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Ultrafast demagnetisation as a Terahertz source

Rhys Hargreaves

University of Wollongong

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Ultrafast Demagnetisation as a Terahertz Source

A thesis submitted in partial fulfillment of the requirements for the award of the degree:

Master of Science – Research

from

University of Wollongong

by

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August 2014
Declaration

I, Rhys Hargreaves, declare that this thesis, submitted in partial fulfilment of the requirements for the award of the degree of Master of Science – Research, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Rhys Hargreaves
1st of August, 2014
For Nikki,
Abstract

Ultrafast demagnetisation of ferromagnets by ultrafast laser pulses provides a unique window for the investigation of spin dynamics in ferromagnets. Ultrafast demagnetisation has previously been observed via the generation of Terahertz emissions (among other methods) using amplified lasers, and by magneto-optical methods using non-amplified lasers. Using a fast (short pulse length), low power laser, with lower pulse energies, but comparable peak pulse power density, models of ultrafast demagnetisation were compared.

The models compared were the Two Temperature model proposed by Vaterlaus et al.[1], the Three Temperature Model by Beaurepaire et al.[2], the Non-Thermal-Electron model by Ju et al.[3], and the Microscopic Three Temperature Model by Koopmans et al.[4]. A quasi-null result of THz spectral power density $< 10^{-22}$ W $\cdot$ THz$^{-1}$, from Nickel samples, was inconsistent with predictions of the Two Temperature Model. More accurate measurements of Terahertz emission were not possible due to cumulative noise effects from the high pulse repetition frequency, and low pulse energy used.

In addition, theoretical investigations into the Microscopic Three Temperature Model were undertaken. These predicted that the peak Terahertz emission frequency is inversely proportional to the ultrafast pulse length. It was also predicted that (for the laser modelled) peak power output is achieved by initiating demagnetisation from $\approx 80\%$ of the Curie temperature of the material, and that this result is approximately independent of the material.
Acknowledgements

Associate Professor Josip Horvat and Professor Roger Lewis, my supervisors, for their support, guidance and patience.

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Chapter 1

Introduction

Terahertz radiation is a fast developing area of science and technology, aimed at utilising an area of the electromagnetic spectrum that was previously unexplored. Terahertz radiation is typically defined as electromagnetic radiation with a frequencies between 0.3 THz and 3 THz, and hence wavelengths between 1 mm and 0.1 mm (100 µm). Terahertz radiation has historically been difficult to produce and detect because it has frequencies that are too high for the electronic oscillator based methods used to produce radio waves and microwaves, and too low for the (atomic or molecular) energy level transition based methods used to produce infra-red and optical light.

Terahertz generation from magnetic dipoles was observed by Lai et al. in 1998[5]. These experiments used ultrafast laser pulses on semiconductor microstructures to produce high currents around relatively large (∼30 µm) microstructure loops. These current loops acted as classical magnetic dipoles, and radiated energy in the Terahertz region.

Terahertz radiation has also been produced from magnetic dipoles by the phenomenon of ultrafast demagnetisation[7], that is; using an ultrafast pulsed laser to transiently suppress or remove the magnetisation of a ferromagnet. This fast change in magnetisation also forms a changing magnetic dipole, radiating energy in the Terahertz region. This differs from the method used by Lai et al. in that no semiconductor microstructure was involved, and that the mechanisms of the magnetisation change are not fully understood.

The energy emitted as Terahertz radiation by ultrafast demagnetisation processes is very small, but very little information has been published on the actual quantities of energy emitted, and there is still discussion over the mechanisms and processes involved in Terahertz emission from ultrafast demagnetisation.

Previous experiments by Beaurepaire et al.[7], have confirmed that using a high
power, high fluence (1-10 mJ cm$^{-2}$), amplified ultrafast pulse, Terahertz emissions can be obtained from ultrafast demagnetisation of Nickel thin films. Other similar experiments[12] confirm that this occurs similarly for a wide variety of ferromagnet substances and structures. Ultrafast demagnetisation has also been detected by time-resolved magneto-optical methods, using much lower pulse energy, un-amplified ultrafast lasers[13].

By focusing a shorter pulse length (10 fs in this thesis, 60-100 fs is typical in literature), un-amplified, pulse laser, pulses with similar peak power densities, but shorter pulse durations and lower total energies can be produced. Using a focused, un-amplified laser, it was proposed that both quantitative measurements of Terahertz emission by ultrafast demagnetisation could be made, and that insight could be gained into the mechanisms of ultrafast demagnetisation.

The thesis is divided into seven chapters. Chapter 1 is this introduction, which provides a general overview of the aims and scope of the thesis. Chapter 2 is the literature review, which summarises and reviews the published work that lead to the research undertaken in this thesis. Chapter 3 contains the theory, drawn from other published work, which is introduced and explained there, for use elsewhere in the thesis. Chapter 4 is titled model development. In this chapter, models were developed to explore and explain the phenomena being researched, as well as to provide predictions for the experimental work undertaken. Chapter 5 is the methods and materials chapter, where the experimental work undertaken is described, including the apparatus, procedures, and descriptions of the materials used. This chapter also includes quantitative predictions of the experimental results, derived from the models developed in chapter 4. Chapter 6 is the results and discussion chapter, where the experimental results are presented and discussed, along with theoretical results, derived from the models developed in chapter 4. Finally chapter 7 is the conclusions, where the results of the work undertaken in the thesis are assessed with respect to the aims of the work, and where future directions are identified. Attached to the thesis are two appendices, the first, appendix A, contains the values of fundamental constants and material properties used in this thesis. The second, appendix B, contains MATLAB code listings, that implement the models developed in chapter 4.
Chapter 2

Literature Review

In this chapter the literature preceding the thesis topic is summarised and reviewed. The notation used in this chapter is kept from the source, and as such may not be compatible or consistent, either between sources, or with the rest of the thesis. Where notation is changed for use elsewhere in the thesis it is noted when introduced.

2.1 Terahertz Emission by Ultrafast Demagnetisation

The phenomenon of ultrafast demagnetisation was proposed in 1992 by Vaterlaus et al.\cite{1}, but the production of Terahertz radiation was not observed until 2004, by Beaurepaire et al.\cite{7}. Likely mechanisms for demagnetisation were proposed in 2004 by Koopmans et al.\cite{11} but were not proven theoretically until 2009 by Steiauf et al.\cite{14}, and experimentally by Koopmans et al.\cite{4} in 2010.

2.1.1 Terahertz Emission From Magnetic Dipoles

The use of magnetic effects to generate Terahertz radiation was demonstrated by Lai et al.\cite{5} in 1998. These experiments used a biased, metal on semiconductor microstructure, shown in figure 2.1. When a laser pulse was applied to the biased interdigital switch a rapidly changing electric dipole was formed due to the resultant current surge. The current also passed around the loop in the upper section, forming a magnetic dipole. The experiment was designed so that the radiation from the magnetic dipole was larger than that of the electric dipole.

