The assembly went through three stages of implementation: in the first stage we used pulses of the oscillator, in second stage was used amplifier pulses and finally the combination mentioned above. In this chapter we will describe in detail the main components and challenges in the development process.

4.1 Experimental Ultrafast Laser Setup in Porto

The laser system used in this work is a commercially available amplifier (Femtolasers Femto-Power Compact PRO CEP), which is based on a CEP-stabilised ultrafast oscillator (Femto lasers Rainbow). This oscillator is a chirped-mirror based Kerr-lens mode-locking laser, which generates pulses with a duration of 6 fs with spectral bandwidth centered at 800 nm. The repetition rate is 80 MHz and the energy per pulse is of about 2 nJ. The pulses are also sent through a Faraday rotator for optical isolation, and through a glass stretcher, which stretches the pulses to about 20 ps. The beam is then sent to a multipass amplifier. This is a nine pass amplifier, and the beam is focused in the gain medium at each pass (focusing length of 50 cm) with spherical mirrors. After four passes, a Pockels cell pulse-picker selects pulses at 1 kHz repetition rate, and they are sent back into the amplifier. After five more passes the pulses are extracted and compressed with a Proctor-Wise prism compressor [118, 119]. The final compressed pulses have 1 mJ energy per pulse, with a duration of 30 fs.

Figure 4.1: Schematic representation of the laser system used in this work. OSC - oscillator; AOM - acousto-optic modulator; APD - avalanche photodiode; PD - photodiode; AOPDF - acousto-optic programmable dispersion filter; ISO - optical isolator (Faraday rotator); TOD CM - third-order dispersion chirped mirrors; SP - spectrometer; PC - personal computer [extracted from [9].

4.2 Stages of the experimental setup

The implementation of the Femto-MOKE experimental setup went through several stages, ranging from the use of different sources by choosing the appropriate components, dispersion compensation, optical characterisation of pulses, the characteristics of the data acquisition system and eventually reaching the "ideal" stage are described in the following sections throughout this chapter. We will make a brief description of the phases in which we used the oscillator and the amplifier as sources to generate the pump and probe pulses. The method to calculate and compensate the total dispersion of the components, the method used to calculate the spot of the pump and, consequently, the fluence, the method for finding the zero and between the pump and probe pulses and finally the optical characterisation of pulses are shown in detail in individual sections.

4.2.1 Oscillator source

The first proposed setup of the experimental pump-probe apparatus is outlined in simplified form in Figure 4.2. A CEP-stabilized ultrafast oscillator with 6fs pulse, 2nJ, with repetition rate of 80 MHz and spectral width of approximately 640 to 1000nm is used. In this case the system was degenerate, with both beams (pump and probe) having the same spectral bandwidth with the potential to achieve a temporal resolution of the order of 6 femtoseconds.

The beam passes through the dispersion compensation system composed of 3 pairs of DCMS with spectral range between 600 – 1200 nm. Similar calculations which will be presented in subsection 4.3.1 for another source (hollow fiber+amplifier) indicates an estimated 6 reflections in the DCM to compensate the dispersion of the components at this stage. The light is incident on a beam splitter that reflects 5% for probe. The remaining energy of the original beam will be the pump. The reflected beam by the sample with elliptical polarisation then goes through a half wave-plate and an analyser for to separate (and balance) into polarisation components s and p. The intensities of these components are measured by a balanced optical detector. The difference signal between the two components will allow assess the relative magnetisation state of the sample as a function of the time delay between the two beams (pump and probe) after excitation. The temporal characterisation of the pump and probe were performed using only the autocorrelation method (see Section 2.4), and the result pulses had a duration of 6.9 fs in the sample plane. In Figure 4.3 we show the first measurements of MOKE signal using samples of cobalt with a thickness of $\sim 80\text{nm}$ as a test.

In the presence of the pump measurements were made by varying the delay. However, in the literature indicated that the fluence necessary for the complete demagnetisation of cobalt was of the order of $7\text{mJ}/\text{cm}^2$ [120]. The fluence calculated experimentally (see method in subsection 4.2.4) was approximately $1,1\text{mJ}/\text{cm}^2$. Although the literature indicates fluence values above that

Figure 4.2: Experimental setup degenerate pump-probe technique using oscillator as source.

obtained in our experiment, we therefore decided to use the laser amplifier pulses to confirm this possibility.

4.2.2 Amplifier source

In Figure 4.4 we show the simplified experimental setup with the changes. It is possible to observe that only 5% of the total energy of the amplifier is used in our experiment. With the use of these pulses it was possible to obtain higher values of fluence in the sample plane. Changes were made in the part of data acquisition due the laser repetition rate. These changes included the use of a boxcar integrator and lock-in amplifier. Furthermore, it was necessary to incorporate new optical components in order to adapt the setup to the pulses provided by the new source. Also, it was necessary to make a new estimate of the number of reflections in DCMs to compensate the total dispersion, this amount being increased to 18 reflections. We should emphasize that procedures such as zero delay calculation between the pump and probe, measurement of the spot (in the case of change of lenses to focus the beam on the sample) and calculation of the total dispersion are remade everytime that the system undergoes changes.

In the initial studies we have made, we found that we can obtain good signal stability, which is sufficient for the measurement of hysteresis loops at any chosen time delay. The measurements shown in Figure 4.5 were made with pump-on or pump-off for a given fixed delay. The strong demagnetisation that we have observed is due the high fluency obtained from the pump (above of 7 mJ/cm^2).

Although we observed demagnetisation in the test sample for a fixed delay. Measurements of the demagnetisation signal by varying the delay, i.e., TR-MOKE measurements were not possible observed. As discussed in subsection 3.2.3, due to try this degeneracy configuration there was

too much contamination of the pump light in the TR-MOKE measurements. Since the signal we expected to measure was very small, of the order of $5mV$, and the pump signal measured was two orders of magnitude higher, it became impossible to do TR-MOKE measurements in the current configuration, although we have applied some solutions already discussed in subsection 3.2.3. Another problem in this configuration is the temporal resolution that is limited by the duration of the pulses $25fs$. Therefore, our system needed new changes to eliminate contamination of the pump in the TR-MOKE measurements and at the same time achieve the main aim that was a high temporal resolution. A solution was proposed to use a non-degenerate system using laser pulses resulting from a combination amplifier + hollow fiber, which will be discussed in the following sections. This was the final solution opted for since it allowed us to achieve an aim of performing ultrafast pump-probe measurements as unprecedented temporal resolution ($t_{pulse} \sim 8fs$)

Figure 4.3: Measurements of the static MOKE signal without the presence of the pump in cobalt samples with a thickness of $\sim 80\text{nm}$ for different intensities of the probe (different beam splitters with 5% and 0.7% reflecting, were used).

Figure 4.4: Experimental setup for the degenerate pump-probe technique using the amplifier as source.

Figure 4.5: Hysteresis loops for different pump-probe delays, demonstrating the ultrafast demagnetisation. The chosen pump fluence is 10 mJ/cm^2 . The black loop was recorded without the pump pulse and is the same in all figures.

4.3 Generation of the pump and probe pulses from broadband hollow fiber compressor

Figure 4.6: Illustration of our experimental setup for spectral broadening through nonlinear propagation. Adapted from [14].

As explained in Chapter 3, conventional dual-colour systems usually employ one or more optical parametric amplifiers (OPAs) as a secondary source of spectrally tuneable femtosecond pulses in the visible to near-infrared range. Our methodology consists in obtaining the two-colour pump and probe pulses from the same broadband hollow fiber source. This approach has several advantages. Unlike in OPA systems, the pump and probe pulses are very broadband and both support pulse with durations below 10 fs; the pulses may also have similar energies since the BS is changed to 50:50, which is relatively simple. This enables us to exchange their roles when studying specific samples that may benefit from a particular combination of central wavelengths for the pump and the probe pulses [5]. Also, the full spectrum of the broadband source can be used for both pump and probe pulses with only minimal changes in the setup, which is expected to result in unprecedented temporal resolutions of the order of 6 fs. In our setup, the output from the amplifier is coupled to a hollow fiber through a lens with a focal length of 1.5 m [121] (Figure 4.6). The hollow fiber is placed inside a chamber with an argon gas pressure of 1 mbar. Spatial coupling into the fiber is optimised using an iris placed before the lens, transmitting roughly 400 μJ out of 580 μJ . After propagation through the fiber and output window, the beam contains 200 μJ , corresponding to 50% transmission, with a typical RMS power stability of 0.5% over 1 hour. Also, after propagation through the hollow fiber, the pulse is sent to a system of chirp mirrors for compensating the dispersion obtained in the step of generating new frequencies.

The spectrum of the beam after the hollow fiber compressor and the chirped mirrors is shown in Figure 4.7, which spans from 500 nm to 1050 nm and supports a sub-4 fs pulse. This spatio-temporal domain characterisation of sub-4fs pulses has been carried out by using a new technique for the characterisation of ultrashort pulses: D-scan. For more details see references [14, 122]. A typical experimental dispersion-scan trace of the hollow fiber is shown in Figure 4.7, along with the retrieved scan and temporal and spectral analysis.

As mentioned above, our method consists in obtaining the two-colour pump and probe pulses from the hollow fiber source. To these ends we use a glass windows (or dichroic mirror) as beam splitter, 95% of the pulse energy is transmitted and is used in the pump; the remaining is reflected and used as the probe (see Figure 4.8). In the case of the dichroic mirror the separation between pump and probe is performed by separating the spatial regions, which are either reflected and

Figure 4.7: (a) Representative measured and (b) retrieved d-scans for the hollow fiber compressor. (c) Measured spectral intensity (black) and retrieved phase (thick red line, with the standard deviation indicated by thin red lines). (d) Retrieved electric field of the pulses for the BK7 wedge insertion that minimizes the intensity FWHM duration, corresponding to a sub-4 fs pulse

transmitted by the dichroic mirror, in other words, reflection of the spectral range of 700-950 nm and transmits the remaining spectral range. In both cases, using colour filters, we can then limit the spectral width of each beam. Pump and probe pulses show large spectral width (550-650 nm and 700-950 nm respectively) supporting pulses durations below 10 fs. Here, it is worth mentioning that we simulate the dispersion and temporal characterisation of the pump and probe in the two situations presented here. We chose to maintain separation through the glass plate because the dichroic mirror has a very thick substrate (6 mm) and many reflections in the chirp mirrors are needed to compensate dispersion introduced by dichroic mirror. Thus the energy losses caused by reflections in chirp mirrors were high (over 30% of the energy of the pump) and, consequently, decreased the maximum fluence of the pump (see section 4.2.4). In the next section will show the simulation of dispersion in the case of glass windows and the high number of reflections in chirp mirrors to compensate the total dispersion of the optical components.

Dispersion simulation

Component	Pump	Probe
Air (2, 1 atm)	1,5 m $\simeq$ 2 mm BK7	1,5 m $\simeq$ 2 mm BK7
Lens	2,5 mm BK7	2,8 mm BK7
Glan-taylor polariser	7,5 mm calcite	7,5 mm calcite
Half wave-plate	1,5 mm quartz	1,5 mm quartz
BS (glass windows)	0,57 mm BK7	-
Filter	0,5 mm BK7	0,5 mm BK7
Reducer telescope	6,5 mm BK7	6,5 mm BK7

Table 4.1: Optical elements and their respective thickness. Each beam will pass through the specified thickness.