The apparatus used by Lai et al. is illustrated in figure 2.2. The laser used was a mode-locked Titanium-Sapphire laser, with a central wavelength of 810 nm. The pulse rate was 82 MHz and the pulse duration was 100 fs. The laser was coupled to
Figure 2.1: Image of the Ti-Au on GaAs microstructure used by Lai et al.\cite{5}. Ultrafast pulse was applied to the digital substructure on the left. Large transient currents moving around the curve to the top are the cause of the changing magnetic dipole moment. The structure is 300 $\mu$m by 300 $\mu$m, the emitter section is 30 $\mu$m by 30 $\mu$m and the interdigital spacing in the emitter section is 1 $\mu$m.

the emitter and detector by optic fibres and the semiconductor microstructure was biased with a DC voltage. The fibre to the emitter was connected via an acousto-optical modulator, coupled to a lock-in amplifier. This modulation was used to exclude noise uncorrelated with the signal. The Emitter was a 300 $\mu$m $\times$ 300 $\mu$m $\times$ 1 $\mu$m Titanium-Gold alloy, deposited on a low temperature grown Gallium Arsenide substrate (see figure 2.1). The left leg was connected to a DC voltage, the right to ground. The laser pulse was coupled by optic fibre to the interdigital switch section, which consisted of 2 $\mu$m wide Ti/Au fingers, separated by a 1 $\mu$m wide area of GaAs substrate. The detector was a photoconductive probe, which was coupled to the ultrafast pulse by an optic fibre. The detector is connected to a junction gate field-effect transistor (JFET) amplifier, whose role was to pre-amplify the current produced by the detector, so that it could be properly detected by the lock-in amplifier. The lock-in amplifier then extracted the component of the signal that was modulated at the frequency of the AO modulator, and amplified it, then transmitted the signal for recording.

When a pulse is emitted from the detector, the major part will be modulated by the AO modulator, then be directed onto the interdigital switch. The photons will generate carrier pairs in the substrate which will be swept by the bias voltage.

2.1. Terahertz Emission by Ultrafast Demagnetisation

Figure 2.2: Apparatus used by Lai et al.\cite{5}. A pulse from the Ti:Sapphire laser is split, with the main component used to trigger the photoconductive emitter, then the remaining component used to trigger the JFET detector after a variable delay.

An electric dipole forms when a short, intense current is created to the appropriate electrode. This current also occurs throughout the microstructure, with the upper part of the microstructure forming a current loop. Rapid changes in the current in this loop emit radiation as a magnetic dipole.

The remaining part of the pulse (which was not coupled onto the emitter) passes through a variable delay line, then to the photoconductive detector. When the pulse is incident on the photoconductive detector, the electric field of the Terahertz radiation emitted from the emitter is sampled. The signal is then amplified and recorded. By varying the delay line, a time domain representation of the electric field at the detector is produced. This procedure is necessary since Terahertz frequencies are too high to be directly sensed by current electronic detectors.

It was discovered that due to the arrangement of the microstructure, the current loop dipole being much larger ($\sim 100 \mu$m) than the interdigital dipoles ($\sim 1 \mu$m), that the magnetic dipole emissions were greater than the electric dipole emissions. Measurements were also taken in the sample plane of the emitter, on either side (in the $+x$ and $-x$ directions from figure 2.2). These measurements showed Terahertz radiation with opposite phases, which would not have occurred in the sample plane, from electric dipole emission. These measurements were however consistent with emission from a magnetic dipole oriented out of the plane, which would be generated by a current loop in the microstructure.

The results obtained by Lai et al. are reproduced in figure 2.3. The results show broadband Terahertz emissions from $\approx 0.25$ to $\approx 1.5$ Terahertz, with a peak at $\approx 0.4$ Terahertz. While these results were produced by novel means, they showed
that Terahertz radiation can be produced in detectable quantities, from magnetic sources.

### 2.1.2 Non-Equilibrium Heating

The heating of the electron shell of a substance separately from the lattice was first demonstrated by Anisimov et al. in 1974[15], and was described using the so-called two temperature model (2TM). It was nearly two decades however until the effects of this non-equilibrium heating on ferromagnetic materials was demonstrated.

Vaterlaus et al.[1][6] in 1991, first measured the non-equilibrium spin-heating of a solid using 10 ns, 2.1 eV pump pulses and 60 ps, 3.2 eV probe pulses, on a Gadolinium sample, saturated with a 0.38 T magnetic field. Using Spin-Resolved Two-Photon Photoemission (SR-2PPE), the population of the conduction electrons was examined. It was hypothesised that heating of the electron cloud was conducted so quickly that the material (partially) demagnetised, with the electrons approaching the Curie temperature, with only delayed heating of the crystal lattice. The value reported by Vaterlaus et al. for the spin-lattice relaxation time in Gadolinium was reported to be \(100 \pm 80\) ps, far larger than later measurements on other ferromagnets (even taking into account the large error margin). This was only recently explained by Koopmans et al. in 2010 as being the result of delayed interactions between magnetic electrons in the \(5f\) and \(5d6s\) shells[4]. The experiments by Vaterlaus et al. involved a high energy pulsed pump laser and two lower energy dye lasers. The pump laser was a 5 eV Krypton-Fluorine excimer laser. The photon energy of the higher energy dye laser was 3.2 eV, and the lower energy laser 2.1 eV. Light from the pump...
2.1. Terahertz Emission by Ultrafast Demagnetisation

Figure 2.4: Evolution of photoemitted electron polarisation and spin temperature, as determined by the spin populations of photoemitted electrons, as reported by Vaterlaus et al.[6]. Copyright 1992, American Physical Society. Reproduced with permission. The polarisation of electrons emitted by the sample decreased by 60% over \( \approx 1.5 \) ns. From this change in polarisation, a change in magnetisation, and therefore a change in spin temperature of \( \approx 175 \) K, can be inferred over the same period.

The change in electron polarisation produced by the first, lower photon energy pulse is shown in figure 2.4. Under the hypothesis that the change in electron polarisation was due to a change in magnetisation, itself induced by the rapid heating of the sample by the first pulse, a spin temperature associated with the magnetisation

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was derived. This spin temperature is also plotted in figure 2.4, and shows a change of \( \approx 175 \text{ K} \) over \( \approx 1.5 \text{ ns} \).

2.1.3 Ultrafast Demagnetisation

Ultrafast demagnetisation of ferromagnets was first reported by Beaurepaire et al.\cite{2} in 1996, using 60 fs laser pulses on polycrystalline Nickel thin film. The magnetisation of the sample was measured using a time resolved magneto-optical Kerr effect apparatus. It was proposed that the demagnetisation was a result of non-equilibrium spin temperatures induced by the pulse. In this experiment, Beaurepaire et al. used a 620 nm colliding pulse mode locked dye laser, producing 60 fs pulses. These

\[ \text{H-(Oe)} \]
\[ \Delta t-(\text{ps}) \]
\[ \text{no pump} \]
\[ \text{Kerr reflectivity} \]
\[ \text{Probe-(time delayed)} \]
\[ \text{Pump Kerr-signal-(a.u.)} \]
\[ \text{Transmission-(a.u.)} \]
\[ -50 \ 0 \ 50 \ 0 \ 2 \ 4 \ 6 \]

\[ \text{H-(Oe)} \]
\[ \Delta t=2.3 \text{ ps} \]

\[ \text{no-pump} \]

\[ \text{Kerr} \]

\[ \text{reflectivity} \]

\[ \text{Probe-(time delayed)} \]

\[ \text{Pump} \]

\[ \text{Kerr-signal-(a.u.)} \]

\[ \text{Transmission-(a.u.)} \]

\[ -50 \ 0 \ 50 \ 0 \ 2 \ 4 \ 6 \]

\[ \text{H-(Oe)} \]
\[ \Delta t-(\text{ps}) \]
\[ \text{no-pump} \]

\[ \text{Kerr reflectivity} \]

\[ \text{Probe-(time delayed)} \]

\[ \text{Pump} \]

\[ \text{Kerr-signal-(a.u.)} \]

\[ \text{Transmission-(a.u.)} \]

\[ -50 \ 0 \ 50 \ 0 \ 2 \ 4 \ 6 \]

\[ \text{H-(Oe)} \]
\[ \Delta t-(\text{ps}) \]
\[ \text{no-pump} \]

\[ \text{Kerr} \]

\[ \text{reflectivity} \]

\[ \text{Probe-(time delayed)} \]

\[ \text{Pump} \]

\[ \text{Kerr-signal-(a.u.)} \]

\[ \text{Transmission-(a.u.)} \]

\[ -50 \ 0 \ 50 \ 0 \ 2 \ 4 \ 6 \]

\[ \text{Figure 2.5: Ultrafast Demagnetisation Measurement using TR-MOKE by Beaurepaire et al.\cite{2}.} \]

\[ \text{a) Diagram of the 1996 experiment by Beaurepaire et al.\cite{2}. Rotation of polarisation, or change in ellipticity of the probe pulse depends on the B-field in the sample. Both the pump-probe delay and the H-field can be altered. This allows the effective measurement of M(H,t) during the relaxation after the pump pulse.} \]

\[ \text{b) Hysteresis loops taken by varying the applied magnetic field and comparing with the reflected polarisation. This shows the loss of roughly half of the remnant and saturation magnetisation at a pump-probe delay of 2.3 ps. This is the basis for the magnetisation results in figure 2.6 and the spin temperature results in figure 2.7.} \]

\[ \text{c) Transmittivity of Nickel thin film as a function of probe pulse delay time. This change was attributed to the loss of reflectivity via electronic heating, although it was also suggested that it was the result of a loss of absorptivity due to depletion of electrons in states able to absorb the pump pulse photons (referred to as dichroic bleaching). The inferred loss of reflectivity is the basis for the electron temperature results in figure 2.7.} \]


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2.1. Terahertz Emission by Ultrafast Demagnetisation

Figure 2.6: Ultrafast change in remnant magnetisation of Nickel thin film, by Beaurepaire et al.\cite{2}. This shows a loss of nearly half the remnant magnetisation of Nickel at a time delay of 2 ps after the pump pulse, i.e. ultrafast demagnetisation. The loss of magnetisation recovers completely over long (100s of ps) timescales, which correspond to the macroscopic cooling of the material.

Ultrafast pulses were amplified using copper vapour laser, resulting in pulse rate of 5 kHz. The sample used was a 22 nm thick polycrystalline Nickel thin film with a 100 nm MgF$_2$ coating, mounted in an electromagnet, with the field in parallel to the sample plane, and the plane of polarisation. The laser was split into two components, with the major component directed onto the sample as the pump beam, and a smaller component directed into a delay line. The pump beam induced non-equilibrium heating in the sample, while the probe beam was directed onto the sample at a more oblique angle. Due to the magneto-optic Kerr effect the polarisation of the reflected beam is dependent on the magnetisation of the sample. This is illustrated in figure 2.5a. By varying the applied magnetic field, a hysteresis loop could be taken at any time delay after the pump beam, allowing the time-dependent remnant magnetisation to be measured. An example of this is shown in figure 2.5b, and the change of remanence as a function of probe delay time is shown in figure 2.6. The transmissivity of the sample was also affected by the heating, and was recorded as a function of path delay. This is depicted in figure 2.5c. This change in transmissivity was used as the basis of the electron temperature, shown in figure 2.7a.

To measure the temperatures of the components of the material, the assumption was made that, during non-equilibrium heating, components of the material have the same properties that they would have at equilibrium. The electron temperature was taken to be the temperature of Nickel, as measured by the transmittivity.
2.1.4 Terahertz Emission From Ultrafast Demagnetisation

In a search for methods to observe ultrafast demagnetisation that do not rely on the optical properties of the magnetised surface, in 2004, Beaurepaire et al. used Terahertz time domain spectroscopy (THz-TDS) to observe Terahertz radiation emission
2.1. Terahertz Emission by Ultrafast Demagnetisation

as a result of ultrafast changes in the magnetisation of a Nickel thin film. The ex-

periment was performed using a regeneratively amplified Titanium Sapphire laser producing 1 mJ pulses, 100 fs long, at a rate of 1 kHz. The sample used was a multilayer thin film consisting of 30 Å of Chromium, 42 Å of Nickel, and 70 Å of Chromium deposited by electron beam evaporation onto a glass substrate. Pulses from the laser were split into a small < 0.1% reference beam, with the remainder continuing as pump beam. The reference beam is distinguished from probe beams used in other techniques, by not interacting with the sample. Whereas a probe beam interacts with the sample, the reference beam interacts with the detection apparatus.

The pump beam was directed onto the sample, and the reference beam was directed into an optical delay line. The pump beam then induced ultrafast demagnetisation within the magnetised sample, which resulted in magnetic dipole emission of Terahertz radiation. This emission was directed onto a ⟨110⟩ Zinc Telluride crystal. Zinc Telluride exhibits the Pockels effect, that is that a low (<5 THz) electric field


Figure 2.8: Diagram of Terahertz time domain spectroscopy, as used by Beaurepaire at al.\[7\]^4. A high intensity pump pulse has a portion split off into a reference beam. Terahertz radiation emitted by the sample rotates the polarization of the reference beam at an electro-optical crystal, which is then detected by an analyser. Varying the delay of the reference beam provides a time-domain representation of the Terahertz emitted by the sample as a result of the ultrafast pulse.
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Figure 2.9: Terahertz emissions from ultrafast demagnetisation by Beaurepaire et al. [7].

a) Time-domain Terahertz signal generated by the above experiment (figure 2.8). This shows a pulse of electromagnetic energy, with a poorly defined frequency, but the pulse duration of 1 ps implies a peak frequency of 1 THz. Normally frequency analysis would be performed on a Fourier transform of the time domain data, or a power spectrum derived from it.

b) The change in magnetisation implied by the Terahertz emission, assuming the emission is from a magnetic dipole. The demagnetisation inferred here has a different profile, but similar timescale to that measured earlier [2], depicted in figure 2.6.

causes it to become birefringent to higher frequency light (optical and near infra-red in this technique). The reference beam was directed to the Zinc Telluride crystal, then to an analyser. This apparatus is illustrated in figure 2.8.

The Terahertz induced birefringence caused the reference beam polarisation to be rotated proportionally to the Terahertz radiation emitted. By varying the length of the delay line, a time domain picture of the Terahertz emissions was constructed, as shown in figure 2.9a. Both the Terahertz emission frequency, and the polarisation of the radiation pattern were consistent with ultrafast demagnetisation occurring with a characteristic time of hundreds of femtoseconds. The time domain signal produced by the modulated reference beam was also consistent with Terahertz emission from a magnetic dipole, formed by ultrafast demagnetisation of a ferromagnet. The ultrafast change in magnetisation inferred from this relationship is shown in 2.9b. Together, the curves in figure 2.9 show ultrafast demagnetisation, occurring over timescale of picoseconds (≈2 ps) resulting in the emission of Terahertz radiation.
2.2 Experimental Techniques

Multiple experimental techniques have been used to investigate ultrafast demagnetisation. Since the precise mechanisms of ultrafast demagnetisation are still becoming clear, multiple techniques have been used to gain insight into the internal causes and effects of ultrafast demagnetisation.