The temporal resolution of the pump-probe system is essential to study the magnetic phenomena in femtosecond time scales. Therefore, the control of dispersion is extremely important so as

Figure 4.8: A glass window is used as beam splitter and colour filters are used to split the main beam into the pump (transmitted) and probe (reflected) pulses. The relevant measurements are shown for the main beam as well as those for the pump and probe after the beamsplitter.

to maintain the high temporal resolution. To achieve this aim, we use dispersion compensation through DCMs with bandwidth 450–950 nm (see Chapter 2). These mirrors introduce a negative dispersion that compensates the positive dispersion introduced by the optical components in the experimental setup. The quantity of negative dispersion introduced by the DCMs is determined by the number of reflections on these mirrors. Each reflection corresponds to compensation of negative GDD of -60 fs^2 for the mirror pair. Therefore the first step was to find the total dispersion in each "arm" of the experimental setup.

In Table 4.1, the optical components of each arm and their thicknesses are indicated. Thus, to find the dispersion associated with each component we must calculate the GDD which is the product of group velocity dispersion with the thickness of the material. After, we sum all the contributions of each optical element obtaining the total dispersion for both the pump and probe. We should mention that the total dispersion of both beams must be equal and, therefore, in the optical path of both we introduce a wedge pair to make those fine tuning necessary to ensure an equivalent dispersion for both beams since the pre composition is made before the beam-splitter. In Figure 4.9(a) show the estimated total dispersion. Thus, to compensate for this dispersion we used 21 reflections in the DCM9. As shown in Figure 4.9(b) adding the dispersion of the elements with the dispersion of DCM9 the curve becomes flat around zero.

4.3.1 Characterisation of the pulses by autocorrelation and d-scan techniques

As shown in section 4.3 the separation between pump and probe was obtained using dichroic mirror and in a later using glass windows. In the first alternative optical characterisation was performed by the conventional method of autocorrelation. In the second this was performed using the new D-scan technique [11]. Both situations are shown below.

Figure 4.9: (a) Simulation of the total dispersion of the pump, GDD vs λ . (b) Compensation of the total dispersion with 21 reflections in DCM9.

Autocorrelation

To measure the autocorrelations we use a commercial autocorrelator femtometer (available in the Femtolasers). In Figure 4.11 show the measurements of the pulse performed by collinear (interferometric autocorrelation- IAC) and noncollinear (intensity autocorrelation- IA) configurations (see Chapter 2, section 2.4). In the IA configuration the beams are focused in a nonlinear-optical crystal, varying the delay between them and then the signal pulse energy vs. delay is measured. While in the IAC we use the collinear beams, so that the second harmonic pulse created by the interaction of the two different beams combines coherently with that created by each individual beam. As a result, interference occurs due to the coherent addition of the two beams, and interference fringes occur vs. line delay (see section 2.5).

D-scan

The experimental implementation of d-scan consists in measuring the SHG spectrum of the pulse while the dispersion is varied via the translation of one of the glass wedges around the point of maximum compression (minimum pulse duration). As a result, a spectrally resolved SHG trace as a function of wedge insertion (dispersion) is obtained. In the present setup, we focus the pulses pump (probe) with a lens with focal length of 200 mm (100 mm) in a nonlinear crystal placed in the position where the pump and probe are overlapped in the sample plane (BBO, 20 μm thick, cut for type I SHG at 800 nm). The SHG signal is collimated with a lens and a blue filter is used

Figure 4.10: Picture of the double chirped mirrors used in the experimental setup with 21 reflections.

to remove the remaining fundamental frequency signal before detection with the spectrometer (HR4000, Ocean Optics Inc.). In Figures 4.12 and 4.13 show the measurements obtained for the probe and pump with temporal duration 7.2 fs and 7.3 fs, respectively.

4.3.2 Zero delay between pump and probe by spectral interference method

In chapter 3 it was shown that the principle of pump-probe spectroscopy is fairly simple. An intense laser pulse (pump) arrives at the sample at a time t_0 , and interacts with the sample in a way that changes some property of the sample. When the second pulse (probe) arrives at a later time $t_0 + \tau$, its interaction with the sample will reflect this property change. By varying the time delay τ , the relaxation of the perturbation induced by the pump can be mapped out by detecting the outgoing probe signal. Therefore, to find the zero delay between the two beams is another key parameter in pump-probe techniques. To calculate the zero delay we consider that despite beams having different spectral ranges, there is a small overlap between them (690 nm -740 nm) which allow us to find the zero delay position by a method of spectral interference as shown in Figure 4.14. With the use of a spectrometer we observed the pattern of interference fringes (Figure 4.15).

4.3.3 Measurement of the pump beam spot size

The pump fluence of the excitation pulse plays a crucial role, i.e., it is through this parameter that the sample is perturbed to a state of non-equilibrium and subsequently the changes experienced by it are monitored through the probe. Therefore, it is essential to know the fluence provided by the pump. In order to calculate this variable, it is necessary to determine the diameter of the

Figure 4.11: (a) Spectra for the pump and probe beams from the dichroic mirror, (b) measured intensity autocorrelation of probe beam and (c) measured interferometric autocorrelation of pump beam and corresponding (calculated) intensity autocorrelation. Retrieved pulse duration (assuming sech2 shapes) is 8 fs for both pulses.

beam (spot) at the sample plane. Knowing the diameter, the fluence is given by:

$$Fluence = \frac{Energy(mJ)}{\pi r^2(cm^2)} \quad (4.1)$$

where r is the radius of the spot. To calculate the diameter of the spot we used a charge-coupled device (CCD) camera with a proper imaging system. We can measure the spot at the surface of the sample by measuring its scattering. This technique offers a simple setup, fast in implementation and analysis. It also has an important advantage: since we are measuring the scattering from the sample surface, the spot can only be overestimated. Thus, if the measured spot radius is smaller than what is needed for the fluence values that we need to start the dynamics of demagnetisation, we need not worry about experimental errors, since it can only be smaller than what is measured. A 2f-2f imaging system was used to create a 1:1 image of the spot in the sample (Figure 4.16).

To analyse the results, the image obtained from the CCD is imported as a numerical array to a Python program. The spot is then fitted using gaussian functions both vertically and horizontally, and the width is calculated at $1/e^2$, since as we are measuring an intensity. In literature we find that for GdCoFe sample the fluence values needed are between $0,3 - 3 mJ/cm^2$ to initiate the process of demagnetisation of the sample. Therefore, to obtain these values of fluence the spot in the sample plane must have a diameter of approximately $380 \mu m$ or less. In Figure 4.17 we show experimental measurements of the pump spot in the sample plane. Doing a Gaussian fit for

Figure 4.12: (a) Measured and (b) retrieved d-scan traces for the probe pulse (central wavelength of approx. 600 nm); retrieved probe pulse in the spectral (c) and temporal (d) domains; probe pulse width is 7.2 fs (FWHM).

each axis and calculating the value FWHM we obtain that $X \simeq 327 \mu m$ and $Y \simeq 422 \mu m$. Thus, we ensure that the fluence values in the sample plane will be within the range mentioned above.

Figure 4.13: (a) Measured and (b) retrieved d-scan traces for the pump pulse (central wavelength of approx. 800 nm); retrieved pump pulse in the spectral (c) and temporal (d) domains; pump pulse width is 7.3 fs (FWHM).

Figure 4.14: Experimental scheme to find the zero delay between pump and probe.

Figure 4.15: Experimental results of spectral interferometry using pump and probe beams

Figure 4.16: Experimental setup used to measure the spot of the pump.

Figure 4.17: Laser spotsize as viewed by the CCD camera and imported to a Python color map. Spot size measurements in X and Y axis. The data is fitted using a gaussian curve and the width is measure at $1/e^2$ of the maximum, since we are measuring an intensity

4.4 Femto MOKE setup

Our pump-probe system (Figure 4.18) is based on a commercial titanium:sapphire laser amplifier (Femtolasers Compact Pro CE-phase) delivering sub-30-fs laser pulses (approximately 40 nm bandwidth centered at 800 nm) with 1 mJ of energy at a repetition rate of 1 kHz and with CEP stabilisation. These pulses are further post-compressed in a home-built state-of-the-art HCF and chirped-mirror compressor that uses the dispersion-scan (d-scan) technique for the simultaneous measurement of the pulses (as described in subsection 4.3.1). We make use of a refractive telescope, consisting of two lenses with a focal length of -100 and 400 mm, to reduce the diameter of the beam prior to sending the pulses through a second chirped-mirror set. These chirped-mirrors effectively compensate the dispersion induced by the different optical elements along the beam paths. They have a working spectral bandwidth between 500 and 950 nm and are capable of compensating, up to high-order, the material dispersion associated with the telescope, the air paths and all remaining optical components (beamsplitter, filters, lenses, wave-plates and polarizers) traversed by the pulsed beams on their way to the sample under study.

After the chirped mirrors, we place a glass plate which act as beam splitter that reflects 4% of the energy which is used as the probe. The rest of the beam is transmitted and is used as the pump pulse. For limiting the spectral bandwidth of the pump, we use a colour filter with transmission ranging from 700 to 950 nm. Moreover, in the optical path of the pump beam, a polariser cube and a half-wave plate for controlling the intensity of the beam at the sample plane have been added. The pump pulse is then sent through a mechanical delay line (0, 1 μ m step, corresponding to a minimum step size of 0, 3 fs resolution). On the other hand, the spectral range of the probe beam is selected using a colour filter that transmits in the range of 550 – 650 nm. In order to obtain a more homogeneous polarisation of the probe beam, a polariser cube, similar to the one placed in the optical pump, is introduced. In both pump and probe beams, we place lenses with 200 mm and 100 mm focal length which produce focused spots of about 380 μ m and 180 μ m, respectively. In any optical pumping experiment, these spots must be accurately focused and overlapping on the sample surface. The presently installed magnet and associated bipolar power supply can generate a magnetic field of up to 1 T in the sample plane.

The detection of the sample magnetic state is performed via the measurement of the MOKE signal obtained from the probe beam reflected from the sample surface (see Chapter 3 in section 3.3). We have used the longitudinal Kerr effect where the rotation angle of the polarisation is directly proportional to the in-plane magnetisation contribution. While the pump beam was set at normal incidence, the probe beam was set to 45° in order to maximize the magneto-optical response. Then, the reflected beam is directed through a broadband half-wave-plate and an analyser to separate (and balance) the *s* and *p* polarised components prior to measuring their corresponding intensities using a balanced amplified photodetector. The difference in the signals allows us to evaluate the relative magnetisation state of the sample as a function of the time delay introduced between pump and probe beams.

Figure 4.18: Schematic illustration of the pump-probe apparatus

4.5 Data acquisition

The data acquisition system in our experiment includes an optical delay and a network of electronic acquisition tools such as the optical detector, an integration / filtering device and a data acquisition board (DAQ). In order to choose the appropriate detector for the acquisition system, we must pay attention to some important criteria such as the repetition rate of the laser system and sensitivity [98]. As our system is based on a low-repetition rate and, also, since the TR-MOKE signal is very small being in order of mV , our adopted detection system is composed by combination boxcar averager (see chapter 3, section 3.3.4) and lock-in amplifier (next section).