2.2.1 Time-Resolved Magneto-Optical Effects

The Magneto-Optical Kerr effect (MOKE) is the phenomena that light reflected from, or transmitted through, a magnetised material undergoes a change in polarisation, proportional to the Magnetisation of the substance.

Time Resolved Magneto-Optical Kerr effect (TR-MOKE) techniques use an optical pump-probe method, in which a pulsed laser beam is periodically interrupted by a chopper, then split in to a pump and probe beam, with the vast majority of laser light remaining in the pump beam. The pump beam is then used to excite the sample, while the probe beam is diverted into a variable optical delay line. The probe beam is then directed onto the sample at an oblique angle and either reflected or transmitted (or both) to a polarisation analyser. These signals are then integrated over many pulses by a lock in amplifier, tuned to the frequency at which the original beam is chopped. A general diagram of TR-MOKE is shown in figure 2.10.

Since the change in polarisation depends on the magnetisation of the sample, varying the length of the optical delay line allows the creation of a time domain representation of the magnetisation of the sample. The delay line can also be held constant, while the applied magnetic field is altered, effectively taking a hysteresis loop, at a variable delay from the pump pulse. This also allows the measurement of other magnetic properties of the sample, such as coercivity and remanence, at any point of the ultrafast demagnetisation process.

Measurements based on the reflected polarisation measure the magnetic field only to the penetration depth for the laser into the material, whereas transmission measurements are affected by the entire bulk of the material they pass through. MOKE contrast had been assumed to be a reliable method of determining the change in magnetisation of a sample, however Koopmans et al.\cite{16} questioned whether demagnetisation on sub-picosecond timescales was possible, since the proposed mechanisms that operate on these timescales are purely electronic and as such must conserve the total electronic angular momentum. Experiments were conducted to distinguish between ellipticity and rotation of the reflected probe beam. These showed that for times less than 1.5 picoseconds after a pump pulse, MOKE contrast does not provide
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Figure 2.10: Diagram of the typical Magneto Optical Kerr Effect apparatus by Zhang et al.\cite{zhang2002laser}. The time delay between a high power pump pulse and a low power probe pulse is varied, then the correlation between the pulses is measured for transmission, reflection, or both. Copyright 2002, Springer-Verlag. Reproduced with permission.

The polarisation of the reflected pulse component is dependent on the magnetic field in the sample. In the absence of a pump beam, the analyser can be adjusted to zero, then, at variable pump-probe delay, the time dependent change in magnetisation of the sample can be determined from the passage of reflected probe pulses through the analyser.

The magnitude of the transmitted pulse is dependent on the temperature of the electrons in the sample. The change in transmission of probe pulses as a function of pump-probe delay allows measurement of non-equilibrium heating by the pump pulse, and subsequent relaxation, as a function of time

an accurate representation of the magnetisation. It was proposed that the depletion of electrons at suitable energy levels to facilitate transmission, caused by the intense laser pulse, produced a transient loss of transmittivity, which was misinterpreted as a magnetisation induced polarisation change. However in 2002, Guidoni et al. conducted experiments comparing Magneto-Optical Kerr Effect measurements in transmission and reflection geometry\cite{guidoni2002laser} and found that while transmission experiments were affected at optical energies, demagnetisation still did occur on ultrafast timescales.

2.2. Magnetisation Dependent Surface Second Harmonic Generation

Magnetisation dependent surface second harmonic generation is a technique whereby high intensity laser light is used to measure the magnetisation of a sample via non-linear surface effects. The experimental apparatus is similar to other time resolved magneto optical measurements, with a high power pump beam, and a lower power, time delayed reference beam. The difference lies in the detection apparatus, since the second harmonic is a different frequency (colour) to the pump and probe beams, they can easily be filtered out, leaving only magnetisation dependent second harmonic signals. By varying the delay stage a time resolved representation of the non-linear optics of the sample, down to the penetration depths, can be obtained.

The connection between the magnetisation and spin temperatures was examined by Hohlfield et al. [18]. Experiments were conducted on bulk polycrystalline Nickel, using pump-probe second harmonic generation. It was shown that shortly after the pump pulse, where the electron reservoir was not thermalised, the magnetisation deviated strongly from that predicted by the electron temperature. For the time when electron temperature was not in equilibrium with the lattice temperature, Hohlfield et al. found that magnetisation was a function of electron temperature. Developments such as this lead to the development of non-thermal electron models in an attempt to explain ultrafast demagnetisation. These models are explored in section 2.5.3.

2.2.3 Spin-Resolved Two-Photon Photoemission

Spin resolved two-photon Photoemission (SR-2PPE) is a technique where the magnetisation of a sample is measured by directly sampling the spin of the surface electrons. While the technique appears similar to other time resolved optical methods, the apparatus is complicated by the need for two, synchronised, pulse lasers of different energies, at least one of which must be higher than the photothreshold. Another difficulty is the need for the apparatus to be enclosed in vacuum, to prevent atmospheric absorption of the photoemitted electrons. Typically a UV laser is used to excite ultrafast pulses from two dye lasers, one ultraviolet, the other visible. The visible pulse, which has an energy below the photothreshold of the material, is used to excite the sample. The ultraviolet laser is passed through a delay stage and then directed onto the material at a variable time delay. The ultraviolet pulse has energies above the photothreshold and therefore causes electrons to be photoemitted from the sample. These electrons are captured in a spin sensitive manner, typically
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by a Mott detector. A diagram is provided at figure 2.11.

The spin polarisation of the photoemitted electrons reflects that of the spin population at the surface of the sample. In this way a time resolved picture of the spin dynamics following an ultrafast pulse can be measured. Since the distance through which the photoemitted electrons can travel through a solid is so short, the depth tested by SR-2PPE is even shorter than that of surface magneto optical methods, being of the order of femtometers.

![Diagram of a typical SR-2PPE experiment by Scholl et al.](image)

Figure 2.11: Diagram of a typical SR-2PPE experiment by Scholl et al.[9]. The sample is placed in a variable magnetic field and in a vacuum chamber. A sub photothreshold energy pump pulse is used to heat the sample, then, at a variable time delay, a higher energy pump pulse is used to excite electrons from the surface. These electrons are spin-analysed by a Mott detector. The overall effect is to sample the surface electron spin polarisation, at any time delay after the pulse.

### 2.2.4 Terahertz Time Domain Spectroscopy

Classically, a changing magnetic dipole will emit electromagnetic radiation similarly to the more familiar electric dipole[19]. Demagnetisation of a classical magnetic dipole over hundreds of femtoseconds, will produce a electromagnetic radiation at Terahertz frequencies. Searching for non-optical methods for investigating ultrafast demagnetisation, Beaurepaire et al.[7] used Terahertz time domain spectroscopy to find Terahertz emissions from Nickel thin film. These emissions were consistent with prior measurements of the time dependent magnetisation.

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2.3 Range of Materials

Terahertz time domain spectroscopy (THz-TDS) uses an electro-optic crystal sensitive to Terahertz radiation, produced by the action of a pulse beam on a sample, to modulate a time delayed reference beam. This is detailed in reference to the literature in section 2.1.4 and figure 2.8, as well as later in section 5.1 as used experimentally in this thesis. As a method of measuring ultrafast demagnetisation, THz-TDS has the advantage of not relying of the optical properties of a system which may be significantly different in the time following absorption of an ultrafast pulse, a problem raised by Koopmans et al., and referred to in section 2.2.1.

2.3 Range of Materials

Similar ultrafast demagnetisations have been observed across the full range of ferromagnetic materials, from elemental ferromagnets, to alloys, to half-metallic compounds. Effects have also been observed across the full spectrum of relevant structures, bulk metals, foils and thin films, in polycrystalline and monocrystalline forms, to multilayer films and nanostructures.

By far the most popular material used in ultrafast demagnetisation experiments are nickel thin films, both poly and monocrystalline, for the full range of experimental techniques[9, 2, 7, 20, 16]. Bulk Nickel was also used with Magnetisation Dependent Second Harmonic Generation (MSSHG) by Hohlfield et al.[18] and Time Resolved Magneto-Optical Kerr Effect (TR-MOKE) methods by Wu et al.[13]. Other elemental ferromagnets used have been Cobalt thin film by Cinchetti et al.[21], Iron thin films by Kampfrath et al.[22] and Carpene et al.[23], and bulk Gadolinium by Vaterlaus et al.[1, 6].

Ferromagnetic alloys have also been used, primarily CoPt$_3$ thin films by Ju et al.[3], Beaurepaire et al.[24] and Guidoni et al.[17]. Ultrafast demagnetisation has also been observed in lanthanide containing ferromagnets such as TbFe by Kim et al.[25]. Half-metallic ferromagnets also exhibit the effect with Zhang et al.[26] using CrO$_2$ and Kise et al.[27] using Sr$_2$FeMoO$_6$.

This demonstrates that ultrafast demagnetisation is an effect in all ferromagnets, and is not a result of peculiarities of structure or chemistry. Similarly, experiments with antiferromagnetic materials show analogous ultrafast magnetic effects [28][29].

2.4 Mechanisms of Demagnetisation

Since fundamentally ferromagnetism is the result of an excess of total angular momentum of the electrons in a ferromagnet, any reduction in the magnetic moment
of a ferromagnet must involve a reduction of the angular momentum of the relevant electrons\cite{10}. In this case the relevant unpaired electrons are those in the 3d (for Iron, Cobalt, Nickel) or 4f (for Gadolinium) shells. Since angular momentum is a conserved quantity, the loss of angular momentum of the electrons must take the form of an interaction, transferring angular momentum from an electron to another entity with lower or zero magnetic moment (lower magnetic moment is necessary for the interaction to decrease the magnetisation).

Unlike a linearly polarised pulse, a circularly polarised pulse will deliver net angular momentum to the electrons, and may assist or inhibit demagnetisation. However the angular momentum carried by the pulse is far less than is required to demagnetise the sample by any significant amount. This is compounded by the fact that most lasers used in ultrafast demagnetisation are linearly polarised and as such carry no net angular momentum. This was demonstrated by Dalla Longa \textit{et al.}\cite{20}, who showed using TR-MOKE methods, that while transmission and reflection magnitudes were both dependent on the helicity of the laser, the demagnetisation effect was not.

2.4.1 Spin-Orbit Coupling Meditated Demagnetisation

Zhang \textit{et al.} proposed in 2000 that spin-orbit coupling based interactions may allow the transfer of angular momentum from conduction band electrons to inner electrons\cite{10}. While these interactions are forbidden according to the semiclassical models of the electron shell, these models are not strictly applicable due to relativistic effects on outer electrons, interactions with electrons from neighbouring atoms, and the splitting of spin sub-bands in a ferromagnet.

In normal ferromagnets, orbital angular momentum is quenched. In the presence of a high energy laser field and spin orbit coupling, or in similar situations following an ultrafast pulse, it is hypothesised that this will not longer be the case, and that partially demagnetising transitions to $L \neq 0$ states may become available. It was hypothesised that in the presence of the laser field, the density of triplet states is decreased and the density of singlet states increased, allowing spin-orbit coupling mediated transitions between the two. The predicted change in the density of states is depicted in figure 2.13a. Without either spin-orbit coupling, or the laser field, these transition, and hence demagnetisation cannot occur, as illustrated in figure 2.14. The mechanism proposed by Zhang \textit{et al.} is problematic, since the laser field is only present during the laser pulse, and the optical electrons return to thermal equilibrium shortly after. This requires either that ultrafast demagnetisation occurs on the timescale of the pulse, rather than that of electron thermalisation.
2.4. Mechanisms of Demagnetisation

The problematically short demagnetisation time is evident here. Demagnetisation via spin orbit coupling is predicted to occur over 10 fs, more than an order of magnitude faster than is experimentally observed.

Inset: Experimental dependence of magnetisations on pulse intensity. This illustrates the limit to which spin-orbit coupling based demagnetisation can reduce magnetisation, being limited to 55% reductions regardless of the pulse intensity.

or electron-lattice relaxation, or that laser field induced SO coupling is part of a multi-step process. This multi-step process would entail electrons rapidly transitioning to an intermediate state, without demagnetisation or Terahertz emission, then undergoing a demagnetising transition at a later time. This problem was not particularly apparent when the shortest pulse durations available were of comparable length to the demagnetisation times (∼100 fs). It is now much more evident, due to the development of lasers with shorter pulse durations, such as the 10 fs used experimentally in this thesis. Also problematic is the limitation on the degree of demagnetisation to approximately half, regardless of the pulse intensity. This is illustrated in figure 2.12.

2.4.2 Elliot-Yafet Spin Flip Interactions

An Elliot-Yafet (EY) interaction is an electron lattice interaction in which angular momentum is transferred from an electron to the lattice[14]. The net result of an E-Y interaction is that an electron undergoes a spin flip and an angular momentum carrying phonon is formed in the lattice. In the case of a ferromagnet the spin

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Figure 2.13: SO coupling overview by Zhang et al.[10].

a) Diagram of singlet and triplet energy levels, showing decreasing density of triplet states and increasing density of singlets in the presence of the laser field, with spin-orbit coupling allowing demagnetising transitions between the two.

b) The effect of successive pulses on demagnetisation at 0, 50 and 80 fs, showing cumulative demagnetisation.

flip of the electron requires an input of energy, in order to overcome the exchange interaction. Studies of EY interactions had previously been conducted on non-magnetic materials, and were thought to be rare, however ab initio calculations, by Steiauf et al.[14] and Koopmans et al.[4] show that the probability of spin-flip interactions is significant for the ferromagnets Iron, Cobalt and Nickel, and to a lesser extent Gadolinium. The anomalously long, in comparison to other ferromagnets, demagnetisation and remagnetisation times of Gadolinium are explained in terms of differing probabilities of spin-flip interactions between 4f and 5d6s electrons, and long timescale interactions between the two shells.

The effects of differing spin-flip probabilities in a three temperature system are illustrated in figure 2.15. A material with a high spin-flip probability will transfer energy from the electron to the spin system more rapidly. Since the electron system is also coupled to the lattice, stronger coupling of the electrons to the spin system will allow greater demagnetisation, since more energy (initially) is coupled to the spin system rather than the lattice. In figure 2.15, the spin-flip probabilities traditionally assumed correspond to the lower spin temperature curve. Due to the higher spin-flip probabilities of ferromagnets undergoing ultrafast demagnetisation, a spin-temperature curve between the upper two curves is expected.
2.4. Mechanisms of Demagnetisation

Figure 2.14: Conditions for SO coupling from Zhang et al.[10]. Demagnetisation is absent without spin orbit coupling $\lambda$, and minimal demagnetisation is present without the laser field $I$. This limits the demagnetising effect to the duration of the ultrafast pulse.