4.5.1 Lock-in amplifier

As mentioned in Chapter 3 the principle the boxcar averager is very simple. The laser trigger signal synchronises the gate times with the laser pulse. During a controlled time, the gate is opened (for a specific time on time windows) and the signal is measured. Then, the gate closes until a new trigger signal is received and new data are acquired. The measured signal for each gate is proportional to the selected time-window. The Signal/Noise ratio is controlled by changing the size and position of the gate. The signal output from the box boxcar averager is sent to the lock-in amplifier.

Lock-in measurements require a frequency reference. Typically an experiment is excited at a fixed frequency and the lock-in detects the response from the experiment at the reference frequency. In other words, in pump-probe experiment, the power of the pump beam is modulated on and off (Figure 4.19) at a known frequency f_c ($f_c = 0.500$ kHz in our experiment). If the pump laser has a repetition rate f_{laser} , and is chopped with a synchronized chopper (e.g., $f_c = f_{laser}/2$), then on will represent one pulse transmitted by the chopper and off will be one pulse blocked by the chopper.

Therefore, in the presence of modulated excitation by chopper with frequency f_c , the signal at the input of the lock-in, in first order of perturbation produced by excitation, is given by:

Figure 4.19: (a) In the case where the delay is fixed, the amplitude of the measured signal is constant. (b) In the case of variable delay between pump and probe the amplitude of the measured signal varies with it. Dashed line represents an illustration of the TR-MOKE signal measured using the lock-in.

$$S = I + \Delta I \cdot f(t) \quad (4.2)$$

I being the MOKE signal, ΔI the induced perturbation by excitation and $f(t)$ a square wave of frequency $\omega_c/2\pi$ that modulates the excitation, being that different frequencies this value will be deleted by the lock-in. In the next chapter will be presented and discussed the results obtained with our new experimental setup.

4.6 Summary

In this chapter, we described all stages of the development of pump-probe experimental setup with resolution sub-8fs. In each stage was used a different laser source to generate the pump and probe. Also, were necessary inserting or removing optical components and adapt the system to acquire data. Finally, we chosen to use the pulses generated from the combination hollow fiber + amplifier. This combination provided pulses with a large spectral bandwidth capable of supporting sub-4fs duration, fundamental for the pump and probe with a large spectral width and, therefore, short duration. Procedures for calculate the zero delay temporal between pump and probe, fluence and spots of pump and the acquisition of data by boxcar + lock-in were described in detail in this chapter.

Chapter 5

Results and Analysis

In this chapter, we present the measurements performed using our home-made experimental set-up described in Chapter 4. In order to demonstrate the capabilities of our apparatus, we have studied the magnetic behavior of a ferrimagnetic rare earth-transition metal (RE-TM) thin film, in the form of a *GdFeCo* alloy. In this alloy, the *Co* and *Fe* sublattice magnetisations are coupled ferromagnetically with each other and the total magnetisation of *Fe* and *Co* is coupled antiferromagnetically with that of Gd, yielding a ferrimagnetic order. This RE-TM alloy has been extensively studied due to its strong magneto-optical response [13]. In particular, we carried out our measurements on a 20 nm thick $Gd_{23}Fe_{68}Co_9$ thin film which was grown by magnetron sputtering in the following multilayer structure: glass/AlTi (10 nm)/SiN(5nm)/GdFeCo(20 nm)/SiN(60 nm) (see section 3.3.3). The AlTi layer serves as a heat sink and the SiN as buffer and capping layers. The latter also serves as an antireflection coating. This film shows out-of-plane magnetic anisotropy and the Curie temperature (T_C) is about $\approx 500 K$

5.1 Introduction

After energy transfer from the pump pulse, two main effects can locally take place in a ferromagnetic thin film: (i) a decrease of the macroscopic magnetisation due to its temperature dependence [17, 3, 24], and (ii) the different anisotropy contributions that determine the equilibrium magnetisation direction can be altered [32, 41]. In other words, both the length and the direction of the magnetisation vector can be modified by an optical pulse. Therefore we can identify two characteristic times in TR-MOKE measurements [123]. According to the three-temperature model (see section 5.3), the rate of demagnetisation is characterised by the demagnetisation time τ_M . This time constant is approximately the same as the electron-spin relaxation time τ_{e-s} , namely the time constant for the energy relaxation process between conduction electrons and the spin system. Also, on a longer time scale we can observe an oscillation with damping on a time scale of ps, corresponding to the magnetisation precession [124] around its equilibrium direction according to the Landau-Lifschitz-Gilbert equation (see Equation 1.31).

5.2 Lase-induced precession dynamics

The laser-induced dynamics were firstly confirmed by measuring the in-plane hysteresis loops of the ferromagnetic GdFeCo thin film with and without applying the pump beam (Figure 5.1). While in the latter case we obtain the standard static MOKE hysteresis loop, the curve, obtained in the presence of a pump fluence of $2.7 mJ/cm^2$ with a pulse width lower than 8 fs and for the time delay when the observed demagnetisation was maximum, shows that the sample magnetisation is reduced to about 70 % of its normal saturation value. This demagnetisation upon laser excitation can be attributed to the increased spin temperature from absorption of the pump-laser pulse [22]. The energy of the photons is transferred to the electron system by creating high-energy

electronic excitations (hot electrons). It is known that energy from the hot electron system to thermal electrons, lattice (phonons), and spin degree of freedom proceeds at an enormously fast timescale down to subpicosecond-timescale. Before the excitation induced by the pump-laser pulse, the electrons constitute a system with defined temperature T , distributed according to the Fermi Dirac distribution. The pump pulse excites a small quantity of electrons to a non-fermionic distribution without set temperature i.e. non-thermalised electrons (hot electrons). Due to electron-electron scattering, the electron system thermalises to the Fermi-Dirac distribution at the higher temperature $T + \Delta T$. The energy is then transferred from the thermalised electron system to the lattice and spin system by the electron-phonon and electron-spin scattering processes. Therefore, the increased sample temperature causes the loss of the ferromagnetic order (Figure 5.1).

Figure 5.1: In-plane hysteresis loops of the GdFeCo thin film without ($\bullet$) and with pump pulse ($\circ$) and using a pump fluence of 2.7 mJ/cm^2 .

Once we verified that the ferrimagnetic system could be excited using sub-10-fs pulses, we studied its time-resolved magnetisation dynamics. However, we should note that with our set-up configuration, which uses linearly polarised laser pulses with a fluence of 2.7 mJ/cm^2 and an in-plane external magnetic field, magnetisation switching of the sample is not allowed and we can focus our attention on the ultrafast demagnetisation and precessional processes [13, 125]

As was previously observed [126, 127], the magnetisation shows a sudden drop within the first picosecond after the pump pulse, a fast recovery (remagnetisation) within a few picoseconds, followed by a clear oscillation or precession during a slower magnetisation recovery, which is characterised by the ferromagnetic resonance frequency ω_{FMR} and the Gilbert damping parameter α . Our TR-MOKE results are summarised in Figure 5.2 where different in-plane external magnetic fields were applied to the sample. The displayed measurements are obtained making the difference between the acquired measurements for external magnetic field H^+ and H^- , because the differentiation with respect to $\vec{H}$ removes the electronic component, as is usually done in properly processed magneto-optical experiments [1]. The damped precessional motion of magnetisation originates from heating effect [128]. It is known that the absorption of the intense laser pulse quickly increases the temperature of the sample under the area of the pump laser spot and accordingly decreases the magnitude of the magnetocrystalline anisotropy (only due to change in magnetisation), giving rise to a new equilibrium orientation for magnetisation when combined with the applied magnetic field. The magnetisation starts to precess initially around the new time-dependent equilibrium direction due to the torque rising from the angular difference between the magnetisation

and the new effective field directions. After a couple of picoseconds, the equilibrium orientation of magnetisation progressively returns to its original position. The magnetisation, which is already out of the original equilibrium caused by the sudden change in magnetic anisotropies, has a tendency to align along the original effective field orientation. Therefore, it continues the precession on a timescale of hundreds of picoseconds, until it reaches at the original equilibrium again.

Figure 5.2: Time-dependent MOKE demagnetisation and precessional curves for a GdFeCo ferromagnetic thin film as a function of the external applied field.

We begin our analysis by focusing on the oscillatory behavior of the magnetisations shown in Figure 5.2. In our experiment, we applied an in-plane magnetic field strong enough to keep the sample magnetisation in plane and parallel to the effective anisotropy field, which depends on several factors such as the external applied magnetic field (strength and direction), the sample magnetocrystalline anisotropy energy and the shape anisotropy energy. Usually, this behavior follows a damped precessional motion on a timescale of hundreds of picoseconds, until the original equilibrium state is regained. In order to obtain a correct fit of the precessional processes, without any contamination from the ultrafast demagnetization, the TR-MOKE measurements were fitted, after a delay time of 10 ps, to a damped-harmonic function superposed with an exponential decay background [129, 130]

$$\theta = \theta_0 + A \cdot e^{\frac{t}{t_0}} + B \cdot \sin(2\pi\omega_{FMR}t + \varphi)e^{\frac{-t}{\tau}} \quad (5.1)$$

where θ_0 and A are the background magnitudes, the $e^{\frac{t}{t_0}}$ term is the remagnetisation with relaxation time t_0 . The final term represents the precessional motion with the resonance frequency ω_{FMR} , relaxation time τ and initial phase φ . The experimental precessional curves and the fits using Equation 5.1, with different applied fields, are summarised in Figure 5.3. The obtained results show that the model agrees very well with the experimental data.

From the previous analysis, we have determined the resonance frequency of the precessional motion (ω_{FMR}) can be determined [126] and its field-dependence is shown in Figure 5.4. Assuming that both the external magnetic field and the sample magnetisation are in the sample plane, we have used ω_{FMR} from the Kittel approximation (Equation 5.2).

$$\omega_{FMR} = \frac{\gamma}{2\pi} \cdot \sqrt{H(H - H_u)} \quad (5.2)$$

where γ is the gyromagnetic ratio and H_u is the effective anisotropy field of the sample. This analysis confirms that the *GdFeCo* thin film shows an effective out-of-plane anisotropy energy with an effective anisotropy field of $H_u = (0.7 \pm 0.2) \text{ kOe}$ and an effective g-factor of $g_{\text{eff}} = (3.4 \pm 0.2)$, in agreement with the values obtained by Kato et al. [131].

The Gilbert damping parameter

the relation $(1/\tau)$ versus H can be obtained from the fits and compared with the theoretical calculations (Figure 5.4a) [129]:

$$\frac{1}{\tau} = \pi\alpha\gamma(2H - H_u) \quad (5.3)$$

with α the theoretical damping, H the external applied field, H_u the effective anisotropy field and γ the gyromagnetic ratio. Then, the damping parameter $\alpha = (0.159 \pm 0.001)$ was extracted which is also in agreement with the values reported in other works [131, 126].

However, and although $(1/\tau)$ should be roughly proportional to (ω_{FMR}) , a significant deviation from the theoretical curve has been observed at $H = 3300 \text{ Oe}$. Therefore, we can conclude that while the Gilbert damping dominates at higher fields, the relaxation process in the lower field regime is governed by the extrinsic magnetic relaxation, which may be related to the presence of inhomogeneities and/or defects in the sample [129, 124, 132]. An alternative approach to evaluate is based on defining the effective Gilbert damping constant, α_{eff} , which is expressed by [129]:

$$\alpha_{\text{eff}} = \frac{1}{2\pi\omega_{FMR}\tau} \quad (5.4)$$

where ω_{FMR} and τ values at each applied H were estimated from the experiment (Figure 5.4b). The α_{eff} value is identical to or larger than α , and corresponds to an upper-bound value of α . In theory, α_{eff} does not depend on H , but in contrast, extrinsic magnetic relaxation significantly does, implying that α_{eff} also changes with H [132, 133]. As observed in Figure 9 b, when Gilbert damping dominates the extrinsic magnetic relaxation process, such as for large applied magnetic fields, α_{eff} should be constant, independent of H and close to $\alpha = (0.159 \pm 0.001)$. On the other hand, α_{eff} should be larger than α for lower applied fields. Another possibility about the divergent point in the Figure 5.5 (magnetic field $H = 3300 \text{ Oe}$) is that it could have originated by a defect in the sample. Besides, with this sole point, we cannot draw many conclusions. It is necessary to make more measurements.

Figure 5.3: Precessional curves (o) and fittings (—) for a GdFeCo ferromagnetic thin film as a function of the external applied field: (a) 4150 Oe, (b) 3980 Oe, (c) 3680 Oe and (d) 3300.

Figure 5.4: Field dependence of the resonance frequency ($\circ$) and the theoretical fitting using the Kittel approximation ($-$).

Figure 5.5: (a) Field dependence of $(1/\tau)$: Experimental data ($\circ$) and theoretical fit ($(-)$) using Equation 5.3. (b) Field dependence of α_{eff} : Experimental data ($\circ$) and theoretical damping coefficient ($(-)$) calculated from Equation 5.3.

5.3 Ultrafast demagnetisation

Next, we focus our attention on the ultrafast demagnetisation and the fast remagnetisation processes within the initial picoseconds after excitation by the pump pulse. For this purpose, we performed time-resolved pump-probe experiments using a pump-laser fluence of 2.7 mJ/cm^2 , with a pulse width of $\approx 7.8 \text{ fs}$, an external applied field of $33000e$ and ranging the time-delay from -1 to 2 ps . Under these experimental conditions, we previously determined that the sample was demagnetised up to 70% of its normal saturation (Figure 5.1). The normalised demagnetisation signal is shown in Figure 5.6a. An ultrafast laser-induced demagnetisation process is observed, with a minimum at a delay t of $\approx 800 \text{ fs}$, followed by a recovery of the magnetisation, which is consistent with previous studies [134, 135].

Figure 5.6: (a) The experimental demagnetisation data of GdFeCo and (b) expected temporal evolution of the spin temperature using Equation 5.8 (open black symbols). Both curves were fitted within the 3T model (—).

The ultrafast demagnetisation and restoration of the ferromagnetic order on the ps timescale upon laser excitation can be described using the three-model temperature (TTM) [136, 22], where it has been assumed that the energy supplied to the sample by the photons can be worked on different timescales in three different ways: the energy of the electrons (e), the phonon or lattice energy

(l) and the spin energy (s), which is related with the magnetisation change. Therefore, within the 3T model, the electron temperature, $T_e(t)$, is coupled to the lattice temperature, $T_l(t)$, and the spin temperature, $T_s(t)$, in the form of the following three coupled differential equations [136, 22]:

$$C_e(T_e) \frac{\partial T_e}{\partial t} = -G_{el}(T_e - T_l) - G_{es}(T_e - T_s) + P(t) \quad (5.5)$$

$$C_l(T_l) \frac{\partial T_l}{\partial t} = -G_{el}(T_l - T_s) - G_{sl}(T_l - T_s) \quad (5.6)$$

$$C_s(T_s) \frac{\partial T_s}{\partial t} = -G_{es}(T_s - T_e) - G_{sl}(T_s - T_l) \quad (5.7)$$

where $C_e(T_e)$, $C_l(T_l)$ and $C_s(T_s)$ are the electronic, lattice and spin specific heats, respectively. G_{el} , G_{es} and G_{sl} are the electron-lattice, the electron-spin and the spin-lattice coupling constants which determines the rate of the energy exchange between the electrons, the lattice and the spin. $P(t)$ is the laser power density absorbed in the material, which is described by a Gaussian function with a 8 fs pulse width (FWHM) and a fluence of 2.7 mJ/cm². Note that the three-model temperature is purely thermodynamic in nature and hence fails to account for the wavelength of the excitation.

Figure 5.7: (Calculated temperature profiles for a GdFeCo thin film excited by a 8 fs laser pulse and a fluence of 2.7 mJ/cm², ((-) $T_e(t)$, (-) $T_l(t)$ and (-) $T_s(t)$).

Therefore, and in order to study the evolution of the magnetisation, we firstly need to extract the experimental spin temperature (Figure 5.6b) using the Bloch $T^{3/2}$ law [134]:

$$M(T_s)/M(T_{\text{room}}) = \left[1 - \left(T_s/T_C \right)^{3/2} \right] \quad (5.8)$$

where T_C is the Curie Temperature ($T_C = 500\text{K}$ for *GdCoFe*) [134, 137]. T_s reaches a maximum temperature of around 365 K at ≈ 800 fs after the pump pulse. Considering that the specific heat of the electrons is proportional to the electronic temperature as $C_e(T_e) = \tilde{a}T_e$ with $\tilde{a} = 714\text{J/m}^3\text{K}^2$ [134, 36] and solving the three coupled differential equations (3T model), the experimental spin temperature has been tuned until a reasonable agreement was obtained between the calculation

and the experiment (Figure 5.6b). Our best fit was achieved for $C_l(T_l) = (2.33 \times 10^6) J/m^3 K$, $C_s(T_s) = (0.34 \times 10^4) J/m^3 K$, $G_{el} = (8.19 \times 10^{17}) W/m^3 K$, $G_{es} = (0.2 \times 10^{16}) W/m^3 K$ and $G_{sl} = (0.55 \times 10^{16}) W/m^3 K$ which are reasonable values when we compare them with the typical values of metals [22] and a GdFeCo alloy with similar chemical composition [134]. Finally, and using the Equation 5.8, the evolution of the fitted magnetisation was represented in Figure 5.6a.

Figure 5.6 shows the temporal dependence of the calculated $T_e(t)$, $T_l(t)$ and $T_s(t)$. While the laser energy acts on the electron subsystem reaching a maximum temperature of around $670 K$ just after excitation, the increase of the spin temperature is slower and it reaches a maximum value of around $365 K$ at $\approx 1 ps$ after laser excitation. Moreover, the curves also show the energy transfer from electrons and spins to the lattice and $T_e(t)$, $T_l(t)$ and $T_s(t)$ reach the same temperature after few ps.

The double pump pulse

In our first measurements, obtained with our experimental setup, we observe the appearance of two demagnetisation peaks (see Figure 5.8(a)). To understand why this occurs we need to report some concepts of optics.

Figure 5.8: TR-MOKE measurements in GdFeCo sample (a) with a waveplate and (b) without waveplate in the optical path of the pump.

When light impinges an anisotropic medium, independent of the initial state of polarisation, the direction of oscillation of its electric field can be decomposed into two components known

as extraordinary ray (parallel to the direction of the optical axis of the medium) and ordinary ray (perpendicular to the optical axis of the medium), which travel with different propagation velocities. This means that there are two distinct refractive indices, n_e and n_o related to the extraordinary and ordinary rays, respectively (Figure 5.9). Such a the medium is called birefringent. An application of these types of materials is the construction of wave plates i.e. optical components whose aim is to change the phases between the o and e components of the incident light.

Figure 5.9: Diagram illustrating of a linearly polarized plane wave incidence in a birefringent medium with the angle θ with relative to the optical axis of the medium (in the y direction), where the extraordinary (E) and ordinary (O) components are indicated.

In our experimental setup we used a half-wave plate+polariser to change the polarisation and energy of the pump. However, due to the birefringence of the material which constitutes the half-wave plate a replica of the pump is generated and reaches the sample plane with a delay of the order of $3ps$ relative to the original beam. Thus, these two pumps in the sample plane, generate two demagnetisation signals. In Figure 5.8(b) shows plot of the temporal evolution TR-MOKE signal without waveplate in the optical path of the pump. The parameters used were: pump fluence $2.7 mJ/cm^2$, magnetic field $3300 Oe$ and time delay step of $8 fs$. Measurements were performed in H^+ and H^- directions of the magnetic field. After removal of the half-wave plate, it is necessary to make an adjustment using wedges (moving the same thickness of the component) to compensate the absence of $3 mm$ of thickness of the half-wave plate, in order to maintain unchanged pulse duration. The measure presented here confirm that by removing only the wave plate the double demagnetisation signal disappeared. We should mention that the measurements of temporal evolution TR-MOKE signal and analysed in the previous sections were acquired without the presence of wave plate.

5.4 Summary

In this chapter, we reported results dynamically measurements pressure induced magnetisation and demagnetization ultrafast laser in GdFeCo samples using our femto-MOKE experimental setup. Once this sample is well characterized in the literature, our aim was to reproduce some results and compare with the existing, in order to show the reliability and versatility of our setup for the study of ferromagnetic materials. Initially, measurements were made of the precession of the magnetisation as a function of the effective field. Parameter as frequency of precession and damping factor are obtained in our analysis. In the second phase of testing of our system was made measures around the zero delay position (zoom) with high resolution. These results were compared with the existing literature and showed that using our new system is possible to access

the dynamics of magnetisation of ferromagnetic materials.

Chapter 6

Conclusion and future perspectives

We have developed a new dual-colour pump-probe MOKE spectrometer dedicated to the study of ultrafast demagnetisation processes in a range of magnetic materials and structures. This versatile setup uses state-of-the-art ultrafast optical methods to deliver ultrashort laser pump and probe pulses permitting the observation of magnetization dynamics at unprecedented temporal resolutions for a system of its type. Contrary to conventional dual-colour systems, which usually employ one or more OPAs as a secondary source of spectrally tuneable femtosecond pulses, our approach consists in obtaining the dual-colour pump and probe pulses from the same broadband hollow-fibre source. This approach has several advantages. Unlike OPA systems, the pump and probe pulses are very broadband ($450 - 700\text{ nm}$ and $700 - 950\text{ nm}$, respectively) and can both support pulse durations below sub-8 fs range. The setup permits control of both polarisation and energy of the pulses, allowing the detection of both polarisation rotation and ellipticity. This few-cycle regime is also highly promising for the direct excitation and observation of coherent ultrafast magneto-dynamic behavior, which is expected to help us to get a deeper understanding on both the conservation of angular momentum associated with the demagnetization process, and the relation between the spin thermalisation and the corresponding quasi-equilibrium magnetisation. Furthermore, CEP-stabilized sub-5-fs pulses open the way for exploring the possible dependence of the induced magnetization dynamics on the electric field of the excitation pulses.