Figure 2.15: Theoretical model by Koopmans et al.[11], showing the effect of different values of spin-flip probability (0.5, 0.1, and 0.01) on the evolution of a three temperature system. Experimental values and more detailed theory predict values of $\sim0.2$ for the spin flip probability[4]. Higher spin temperatures result in lower magnetisation. This shows the strong effect of the spin-flip probability on the degree of demagnetisation.
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2.5 Models of Ultrafast Demagnetisation

Since the discovery of ultrafast demagnetisation effects, multiple models, of increasing complexity, have been used to describe the phenomenon. The models vary in their aims, that is the aspects of the system they aim to model most accurately, as well as the balance between theoretical and phenomenological approaches used in their development.

2.5.1 Two Temperature Model

The Two-Temperature Model is the original model of ultrafast magnetisation used by Vaterlaus et al.\cite{1}. It is an application of the two temperature model of Anisimov et al.\cite{15}, applied to a ferromagnetic system. The Two Temperature Model, models the temperature of two coupled components of a solid; the lattice, and a reservoir of spins (the electrons). In the model featured in the source literature, the initial perturbation from the ultrafast pulse has already occurred and is incorporated through an initial condition. It was assumed that the spin heat capacity $C_{\text{spin}}$, was a function of temperature but that the spin-lattice coupling constant $G$, was a constant.

$$C_{\text{spin}} \frac{dT_{\text{spin}}}{dt} = G (T_{\text{lattice}} - T_{\text{spin}})$$  \hspace{1cm} (2.1)

with the spin-lattice relaxation time $\tau_{\text{sl}}$:

$$\tau_{\text{sl}} = \frac{C_{\text{spin}}}{G}.$$

(2.2)

In order to solve the problem analytically, it was assumed that $\tau_{\text{sl}}$ was independent of temperature, and that $T_{\text{lattice}}$ increased linearly with time at rate $q$, giving:

$$T_{\text{lattice}} = T_0 + qt$$  \hspace{1cm} (2.3a)

$$T_{\text{spin}} = T_0 + q \left( t - \tau_{\text{sl}} \left( 1 - e^{-\frac{t}{\tau_{\text{sl}}}} \right) \right).$$  \hspace{1cm} (2.3b)

The two temperature model suffers from the problem that, theoretically, a pulse cannot directly couple to the spin system. This is due to conservation of angular momentum requiring that spin-changing interactions transfer angular momentum to or from another system, and the insufficiency of the angular momentum of the laser field\cite{20}. Whether the model can be modified to interpret the spins as either the


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2.5. Models of Ultrafast Demagnetisation

kinetic, magnetic or both, components of the electron system is addressed in section 4.3.1.

2.5.2 Three Temperature Model

The Three-Temperature Model proposed by Beaurepaire et al.\cite{2} expands on the Two-Temperature Model by explicitly including three separate energy reservoirs, coupled to each other. The electron reservoir, with temperature $T_e$ is thermally coupled to the lattice reservoir, of temperature $T_l$ and energy flows between them at a rate proportional to the temperature difference between the two reservoirs, $(T_e - T_l)$. The constant of proportionality for this link is $G_{el}$. Analogous connections exist between the each of the electron and lattice reservoirs and the spin reservoir. The models are explicitly energy conserving (excepting the input of energy by the pulse function), with each coupling term $(G_{12}(T_1 - T_2))$ appearing twice, once in the equation for each reservoir it represents, except with the opposite sign. The effect being that a coupling term is in one equation will have the same magnitude but opposite sign in the other, conserving energy in the system.

The model developed by Beaurepaire et al. is reproduced below, with $C$ representing the heat capacity, $T$ representing temperature, $G$ representing the coupling constants and $P$ representing the input of energy by the pulse. The subscripts define which reservoir the quantity pertains to: $e$ for the electrons, $l$ for the lattice, and $s$ for the spins. The coupling constants relate to a pair of reservoirs, so are doubly subscripted, with their order being unimportant. The units of each side of the equations are $W \cdot m^{-3}$, power volume density in SI;

\[
C_e(T_e)\frac{dT_e}{dt} = -G_{el}(T_e - T_l) - G_{es}(T_e - T_s) + P(t) \tag{2.4a}
\]

\[
C_l(T_l)\frac{dT_l}{dt} = -G_{el}(T_l - T_e) - G_{sl}(T_l - T_s) \tag{2.4b}
\]

\[
C_s(T_s)\frac{dT_s}{dt} = -G_{sl}(T_s - T_l) - G_{es}(T_s - T_e). \tag{2.4c}
\]

The heat capacities were modelled by Beaurepaire et al. with a constant total heat capacity. The lattice specific heat was taken as a constant, as Debye theory predicts a relatively constant value. The electronic specific heat was taken as a linear function of electron temperature, but with a higher value than predicted by theory. This is attributed to singularities in the density of states near the Fermi Level\cite{2}. The spin heat was taken to be the remainder of the total heat capacity.

\[
C = C_l + C_e + C_s
\]
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\[ C_l = 2.2 \times 10^6 \quad J \cdot m^{-3} \cdot K^{-1} \]  
(2.5a)

\[ C_e = (6 \times 10^3) \cdot T_e \quad J \cdot m^{-3} \cdot K^{-1} \]  
(2.5b)

\[ C_s = C - C_l - C_e \]
\[ = (4 \times 10^6) - (6 \times 10^3) \cdot T_e \quad J \cdot m^{-3} \cdot K^{-1} \]  
(2.5d)

The coupling constants represent the degree of thermal conductivity between the reservoirs. Since the reservoirs consist of discrete microscopic components, electrons and phonons, and those components occupy the same space, the coupling represents the probability of an interaction between the reservoirs, multiplied by the energy transferred. The coupling constants below were chosen to align the model with experimental observations:

\[ G_{el} = 8 \times 10^{17} \quad W \cdot m^{-3} \cdot K^{-1} \]  
(2.6a)

\[ G_{es} = 6 \times 10^{17} \quad W \cdot m^{-3} \cdot K^{-1} \]  
(2.6b)

\[ G_{sl} = 3 \times 10^{16} \quad W \cdot m^{-3} \cdot K^{-1} \]  
(2.6c)

The pulse function was adjusted to reproduce the measured electronic temperature, its exact value was not reported, but it was stated that the value was consistent with previous work and estimates of pump fluence.

### 2.5.3 Non-Thermal Electron Model

Non-Thermal Electron Model (NTEM) proposed by Ju et al.[3] introduces a component representing the population of non-thermal electrons. In the original paper, the non-thermal electrons are referred to as non-thermal spins. This appears to be arbitrary, as the spins are physically electrons, and no special spin distribution is ascribed to the non-thermal population. Initially it was proposed that ultrafast demagnetisation, or the ultrafast optical effects ascribed to it, may be connected to the presence of a non-thermal electron population. This is no longer believed to be the case for the magnetisation[17].