To demonstrate the essential capability of our dual-colour set-up described in this thesis, we have measured the ultrafast demagnetisation and precessional dynamics in a ferrimagnetic Gd-FeCo thin film using a pump pulse fluence of 2.7 mJ/cm^2 , with sub-8-fs pulse width and ranging the time delay from -1 to hundred of ps . We observed that the magnetisation shows a sudden drop within the first picosecond after the pump pulse and a fast recovery (remagnetization) within a few picoseconds, followed by a clear oscillation or precession during a slower magnetisation recovery. Regarding the precessional behaviour, we have determined both the ferromagnetic resonance frequency ω_{FMR} and the effective Gilbert damping parameter α_{eff} , in good agreement with the current literature. Moreover, the ultrafast demagnetisation and the fast remagnetisation processes within the initial picoseconds after excitation by the pump pulse has been analysed using an external applied field of 3300 Oe and a time delay ranging from -1 to 2 ps . Under these experimental conditions, measurements of the laser-induced demagnetisation revealed a minimum at $\approx 800\text{ fs}$. Within the three-model, the electronic, lattice and spin specific heats, as well as the electron-lattice, the electron-spin and the spin-lattice coupling constants were calculated. Therefore, we have experimentally confirmed that our sub-8-fs pump pulses are able to efficiently induce demagnetisation in a ferromagnetic material. We expect that the present pump-probe system, when operating in a degenerate configuration with CEP-stabilized sub-5-fs pulses, will enable us to further explore this limit, which we believe is an important aim for future developments in the femtomagnetism research field.

Bibliography

- [1] J.-Y. Bigot, M. Vomir, and E. Beaurepaire, “Coherent ultrafast magnetism induced by femtosecond laser pulses,” *Nature Physics*, vol. 5, pp. 515–520, 2009. vii, 2, 11, 12, 13, 15, 31, 32, 34, 64
- [2] J. H. Mentink, *Magnetism on the timescale of the exchange interaction: explanations and predictions*. PhD thesis, Radboud University Nijmegen, 2012. xi, 10
- [3] A. Kirilyul, A. Kimel, and T. Rasing, “Ultrafast optical manipulation of magnetic order,” *Rev. of Mod. Phys.*, vol. 82, pp. 2731–2784, 2010. xi, 1, 2, 9, 12, 15, 31, 32, 33, 34, 63
- [4] R. Thomson, C. L. Leburn, and D. Reid, *Ultrafast Nonlinear Optics*. New York: Springer, 2013. xi, 20
- [5] A. M. Weiner, *Ultrafast Optics*. New York: John Wiley, 2009. xi, 20, 88, 90
- [6] M. H. Frosz and A. E. Peter, “Supercontinuum generation: Can pulse broadening be stopped?,” *Nature Photonics*, vol. 1, pp. 611–612, 2007. xi, 21
- [7] M. Matuscheki, *Theory and Design Double-Chirped Mirrors*. PhD thesis, Swiss Federal Institute of Technology Zurich, 1999. xi, 22, 23
- [8] I. Jovanovic, “Chirped-pulse amplification,” *Optik and Photonik*, vol. 4, pp. 30–33, 2010. xii, 25
- [9] M. Miranda, *Sources and Diagnostics for Attosecond Science*. PhD thesis, Lund University, 2012. xii, xiii, 26, 44
- [10] Diels and Rudolph, *Ultrashort Laser Pulse Phenomena*. Academic Press, 1996. xii, 27, 28
- [11] M. Miranda, C. L. Arnold, T. Fordell, F. Silva, B. Alonso, R. Weigand, and H. Crespo, “Characterization of broadband few-cycle laser pulses with the d-scan technique,” *Optics Express*, vol. 17, pp. 18732–18743, 2012. xii, 28, 30, 52
- [12] M. V. Lebedev, O. V. Misochko, T. Dekorsy, and N. Georgiev, “On the nature of coherent artifact,” *Journal of Experimental and Theoretical Physics*, vol. 100, pp. 272–282, 2005. xii, 33
- [13] A. Kirilyuk, A. Kimel, and T. Rasing, “Laser-induced magnetization dynamics and reversal in ferrimagnetic alloys,” *Rep. Prog. Phys.*, vol. 72, p. 026501, 2013. xiii, 37, 38, 63, 64
- [14] B. Alonso, M. Miranda, V. Pervak, J. Rauschenberger, J. San Romn, I. J. Sola, and H. Crespo, “Characterization of sub-two-cycle pulses from a hollow-core fiber compressor in the spatiotemporal and spatio-spectral domains,” *Appl. Phys. B*, vol. 112, pp. 105–114, 2013. xiii, 17, 19, 20, 25, 50
- [15] P. Pantazis, J. Maloney, D. Wu, and S. E. Fraser, “Second harmonic generating (shg) nanoprobes for in vivo imaging,” *PNAS, Proceedings of the National Academy of Sciences*, vol. 107, p. 1453514540, 2010. xiv, 91

- [16] C. Rulliere, *Femtosecond Laser Pulses: Principles and Experiments*. New York: Springer, 2005. xv, 17, 18, 21, 91
- [17] M. Dantus and P. Gross, "Ultrafast spectroscopy," *Encyclopedia of Applied Physics*, vol. 82, pp. 431–456, 1998. 1, 63
- [18] G. Reid and K. Wynne, "Ultrafast laser technology and spectroscopy," *Encyclopedia of Analytical Chemistry*, pp. 13644–13670, 2000. 1
- [19] J. Baskin, M. Felker, and A. Zewail, "Purely rotational coherence effect and time-resolved sub-doppler spectroscopy of large molecules. ii. experimental," *J. Chem. Phys.*, vol. 24, pp. 2460–2482, 1987. 2
- [20] P. Felker, "Rotational coherence spectroscopy: Studies of the geometries of large gas-phase species by picosecond time-domain methods," *J. Chem. Phys.*, vol. 96, pp. 7844–7857, 1992. 2
- [21] J. Manz and W. L., *Femtosecond Chemistry*. New York: VCH, 1995. 2
- [22] E. Beaurepaire, J.-C. Merle, A. Daunois, and J.-Y. Bigot, "Ultrafast spin dynamics in ferromagnetic nickel," *Phys. Rev. Lett.*, vol. 76, pp. 4250–4253, 1996. 2, 11, 12, 13, 31, 63, 70, 71, 72
- [23] B. Koopmans, M. Van Kampen, J. T. Kohlhepp, and W. J. M. Jonge, "Ultrafast magneto-optics in nickel: Magnetism or optics?," *Phys. Rev. Lett.*, vol. 85, pp. 844–847, 2000. 2
- [24] J. Wang, *Time-Resolved Magneto-Optical Spectroscopy, Optical Techniques for Solid-State Materials Characterization*. New York: CRC Press, 2011. 2, 11, 63
- [25] R. Hicken, N. D. Hughes, J. R. Moore, D. S. Schmool, R. Wilks, and J. Wu, "Magneto-optical studies of magnetism on pico and femtosecond timescales," *J. Magn. Magn. Mater.*, vol. 242245, Part 1, p. 559564, 2002. 2
- [26] Q. Wang, R. Schoenlein, L. Peteanu, R. Mathies, and C. Shank, "Vibrationally coherent photochemistry in the femtosecond primary event of vision," *Science*, vol. 266, pp. 422–424, 1994. 2
- [27] N. A. Spaldin, *Magnetic Materials: Fundamentals and Applications*. Cambridge: Cambridge University Press, 2010. 2
- [28] P. Weiss, "La variation du ferromagnetisme du temperature," *Comptes Rendus*, vol. 143, pp. 1136–1149, 1909. 2, 7
- [29] K. Kittel, "Physical theory of ferromagnetic domains," *Rev. Mod. Phys.*, vol. 21, pp. 541–583, 1949. 2
- [30] C. Tannous and J. Gieraltowski, *Handbook of Electronic and Photonic Materials*. New York: Springer-Verlag, 2006. 2
- [31] B. Cullity, *Introduction to Magnetic Materials*. Boston: Addison-Wesley Publishing Company, 1972. 4
- [32] A. Aharoni, *Introduction to the Theory of Ferromagnetism*. Oxford: Oxford University Press, 2000. 4, 63
- [33] R. C. Handley, *Modern Magnetic Materials Principles and Applications*. New York: John Wiley and Sons, 2000. 5, 6
- [34] R. Wu and A. Freeman, "Spinorbit induced magnetic phenomena in bulk metals and their surfaces and interfaces," *J. Magn. Magn. Mater.*, vol. 200, pp. 498–514, 1999. 5

-
- [35] Y. Ueda and M. Takahashi, “Structure and magnetic properties in single-crystal iron film electrodeposited on a (110) copper crystal,” *J. Magn. Magn. Mater.*, vol. 71, pp. 212–218, 1988. 6
 - [36] C. Kittel, *Introduction to Solid State Physics*. United States: Wiley, 1995. 6, 7, 71
 - [37] L. Neel, “Anisotropie magnétique superficielle et surstructures d’orientation,” *J. Phys. Radium*, vol. 15, pp. 225–239, 1954. 7
 - [38] D. A. Dimitrov and G. M. Wysin, “Effects of surface anisotropy on hysteresis in fine magnetic particles,” *Phys. Rev. B*, vol. 50, pp. 3077–3084, 1994. 7
 - [39] M. Jamet, W. Wernsdorfer, C. Thirion, D. Mailly, V. Dupuis, and P. Mélinon, “Magnetic anisotropy of a single cobalt nanocluster,” *Phys. Rev. Lett.*, vol. 86, pp. 4676–4679, 2001. 7
 - [40] D. Sander, “The correlation between mechanical stress and magnetic anisotropy in ultrathin films,” *Rep. Prog. Phys.*, vol. 62, p. 809, 1999. 7
 - [41] R. Camley, “Magnetization dynamics in thin films and multilayers,” *J. Magn. mater.*, vol. 200, pp. 583–597, 1999. 9, 63
 - [42] J.-Y. Bigot and M. Vomir, “Ultrafast magnetization dynamics of nanostructures,” *Ann. Phys.*, vol. 525, pp. 2–30, 2013. 11, 12
 - [43] J. Hohlfeld, E. Matthias, R. Knorren, and K. H. Bennemann, “Nonequilibrium magnetization dynamics of nickel,” *J. Magn. mater.*, vol. 78, pp. 4861–4864, 1997. 12
 - [44] E. Carpena, E. Mancini, C. Dallera, M. Brenna, E. Puppini, and S. De Silvestri, “Dynamics of electron-magnon interaction and ultrafast demagnetization in thin iron films,” *Phys. Rev. B*, vol. 78, pp. 174422–174428, 2008. 12
 - [45] M. Vomir, L. H. F. Andrade, L. Guidoni, E. Beaurepaire, and J.-Y. Bigot, “Real space trajectory of the ultrafast magnetization dynamics in ferromagnetic metals,” *Phys. Rev. Lett.*, vol. 94, pp. 237601–237605, 2005. 12
 - [46] J. Wang, L. Cywinski, C. Sun, J. Kono, H. Munekata, and L. J. Sham, “Femtosecond demagnetization and hot-hole relaxation in ferromagnetic $Ga_{1-x}Mn_xAs$,” *Phys. Rev. B*, vol. 77, pp. 235308–235314, 2008. 12
 - [47] A. V. Kimel, R. V. Pisarev, J. Hohlfeld, and T. Rasing, “Ultrafast quenching of the antiferromagnetic order in febo3: Direct optical probing of the phonon-magnon coupling,” *Phys. Rev. Lett.*, vol. 89, pp. 287401–287405, 2002. 12
 - [48] G. Muller, “Spin polarization in half-metals probed by femtosecond spin excitation,” *Nature Materials*, vol. 8, pp. 56–61, 2009. 12
 - [49] A. Scholl, L. Baumgarten, R. Jacquemin, and W. Eberhardt, “Ultrafast spin dynamics of ferromagnetic thin films observed by fs spin-resolved two-photon photoemission,” *Phys. Rev. Lett.*, vol. 79, pp. 5146–5149, 1997. 12
 - [50] G. van der Laan and A. I. Figueroa, “X-ray magnetic circular dichroism versatile tool to study magnetism,” *Surface Review and Letters*, vol. 277278, pp. 95–129, 2014. 12
 - [51] G. P. Zhang and W. Hübner, “Laser-induced ultrafast demagnetization in ferromagnetic metals,” *Phys. Rev. Lett.*, vol. 85, pp. 3025–3028, 2000. 13
 - [52] M. Si and G. Zhang, “Resolving photon-shortage mystery in femtosecond magnetism,” *J. Phys. Condens. Matter*, vol. 22, p. 076005, 2010. 13