When an ultrafast pulse interacts with the electron cloud, each photon transfers its energy to a single (in general) electron, resulting in an electron with optical (\(\sim eV\)) energies instead of thermal energies (\(\sim meV\)). Since the electron reservoir is not in
2.5. Models of Ultrafast Demagnetisation

thermal equilibrium, the notion of a temperature is ill-defined until the reservoir
returns to equilibrium. The symbol $N_s$ represents the population density of non
thermal spins (elsewhere referred to as non-thermal electrons), and the constants $\alpha$
and $\beta$ represent the rate at which the non-thermal distribution decays, transferring
energy to the electron or spin reservoirs;

\[
\frac{\partial N_s}{\partial t} = -\alpha N_s + \beta N_s \tag{2.7a}
\]

\[
C_s(T_s) \frac{\partial T_s}{\partial t} = -G_{es}(T_s - T_e) + \alpha N_s \tag{2.7b}
\]

\[
C_e(T_e) \frac{\partial T_e}{\partial t} = -G_{es}(T_e - T_s) + \beta N_s. \tag{2.7c}
\]

The ultrafast pulse is not explicitly featured but is incorporated by using a non-zero
initial value for the concentration of non-thermal electrons. The electron thermal-
isation time is a similar concept to the momentum relaxation time for electrons at
optical energies. The non-thermal electron population is not modelled as a separate
heat reservoir since the non-thermal spin population does not exist for long enough
to reach an equilibrium with itself, that is, in the time it takes for the non-thermal
population to interact with itself and return to a thermal distribution, the (now ther-
malised, but still high energy) population will have interacted with the non-thermal
population.

These equations were explicitly extended by Zhang et al. in 2006\cite{26} to include a
lattice reservoir denoted by subscript $l$, an explicit pulse function $P(t)$, and dropping
the subscript $s$ for the non-thermal population. The non-thermal decay constants
were also altered, exchanging $\beta$ for $\eta$ as the spin decay constant, and using $\text{beta}$ as
the newly introduced lattice decay constant:

\[
\frac{\partial N}{\partial t} = -\alpha N + \beta N + \eta N + P(t) \tag{2.8a}
\]

\[
c_e(T_e) \frac{\partial T_e}{\partial t} = -g_{el}(T_e - T_l) - g_{es}(T_e - T_s) + \alpha N \tag{2.8b}
\]

\[
c_s(T_s) \frac{\partial T_s}{\partial t} = -g_{es}(T_s - T_e) - g_{sl}(T_s - T_l) + \eta N \tag{2.8c}
\]

\[
c_l(T_l) \frac{\partial T_l}{\partial t} = -g_{el}(T_l - T_e) - g_{sl}(T_l - T_s) + \beta N \tag{2.8d}
\]

shown here with the lowercase $c$ and $g$, as used within the source literature, but not
elsewhere in this thesis.

The assumption was however made by Zhang et al., that the non-thermal cou-
pling was not significantly stronger than the thermal coupling. Therefore the model,
in this incarnation, does not predict a significantly different evolution than the three
temperature system, its purpose being to account for other effects of the non-thermal electron population, such as the change in optical properties described by Koopmans et al. in 2000[16] and detailed in section 2.2.1. The effect of adding a non-thermal electron population to the 3TM is shown by the contrast between figure 2.16a and 2.16b. The principal effect is a lower peak electron temperature. This allows a larger value of P(t) when it’s value is fit to experimental results, and therefore lower values of the coupling constants. This effect not however occur when the magnitude of the pulse is not used as a fitting parameter, as is the case in this thesis. A secondary effect is a minor increase in spin temperature, due to the spin-flip probability typically being higher for electrons with optical energies, int he non-thermal population, than electrons with thermal energies, in the electron system.

Both the NTEM and 3TM become problematic when the electronic heat capcity is not used as a fitting parameter. This is shown in figure 2.16c. A higher value takes into account singularities in the density of states near the Fermi level, but is, on a macroscopic level, far too large. The flat spin temperature profile is due to the lower amount of energy present in the electron system when the heat capacity is lowered, being less able to heat the spin and lattice systems before cooling.
2.5. Models of Ultrafast Demagnetisation

2.5.4 Microscopic Three Temperature Model

The Microscopic Three Temperature Model was proposed by Koopmans et al. in 2010[4]. It replaces the concept of spin temperature with an explicit term for magnetisation. This magnetisation term is derived from modelling individual spin-flip interactions between electrons and phonons, and conserving energy, linear and angular momentum.

The model is reproduced as below with the subscript \( p \) referring to the phonon reservoir, elsewhere described simply as the lattice \( l \), and the coupling constant \( g \) in lower case:

\[
\begin{align*}
C_e(T_e) \frac{dT_e}{dt} &= \nabla_z (\kappa \nabla_z T_e) + g_{ep}(T_p - T_e) \quad (2.9a) \\
C_p \frac{dT_p}{dt} &= g_{ep}(T_e - T_p) \quad (2.9b) \\
\frac{dm}{dt} &= Rm \frac{T_p}{T_c} \left( 1 - m \coth \left( \frac{mT_c}{T_e} \right) \right) \quad (2.9c)
\end{align*}
\]

where \( R \) is a material specific parameter, \( \kappa \) is the electronic thermal conductivity, and \( \nabla_z \) represents differentiation in the \( z \) (depth) direction. The material specific parameter \( R \) is defined as:

\[
R = \frac{8a_{sf}g_{ep}k_B^2V_{at}}{\left( \mu_{at}/\mu_B \right)E_D^2} \quad (2.10)
\]

relating the physical constants \( k_B \), the Boltzmann constant and \( \mu_B \) the Bohr magneton. The material specific constants are: \( a_{sf} \) the Elliot-Yafet spin-flip probability, \( g_{ep} \), the electron-phonon (electron-lattice) coupling constant, \( T_c \) the Curie Temperature, \( V_{at} \), the atomic volume, \( \mu_{at} \), the atomic magnetic moment and \( E_D \), the Debye energy, which is defined as:

\[
E_D = k_BT_D \quad (2.11)
\]

where \( T_D \) is the Debye temperature. This gives \( R \) the units of \( s^{-1} \), meaning it is a constant describing the rate of the demagnetisation, as a function of the material specific parameters above. The model also includes a thermal cooling parameter, describing the diffusion of heat into the sample (in the \( \hat{z} \) direction).

Koopmans et al. also propose a figure of merit of ultrafast demagnetisation of \( T_c/\mu_{at} \), the ratio of Curie temperature to atomic magnetic moment. This figure is proposed as being inversely related to demagnetisation time, i.e. that high Curie temperatures, and low atomic magnetic moments are associated with short demag-
netisation times. This is demonstrated by the comparison of similar values of the figure of merit for Nickel and Cobalt, with similar demagnetisation times. This is contrasted with much lower values of the figure of merit for Gadolinium, and correspondingly much longer demagnetisation times.
Chapter 3

Theory

In this chapter concepts which are not derived from the preceding literature, but which are relied upon for the latter parts of this thesis, are defined and explained for later use. The notation used in this chapter is kept from the source, and as such may not be compatible or consistent, either between sources, or with the rest of the thesis. Where notation is changed for use elsewhere in the thesis it is noted when introduced.