- [53] S. Essert and H. C. Schneider, “Electron-phonon scattering dynamics in ferromagnetic metals and their influence on ultrafast demagnetization processes,” *Phys. Rev. B*, vol. 84, pp. 224405–224416, 2011. 13, 14
- [54] F. Dalla Longa, J. T. Kohlhepp, W. J. M. de Jonge, and B. Koopmans, “Influence of photon angular momentum on ultrafast demagnetization in nickel,” *Phys. Rev. B*, vol. 75, p. 224431, 2007. 13
- [55] C. Stamm, N. Pontius, T. Kachel, M. Wietstruk, and H. A. Dürr, “Femtosecond x-ray absorption spectroscopy of spin and orbital angular momentum in photoexcited ni films during ultrafast demagnetization,” *Phys. Rev. B*, vol. 81, p. 104425, 2010. 13
- [56] M. Wietstruk, A. Melnikov, C. Stamm, T. Kachel, N. Pontius, M. Sultan, C. Gahl, M. Weinelt, H. A. Dürr, and U. Bovensiepen, “Hot-electron-driven enhancement of spin-lattice coupling in gd and tb 4f ferromagnets observed by femtosecond x-ray magnetic circular dichroism,” *Phys. Rev. Lett.*, vol. 106, pp. 127401–127405, 2011. 13
- [57] B. Koopmans, H. Kicken, M. v. Kampen, and W. Jonge, “Microscopic model for femtosecond magnetization dynamics,” *J. Magn. Magn. Mater.*, vol. 286, p. 271275, 2005. 13, 14
- [58] R. J. Elliott, “Theory of the effect of spin-orbit coupling on magnetic resonance in some semiconductors,” *Phys. Rev.*, vol. 96, pp. 266–279, 1954. 13
- [59] M. Wu, J. Jiang, and M. Weng, “Spin dynamics in semiconductors,” *J. Magn. Magn. Mater.*, vol. 493, p. 61236, 2010. 13, 14
- [60] D. Steiauf and M. Illg, C. and Fahnle, “Extension of yafet’s theory of spin relaxation to ferromagnets. j. magn. magn. mater.,” *J. Magn. Magn. Mater.*, vol. 322, pp. L5–L7, 2010. 14
- [61] M. Faahnle, J. Seib, and C. Illg, “Relating gilbert damping and ultrafast laser-induced demagnetization,” *Phys. Rev. B*, vol. 82, p. 144405, 2010. 14
- [62] I. Radu, G. Woltersdorf, M. Kiessling, A. Melnikov, U. Bovensiepen, J.-U. Thiele, and C. H. Back, “Laser-induced magnetization dynamics of lanthanide-doped permalloy thin films,” *Phys. Rev. Lett.*, vol. 102, pp. 117201–117206, 2009. 14
- [63] K. Carva, M. Battiato, and P. M. Oppeneer, “*Ab Initio* investigation of the elliott-yafet electron-phonon mechanism in laser-induced ultrafast demagnetization,” *Phys. Rev. Lett.*, vol. 107, p. 207201, 2011. 14
- [64] M. Battiato, K. Carva, and P. M. Oppeneer, “Superdiffusive spin transport as a mechanism of ultrafast demagnetization,” *Phys. Rev. Lett.*, vol. 105, p. 027203, 2010. 14
- [65] C. Stamm, T. Kachel, N. Pontius, R. Mitzner, T. Quast, K. Holldack, S. Khan, C. Lupulescu, E. F. Aziz, M. Wietstruk, H. A. Drr, and W. Eberhardt, “Femtosecond modification of electron localization and transfer of angular momentum in nickel,” *Nature Materials*, vol. 6, pp. 740–743, 2007. 14
- [66] G. P. Zhang, W. Hbner, G. Lefkidis, Y. Bai, and T. F. George, “Paradigm of the time-resolved magneto-optical kerr effect for femtosecond magnetism,” *Nature Physics*, vol. 5, pp. 499–502, 2009. 15
- [67] D. Jones, S. A. Diddams, J. K. Ranka, A. Stentz, R. S. Windeler, J. L. Hall, and S. T. Cundiff, “Carrier-envelope phase control of femtosecond mode-locked lasers and direct optical frequency synthesis,” *Science*, vol. 288, pp. 635–639, 2000. 19, 20
- [68] B. Alonso, M. Miranda, I. J. Sola, and H. Crespo, “Spatiotemporal characterization of few-cycle laser pulses,” *Opt. Express*, vol. 20, pp. 17880–17893, 2012. 19, 20

-
- [69] M. Hentschel, R. Kienberger, C. Spielmann, G. A. Reider, N. Milosevic, T. Brabec, P. Corkum, U. Heinzmann, M. Drescher, and F. Krausz, “Attosecond metrology,” *Nature*, vol. 414, pp. 509–513, 2001. 19
 - [70] F. Krausz, “Attosecond metrology,” *Rev. Mod. Phys.*, vol. 81, pp. 163–234, 2009. 19
 - [71] W. Sellmeier, “Zur erklärung der abnormen farbenfolge im spektrum einiger substanzen,” *Annalen der Physik*, vol. 143, pp. 272–282, 1871. 21
 - [72] R. L. Fork, O. E. Martinez, and J. P. Gordon, “Negative dispersion using pairs of prisms,” *Optics Letters*, vol. 9, pp. 150–152, 1984. 22
 - [73] E. Treacy, “Optical pulse compression with diffraction gratings,” *IEEE J Quantum Electron*, vol. 9, pp. 454–458, 1969. 22
 - [74] M. Matuschek, F. X. Kartner, and U. Keller, “Theory of double-chirped mirrors,” *IEEE J Quantum Electron*, vol. 4, pp. 197–208, 1998. 22
 - [75] F. X. Kartner, “Design and fabrication of double-chirped mirrors,” *Optics Letters*, vol. 22, pp. 831–833, 1997. 22
 - [76] M. Matuscheki, F. X. Kartner, and U. Keller, “Theory of double-chirped mirrors,” *IEEE Journal of selected topics in Quantum Electronics*, vol. 02, pp. 197–208, 1998. 22
 - [77] S. Yefet and A. Peer, “A review of cavity design for kerr lens mode-locked solid-state lasers,” *Appl. Sci.*, vol. 03, pp. 694–724, 2013. 24
 - [78] O. Svelto, *Principles of Lasers*. New York: Plenum Press, 1989. 24
 - [79] R. Thomson, C. Leburn, and D. Reid, *Ultrafast Nonlinear Optics*. Switzerland: Springer International Publishing, 2013. 24
 - [80] G. Steinmeyer, D. H. Sutter, L. Gallmann, N. Matuschek, and U. Keller, “Frontiers in ultrashort pulse generation: Pushing the limits in linear and nonlinear optics,” *Science*, vol. 286, pp. 1507–1512, 1999. 24
 - [81] J. Simon, “Ultrashort light pulses,” *Rev. Sci. Instrum*, vol. 60, pp. 3597–3624, 1989. 24
 - [82] D. Strickland and G. Mourou, “Compression of amplified chirped optical pulses,” *Optics Comm*, vol. 56, pp. 219–221, 1985. 24
 - [83] M. Z. Hentschel, F. Krausz, and S. Spielmann, “Generation of 0.1-tw optical pulses with single-stage ti:sapphire amplifier at a 1-khz repetition rate,” *Appl. Phys. B*, vol. 70, pp. S161–S164, 2000. 24
 - [84] M. Nisoli, D. De Silvestri, O. Svelto, R. Szepcs, K. Ferencz, C. Spielmann, S. Sartania, and F. Krausz, “Compression of high-energy laser pulses below 5 fs,” *Optics Letters*, vol. 22, pp. 522–524, 1997. 25
 - [85] B. Schenkel, J. Biegert, U. Keller, C. Vozzi, M. Nisoli, G. Sansone, S. Stagira, S. De Silvestri, and O. Svelto, “Generation of 3.8-fs pulses from adaptive compression of a cascaded hollow fiber supercontinuum,” *Optics Letters*, vol. 28, pp. 1987–1989, 2003. 25
 - [86] F. X. Kartner, “Pulse characterization ultrafast optics,” *Spring*, pp. 333–370, 2005. 26
 - [87] D. J. Kane and R. Trebino, “Single-shot measurement of the intensity and phase of an arbitrary ultrashort pulse by using frequency-resolved optical gating,” *Optics Letters*, vol. 18, pp. 823–825, 2013. 26
 - [88] I. C. and W. I. A., “Self-referencing spectral interferometry for measuring ultrashort optical pulses,” *IEEE J. Quantum Electron*, vol. 35, pp. 501–509, 1999. 26

- [89] M. Miranda, T. Fordell, C. Arnold, and H. Crespo, “Simultaneous compression and characterization of ultrashort laser pulses using chirped mirrors and glass wedges,” *Optics Express*, vol. 20, pp. 688–697, 2012. 26
- [90] N. S. Almeida and D. L. Mills, “Effective-medium theory of long-wavelength spin waves in magnetic superlattices,” *Phys. Rev. B*, vol. 38, pp. 6698–6710, 1988. 31
- [91] S. Zapperi, P. Cizeau, G. Durin, and H. E. Stanley, “Dynamics of a ferromagnetic domain wall: Avalanches, depinning transition, and the barkhausen effect,” *Phys. Rev. B*, vol. 58, pp. 6353–6366, 1998. 31
- [92] M. Yamanouchi, D. Chiba, F. Matsukura, and H. Ohno, “Current-induced domain-wall switching in a ferromagnetic semiconductor structure,” *Phys. Rev. B*, vol. 428, pp. 539–542, 2004. 31
- [93] Y. Yokoyama, Y. Suzuki, S. Yuasa, K. Ando, K. Shigeto, T. Shinjo, P. Gogol, J. Miltat, A. Thiaville, T. Ono, and T. Kawagoe, “Kerr microscopy observations of magnetization process in microfabricated ferromagnetic wires,” *J. Appl. Phys.*, vol. 87, pp. 5615–5617, 2000. 31
- [94] D. Pescia, M. Stampanoni, G. L. Bona, A. Vaterlaus, R. F. Willis, and F. Meier, “Magnetism of epitaxial fcc iron films on cu(001) investigated by spin-polarized photoelectron emission,” *Phys. Rev. Lett.*, vol. 58, pp. 2126–2129, 1987. 31
- [95] C. Yu., “Ferromagnetic resonance in ferromagnetic/ferroelectric febio3rtio3 (001),” *J. Appl. Phys.*, vol. 103, p. 07B108, 2008. 31
- [96] M. D. Sihues, C. Durante-Rincon, and J. Fermin, “A ferromagnetic resonance study of nife alloy thin lms. journal of magnetism and magnetic materials,” *J. Appl. Phys.*, vol. 316, p. e462 e465, 2007. 31
- [97] J. R. Dutcher, J. F. Cochran, I. Jacob, and W. F. Egelhoff, “Brillouin light-scattering intensities for thin magnetic films with large perpendicular anisotropies,” *Phys. Rev. B*, vol. 39, pp. 10430–10432, 1989. 31
- [98] J. Wang, *Time-Resolved Magneto-Optical Spectroscopy, Optical Techniques for Solid-State Materials Characterization*. CRC Press, 2012. 31, 32, 61
- [99] Z. Zhang, B. Cui, G. Wang, B. Ma, Q. Y. Jin, and Y. Liu, “Ultrafast laser-induced magnetization precession dynamics in fept/cofe exchange-coupled films,” *Phys. Rev. B*, vol. 97, p. 172508, 2010. 32
- [100] C. La-O-Vorakiat, E. Turgut, C. A. Teale, H. C. Kapteyn, M. M. Murnane, S. Mathias, M. Aeschlimann, C. M. Schneider, J. M. Shaw, H. T. Nembach, and T. J. Silva, “Ultrafast demagnetization measurements using extreme ultraviolet light: Comparison of electronic and magnetic contributions,” *Phys. Rev. X*, vol. 2, p. 011005, 2012. 32, 34
- [101] I. Radu, K. Vahaplar, C. Stamm, T. Kachel, N. Pontius, H. A. Drr, T. A. Ostler, J. Barker, R. F. L. Evans, R. W. Chantrell, A. Tsukamoto, A. Itoh, A. A. Kirilyuk, T. Rasing, and A. V. Kimel, “Transient ferromagnetic-like state mediating ultrafast reversal of antiferromagnetically coupled spins,” *Nature (London)*, vol. 472, p. 011005, 2011. 32
- [102] C. W. Luo, Y. T. Wang, F. W. Chen, H. C. Shih, and T. Kobayashi, “Eliminate coherence spike in reflection-type pump-probe measurements,” *Optics Express*, vol. 17, pp. 11321–11327, 2009. 33, 34
- [103] P. N. Argyres, “Theory of the faraday and kerr effects in ferromagnetics,” *Phys. Rev.*, vol. 97, pp. 334–345, 1955. 34, 35

-
- [104] H. v. Philipsborn, M. Rubinstein, and L. Treitinger, “4.2.3.3.5 magneto-optical effects (faraday, kerr, magnetocircular dichroism, reflectance circular dichroism),” *SpringerMaterials*, vol. 12b. 34
 - [105] J. D. Jackson, *Classical Electrodynamics*. John Wiley and Sons, 1999. 35
 - [106] Z. Qiu and S. Bader, “Surface magneto-optic kerr effect (smoke),” *Optics Express*, vol. 200, pp. 664–678, 1999. 35
 - [107] Z. Qiu and S. Bader, “Surface magneto-optic kerr effect,” *Rev. Sci. Instrum.*, vol. 71, pp. 1243–1255, 2000. 35
 - [108] J. Zak, E. R. Moog, C. Liu, and S. D. Bader, “Fundamental magneto optics,” *J. Appl. Phys.*, vol. 68, pp. 4203–4207, 1996. 35
 - [109] W. Voigt, “Magneto-und elektrooptik,” *Leipzig, B. G. Teubner*, 1908. 35
 - [110] Z. J. Yang and M. R. Scheinfein, “Combined threeaxis surface magneto-optical kerr effects in the study of surface and ultrathin film magnetism,” *J. Appl. Phys.*, vol. 74, pp. 6810–6823, 1993. 36
 - [111] R. P. Hunt, “Magneto optic scattering from thin solid films,” *J. Appl. Phys.*, vol. 38, pp. 1652–1671, 1967. 36
 - [112] E. Hecht, *Optics*. Addison Wesley, 2002. 36
 - [113] U. Nowak, O. N. Mryasov, R. Wieser, K. Guslienko, and R. W. Chantrell, “Spin dynamics of magnetic nanoparticles: Beyond brown’s theory,” *Phys. Rev. B*, vol. 72, p. 172410, 2005. 37
 - [114] R. P. Prasankumar and A. J. Taylor, *Optical techniques for solid-state Materials characterization*. CRC Press, 2011. 38
 - [115] S. Polisetty, J. Scheffler, S. Sahoo, Y. Wang, T. Mukherjee, X. He, and C. Binek, “Optimization of magneto-optical kerr setup: Analyzing experimental assemblies using jones matrix formalism,” *Rev. Sci. Instrum.*, vol. 79, p. 055107, 2008. 39, 40
 - [116] M. Born and E. Wolf, *Principles of Optics*. Cambridge University Press, 1999. 40
 - [117] J. M. Teixeira, R. Lusche, J. Ventura, R. Fermento, F. Carpinteiro, J. P. Araujo, J. B. Sousa, S. Cardoso, and P. P. Freitas, “Versatile, high sensitivity, and automatized angular dependent vectorial kerr magnetometer for the analysis of nanostructured materials,” *Rev. Sci. Instrum.*, vol. 82, p. 043902, 2011. 41
 - [118] Z. Cheng, F. Krausz, and C. Spielmann, “Compression of 2 mJ kilohertz laser pulses to 17.5 fs by pairing double-prism compressor: analysis and performance,” *Optics Communications*, vol. 201, pp. 145–155, 2002. 43
 - [119] B. Proctor and F. Wise, “Quartz prism sequence for reduction of cubic phase in a mode-locked Ti:Sapphire laser,” *Opt. Lett.*, vol. 17, pp. 1295–1297, 1992. 43
 - [120] T. Roth, D. Steil, D. Hoffmann, M. Bauer, M. Cinchetti, and M. Aeschlimann, “Dynamics of the coercivity in ultrafast pump-probe experiments,” *J. Phys. D: Appl. Phys.*, vol. 41, p. 164001, 2008. 44
 - [121] F. Silva, “Femtosecond pulse compression and diagnostics: Towards attosecond pulse generation,” Master’s thesis, University of Porto, 2009. 50

- [122] F. Silva, M. Miranda, B. Alonso, J. Rauschenberger, V. Pervak, and H. Crespo, “Simultaneous compression, characterization and phase stabilization of gw-level 1.4 cycle vis-nir femtosecond pulses using a single dispersion-scan setup,” *Optics Express*, vol. 22, pp. 10181–10190, 2014. 50
- [123] S. Mizukami, S. Tsunegi, T. Kubota, M. Oogane, D. Watanabe, H. Naganuma, Y. Ando, and T. Miyazaki, “Ultrafast demagnetization for $ni_{80}fe_{20}$ and half-metallic co_2mnsi heusler alloy films,” *Journal of Physics: Conference Series*, vol. 200, p. 042017, 2010. 63
- [124] S. Mizukami, D. Watanabe, T. Kubota, X. Zhang, H. Naganuma, M. Oogane, Y. Ando, and T. Miyazaki, “Laser-induced fast magnetization precession and gilbert damping for cocrpt alloy thin films with perpendicular magnetic anisotropy,” *Applied Physics Express*, vol. 3, p. 123001, 2010. 63, 66
- [125] C. D. Stanciu, F. Hansteen, A. V. Kimel, A. Kirilyuk, A. Tsukamoto, A. Itoh, and T. Rasing, “All-optical magnetic recording with circularly polarized light,” *Phys. Rev. Lett.*, vol. 99, p. 047601, 2007. 64
- [126] C. D. Stanciu, A. V. Kimel, F. Hansteen, A. Tsukamoto, A. Itoh, A. Kirilyuk, and T. Rasing, “Ultrafast spin dynamics across compensation points in ferrimagnetic gdfeco: The role of angular momentum compensation,” *Phys. Rev. B*, vol. 73, p. 220402, 2006. 64, 65, 66
- [127] J. Hohlfeld, T. Gerrits, M. Bilderbeek, T. Rasing, H. Awano, and N. Ohta, “Fast magnetization reversal of gdfeco induced by femtosecond laser pulses,” *Phys. Rev. B*, vol. 65, p. 012413, 2001. 64
- [128] Z. Zhang, B. Cui, G. Wang, B. Ma, Q. Y. Jin, and Y. Liu, “Ultrafast laser-induced magnetization precession dynamics in fept/cofe exchange-coupled films,” *Appl. Phys. Lett.*, vol. 97, p. 172508, 2010. 64
- [129] S. Mizukami, S. Iihama, N. Inami, T. Hiratsuka, G. Kim, H. Naganuma, M. Oogane, and Y. Ando, “Fast magnetization precession observed in l10-fept epitaxial thin film,” *Appl. Phys. Lett.*, vol. 98, p. 052501, 2011. 65, 66
- [130] H.-S. Song, K.-D. Lee, J.-W. Sohn, S.-H. Yang, S. S. P. Parkin, C.-Y. You, and S.-C. Shin, “Observation of the intrinsic gilbert damping constant in co/ni multilayers independent of the stack number with perpendicular anisotropy,” *Appl. Phys. Lett.*, vol. 102, p. 102401, 2013. 65
- [131] T. Kato, K. Nakazawa, R. Komiya, N. Nishizawa, S. Tsunashima, and S. Iwata, “Compositional dependence of g-factor and damping constant of gdfeco amorphous alloy films,” *IEEE Trans. Magn.*, vol. 44, pp. 3380–3383, 2008. 66
- [132] e. a. Beaujour, J.-M., “Beaujour, j.-m. and ravelosona, d. and tudosa, i. and fullerton, e. e. and kent, a. d.,” *Phys. Rev. B*, vol. 80, p. 180415(R), 2009. 66
- [133] N. Mor, J. Hohlfeld, M. Islam, C. S. Brown, E. Girt, P. Krivosik, W. Tong, A. Rebei, and C. E. Patton, “Origins of the damping in perpendicular media: Three component ferromagnetic resonance linewidth in co-cr-pt alloy films,” *Appl. Phys. Lett.*, vol. 92, p. 022506, 2008. 66
- [134] A. Mekonnen, A. R. Khorsand, M. Cormier, A. V. Kimel, A. Kirilyuk, A. Hrabec, L. Ranno, A. Tsukamoto, A. Itoh, and T. Rasing, “Role of the inter-sublattice exchange coupling in short-laser-pulse-induced demagnetization dynamics of gdco and gdcofe alloys,” *Phys. Rev. B*, vol. 87, p. 180406, 2013. 70, 71, 72
- [135] C. D. Stanciu, A. Tsukamoto, A. V. Kimel, F. Hansteen, A. Kirilyuk, A. Itoh, and T. Rasing, “Subpicosecond magnetization reversal across ferrimagnetic compensation points,” *Phys. Rev. Lett.*, vol. 99, p. 217204, 2007. 70

- [136] G. P. Zhang, W. Hbner, E. Beaupaire, and J.-Y. Bigot, “Laser-induced ultrafast demagnetization: Femtomagnetism, a new frontier?,” *Topics of Applied Physics: Spin Dynamics in Confined Magnetic Structures I*, edited by B. Hillebrands and K. Ounadjela (Springer-Verlag Berlin Heidelberg 2002), vol. 83, pp. 245–289, 2002. 70, 71
- [137] T. A. Ostler, R. F. L. Evans, R. W. Chantrell, U. Atxitia, O. Chubykalo-Fesenko, I. Radu, R. Abrudan, F. Radu, A. Tsukamoto, A. Itoh, A. Kirilyuk, T. Rasing, and A. Kimel, “Crystallographically amorphous ferrimagnetic alloys: Comparing a localized atomistic spin model with experiments,” *Phys. Rev. B*, vol. 84, p. 024407, 2011. 71
- [138] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, “Interactions between light waves in a nonlinear dielectric,” *Phys. Rev.*, vol. 127, pp. 1918–1939, 1962. 87
- [139] R. W. Body, *Nonlinear Optics*. Boston: Academic Press, 1992. 87
- [140] C. B. Schaffer, *Interaction of Femtosecond Laser Pulses with Transparent Materials*. PhD thesis, Harvard, 2001. 87
- [141] Y. R. Shen, *The principles of Nonlinear Optics*. New York: John Wiley and Sons, 1984. 87
- [142] M. Sheik-Bahae, D. Hutchings, D. Hagan, and E. Stryland, “Dispersion of bound electron nonlinear refraction in solids,” *IEEE J. Quantum Electron*, vol. 27, p. 12961309, 1991. 87

Appendix A

Nonlinear Index of Refraction

The nonlinear dependence of the polarisation of an electric field with high intensity, can be expressed as power series in $\vec{E}$ [138, 139]:

$$\vec{P} = \varepsilon_0(\tilde{\chi}^1 \vec{E} + \tilde{\chi}^2 \vec{E} \vec{E} + \tilde{\chi}^3 \vec{E} \vec{E} \vec{E} + \dots) \quad (\text{A.1})$$

where $\tilde{\chi}^n$ is the n-th order nonlinear susceptibility.

Consider a spatial inversion in a centrosymmetric material. We have $P^{(2)} \rightarrow -P^{(2)}$, $E^{(2)} \rightarrow -E^{(2)}$, but $X^{(2)} \rightarrow X^{(2)}$, because the material has inversion symmetry. When then have that

$$-P^{(2)} = \varepsilon_0(-\vec{E})(\vec{E}) = P^{(2)} \quad (\text{A.2})$$

And so $P^{(2)} = 0$ which implies that $X^{(2)} = 0$. A similar argument holds for higher-order even terms in Equation A.1.

For moderate intensities laser (up to about 10^{12} W/cm^2) in centrosymmetric media, we may terminate the Equation A.1 after the third- order nonlinear polarisation. Because the material is isotropic, P and E are parallel, and will henceforth be represented by scalars. Including all three permutations of the fields on the hand side Equation A.1 which contribute to the third-order nonlinear polarisation, we can write:

$$\vec{P} = \varepsilon_0(\chi^{(1)} + \frac{3}{4}\chi^{(3)}|\vec{E}|^2)E \quad (\text{A.3})$$

The propagation of light in a nonlinear medium is governed by the wave equation which was derived from Maxwells equations for an arbitrary homogeneous, isotropic dielectric medium. This equation is given by:

$$\nabla^2 E^2 - \frac{1}{c} \frac{\partial^2 E}{\partial t^2} = -\frac{1}{\varepsilon_0 c^2} \frac{\partial^2 P}{\partial t^2} \quad (\text{A.4})$$

Substituting Equation A.3 in Equation A.4 leads to a index of refraction given by [140, 141, 142]

$$n = \sqrt{1 + \chi^{(1)} + \frac{3}{4}\chi^{(3)}|\vec{E}|^2} \quad (\text{A.5})$$

Taking the nonlinear term to be small compared to term linear $n_0^2 = 1 + \chi^{(1)}$, we can write:

$$n = \sqrt{n_0^2 \left(1 + \frac{3}{4n_0^2} \chi^{(3)} |\vec{E}|^2 \right)} \quad (\text{A.6})$$

$$n = n_0 \left(1 + \frac{3}{4n_0^2} \chi^{(3)} |\vec{E}|^2 \right)^{\frac{1}{2}} \approx n_0 + n_2 I \quad (\text{A.7})$$

where the intensity of the light is

$$I = \frac{1}{2} \epsilon_0 c n_0 |\vec{E}|^2 \quad (\text{A.8})$$

and the nonlinear refractive index, n_2 , is:

$$n_2 = \frac{3}{4 \epsilon_0 c n_0^2} \chi^{(3)} \quad (\text{A.9})$$

Equation A.7 shows the importance of the intensity laser $I(r, t)$, as the refractive index seen by the pulse follows the local and temporal intensity profile (Kerr Effect). The spatio-temporal dependence of the refractive index results in dramatic alterations of the spatial phase (self-focusing) and of the temporal phase (self-phase modulation) of the incoming pulse.

A.1 Self-focusing: Kerr Lens effect

From of the Equation A.7 highlight the fact that the light itself can alter the index of refraction. When the intensity of the light is high enough the electric field of the light becomes strong enough to distort the atoms of the material and change its refractive index. As the beam is more intense in the centre than the edges, the index of refraction becomes higher in the centre than at the edges, which causes the light to focus. A rod of material that acts like a lens for high intensity light based on the optical Kerr effect becomes known as a Kerr lens. The focusing from the Kerr lens limits when the beams diameter is narrow enough that its linear diffraction is large enough to balance out the Kerr effect (Figure A.1). The effect is known as self-focusing.

Figure A.1: The Kerr lens effect and self-focusing. The index of refraction varies with intensity along the beam diameter. Depending on the sign of the nonlinear term n_2 in the Equation A.7 the index of refraction increases or decreases towards the center of the laser beam. For positive n_2 the laser beam self-focuses.

A.2 Self-phase modulation

Self-phase modulation is due to the time dependence of the beam intensity provoking a temporal dependence of the refractive index [5]. For a quantitative analysis, we consider the propagation of an optical pulse through a medium with a refractive index given by Equation A.7.

In the slowly-varying envelope approximation, the electric field of the pulse has the form:

$$E(z, t) = A(z, t)e^{i(kz - \omega t)} \quad (\text{A.10})$$

where $A(z, t)$ is the slowly-varying envelope of the pulse. The propagation through a length L translates to a phase given by:

$$\phi(t) = kL - \omega t = \frac{\omega L}{c}(n_0 + n_2 I(t)) - \omega t \quad (\text{A.11})$$

The instantaneous frequency ω_{inst} and the phase are related through

$$\omega_{inst} = -\frac{d\phi(t)}{dt} \quad (\text{A.12})$$

By differentiating Equation A.11 finally writes, we can write ωt :

$$\omega(t) = \omega - \frac{\omega L n_2}{c} \frac{dI(t)}{dt} = \omega \left[1 - \frac{L n_2}{c} \frac{dI(t)}{dt} \right] \quad (\text{A.13})$$

From the last equation, it appears that the leading edge of the pulse (for $t < 0$) shifts to lower frequencies while the trailing edge shifts to higher frequencies in a symmetrical fashion. As main result, new frequencies are generated in the pulse spectrum upon nonlinear propagation with consequences on the temporal shape. In Figure A.2, the left-hand column shows the calculated instantaneous frequency and power spectrum for a pulse with an input *sech*(t) amplitude profile with a peak nonlinear phase shift of about 6π . The right-hand column shows a calculation for SPM acting in concert with normal dispersion, with the peak intensity adjusted to yield the same spectral broadening. For the normal case of media with positive nonlinear refractive index ($n_2 > 0$), the frequency modulation assumes the form of an approximately linear up-chirp in the central, most intense region of the pulse. The spectral broadening connected with this chirp can be exploited successfully for optical pulse compression

Figure A.2: Relation between (top) the time-dependent output intensity profile $|I(z, t)|^2$ and (middle) instantaneous frequency shift $\omega(z, t)$ in SPM, as well as (bottom) resultant power spectrum. A medium with $n_2 > 0$ is assumed, and $1 \text{ cm}^{-1} = 30 \text{ GHz}$. The left-hand side shows the case of pure (dispersionless) SPM with a peak nonlinear phase shift of about 6π . In this case the output intensity profile is identical to the input intensity profile. The right-hand column shows a calculation for SPM acting in concert with normal dispersion, with the peak intensity adjusted to yield the same spectral broadening [5].

Appendix B

Second Harmonic Generation

Second harmonic generation (SHG) is a second-order nonlinear optical process in which two photons at the frequency ω interacting with noncentrosymmetrical media (i.e., material lacking a generalised mirror symmetry) combine to form a new photon with twice the energy, and therefore twice the frequency (2ω) and half the wavelength of the initial photons Figure B.1.

Figure B.1: When intense light is shone on materials that do not possess an inversion symmetry, the vibrating electric field of the incident beam results in the polarization of the medium, reemitting light at the original frequency ω_i but also at the frequency $2\omega_i$ that is twice the original one (with half of the wavelength). SHG involves only virtual energy transition. As a result, using ultrafast (femtosecond) pulsed lasers, the response time of SHG is at the femtosecond level allowing very fast and sensitive detection. Adapted from [15]

The electric field induces a nonlinear polarisation $P^{(2)}$ in the material, which can be written as [16]:

$$P_i^{(2)}(\omega) = \sum_{j,k} \chi_{ijk}^{(2)} E_j(\omega) E_k(\omega) \quad (\text{B.1})$$

The polarised dipoles radiate in a frequency 2ω which generates an electric field $E_{2\omega}$, that propagates with phase velocity $v_{(2\omega)} = c/n_{(2\omega)}$. If both waves propagate along the length of the material with the same phase velocity, the energy from the fundamental wave is converted to the second harmonic wave, occurring phase matching between them. However, due to dispersion, waves do not usually propagate with the same velocity. Then, after propagating in a distance, known as the coherence length, both waves will be out of phase. Meaning that both fundamental and second harmonic waves cannot be always added at different positions within the nonlinear material. When the fundamental and second harmonic waves propagate through the nonlinear material in the condition of non-phase matching, SHG power varies along the length of the nonlinear material. In this case, the SHG can be described by [16]:

$$I(2\omega, L) = \frac{2\omega^2 \chi_{eff}^2 L^2}{n_{2\omega} n_{\omega}^2 c^3 \varepsilon_0} \left(\frac{\sin(\Delta k L/2)}{\Delta k L/2} \right)^2 I^2(\omega) \quad (\text{B.2})$$

The dependence on both the length of the material L and the incident intensity $I(\omega)$ is quadratic; c the velocity of light. The intensity of the doubled frequency is proportional to the square of an effective susceptibility χ_{eff}^2 , which depends on the material and reflects the mean doubling properties of this material in a given working direction. For the doubling yield to be maximum, the dephasing quantity $\Delta k = k(2\omega) - k(\omega)$ must be zero. This dephasing term accounts for the propagation effects during the doubling process. At any one point along the propagation axis the electronic oscillators radiate at angular frequency ω and 2ω in the same direction k .