3.1 Magnetisation and Demagnetisation

The magnetisation $M$, is the response of material to an applied external magnetic field $H$, where $M$ is a function of $H$. The total magnetic field $B$, is proportional to the sum of the applied magnetic field and the magnetisation.

\[ B = \mu_0 (H + M) \]  

(3.1)

For a paramagnetic or diamagnetic substance the relationship between $M$ and $H$ is given by $\chi$, the magnetic susceptibility;

\[ M = \chi H \]  

(3.2)

\[ B = \mu_0 (1 + \chi) H \]  

(3.3)

which is small and positive for a paramagnet ($\sim 10^{-4}$ to $10^{-5}$), and very small and negative for a diamagnet ($\sim -10^{-6}$). For a ferromagnet however the relationship between $M$ and $H$ is non-linear, and path dependent. This means that the current value of $\chi$ depends on both the current and past values of $H$. This physically manifests in the concept of hysteresis, and is involved in several important properties
of ferromagnets. Saturation is the state where for a large enough (material and conditions dependent) $H$ field, $\chi(H)$ becomes linear and ceases to be path dependent. Having reached saturation, $\chi$ is also typically much smaller, $\sim 10^{-4}$. This is due to the total alignment of ferromagnetic domains, and any further magnetisation proceeds in a paramagnetic fashion. Remanence is the $B$ field remaining when a previously saturating $H$ field is reduced to zero, with the remanent $B$ field purely being the result of path dependence. Coercivity is the opposing $H$ field required to reduce $B$ to zero after previously being saturated.

The macroscopic magnetisation of a ferromagnet is the product of two separate phenomena, spontaneous magnetisation and magnetic domain alignment. Microscopically, ferromagnets are always at saturation magnetisation, however individually saturated magnetic domains can (and in general will, as opposing domains minimise the magnetic energy of the solid) point in differing directions, reducing or eliminating macroscopic magnetisation. Hysteresis is the result of the work necessary to shift domains from one alignment to another. Ultrafast demagnetisation has been observed similarly at both remanent and saturated magnetisations[2, 7], which implies that ultrafast demagnetisation is the result of reducing the spontaneous magnetisation, not of any realignment of magnetic domains. If ultrafast demagnetisation was the result of domain realignment, demagnetisation from remnant magnetisation would not be followed by subsequent remagnetisation, as energy input would be required to recreate domain boundaries, and return the domains to their original alignment. Also due to the short timescales over which ultrafast demagnetisation occurs (100s of fs), changes propagating across (relatively) large scale structures like magnetic domains are not possible (in 100 fs, light, and therefore any electromagnetic effect, travels only 30 $\mu$m in a vacuum).

### 3.2 Magnetisation and Temperature

The magnetisation of a ferromagnet is greatest at absolute zero and decreases with increasing temperature until the Curie temperature, at which the ferromagnetic component of magnetisation is zero. In the presence of an external field, the much smaller paramagnetic or diamagnetic magnetisations remain, however these exhibit no hysteresis, and hence no coercivity, remanence or saturation. At an equilibrium all components of a solid are at the same temperature. Equilibrium heating of a ferromagnet reduces its magnetisation, and it is assumed that this is also true for non-equilibrium heating (i.e. when the components of the system are thermalised
3.2. Magnetisation and Temperature

themselves, but at differing temperatures). The relevant temperature for determining magnetisation, is the temperature of the magnetic components of the system, which in most models is referred to as the spin temperature $T_s$.

In the Curie-Weiss model of ferromagnetism the microscopic magnetisation experienced by each atomic dipole in a ferromagnet is modelled as being in response to a large internal (and fictitious) magnetising field, $H_{\text{int}}$, also referred to as the effective field. This apparent field is much greater than can be produced in a laboratory (typically hundreds of Tesla) and is the result of quantum mechanical exchange interactions, which arise from the exclusion principle. The internal field seen by each dipole is proportional to the magnetisation[30]:

$$B = \mu_0 (H + H_{\text{int}}) \quad (3.4)$$

$$B = \mu_0 (H + \lambda M) \quad (3.5)$$

where $\lambda$ is the effective field constant.

The constant $\lambda$ is defined by the following expression, where $T_C$ is the material specific Curie temperature, and $C$ is the material specific Curie constant[30]:

$$\lambda = \frac{T_C}{C} \quad (3.6)$$

$$\lambda = \frac{3k_BT_C}{Ng^2\mu_B^2\mu_0 J(J+1)} \quad (3.7)$$

and where $N$ is the density of the elementary dipoles, $J$ is the total angular momentum quantum number of the elementary dipole and $g$ is their g-factor, $\mu_0$ is the magnetic constant and $\mu_B$ is the Bohr magneton.

The magnetisation as a function of temperature is described by[30]:

$$M(T) = NgJ\mu_B B_J \left(\frac{NgJ\mu_BB}{k_BT}\right) \quad (3.8)$$

$$M(T) = NgJ\mu_B B_J \left(\frac{NgJ\mu_B\mu_0 (H + \lambda M)}{k_BT}\right) \quad (3.9)$$

where $B_J$ denotes a Brillouin function of order $J$, i.e. a Brillouin function with the order of the total angular momentum quantum number.

A Brillouin function of order $J$ is defined as[30]:

$$B_J(x) = \frac{2J+1}{2J} \coth \left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth \left(\frac{x}{2J}\right). \quad (3.10)$$

Equation 3.9 has no closed form solution, but can be solved numerically.
Chapter 3. Theory

With increasing temperature, the magnetisation decreases slowly at first, then rapidly as $T \to T_C$. The effect of the $J$ value on the solution is to flatten the shape of the magnetisation curve, from an elliptical shape, towards a square root shape. Increasing the $J$ parameter has the effect of decreasing the magnetisation at all temperatures (except 0 K), with the magnetisation decrease becoming more significant as $T$ increases, then converging as $T \to T_C$. Koopmans et al. [4] give a direct relation between $T_l$, $T_e$ and the relative magnetisation $m$, as a function of time, bypassing $T_s$;

$$m = \frac{M}{M(T = 0)}$$

$$\frac{dm}{dt} = Rm \left( 1 - m \coth \left( \frac{mT_C}{T} \right) \right).$$

This expression can be shown (equation 4.50) to, at equilibrium conditions, reduce to a Langevin equation, which is a Brillouin equation in the limit as $J \to \infty$. This relationship is a component of the Macroscopic Three Temperature Model (M3TM) which is featured in section 4.3.2.

At the critical point ($T = T_C$), in the absence of an applied magnetic field ($H = 0$), the magnetisation curve becomes vertical as $T$ approaches $T_C$ from below, then becomes horizontal and zero for $T > T_C$, creating a singularity, and a discontinuity in the derivative, at $T = T_C$. An applied magnetic field prevents the argument of the Brillouin function from reaching zero at $T = T_C$, this has the physical effect of removing the singularity in the derivative, smoothing the transition between the ferromagnetic and paramagnetic phases. This has repercussions not only for magnetisation, but for heat capacity which is a function of the derivative of the magnetisation with respect to temperature. This effect is modelled in section 4.5.

There is also a simple relationship between the atomic magnetic moment, and the macroscopic saturation magnetisation at 0 K. When fully saturated, and in the absence of thermal energy, all of the atomic magnetic dipoles are aligned (in single domain). Therefore the magnetisation is given by the atomic magnetic moment $\mu_{at}\mu_B$, multiplied by the density of those moments $N$;

$$M_0 = N\mu_{at}\mu_B.$$
A rapidly changing magnetic dipole causes changes in the electromagnetic field to propagate outward in a manner analogous to the more familiar electric dipole. When the demagnetisation occurs in a time $\tau \sim 1\text{ps}$ the emitted radiation will have a frequency of the order $1/\tau = \text{THz}$, viz. Terahertz radiation. The equations describing magnetic dipole emission are identical to those for electric dipole emission, except for the exchange of magnetic for electric dipoles, magnetic for electric fields, and a scaling factor of $c$. In general, the electromagnetic radiation emitted by a magnetic dipole is described by[19, pp. 451-454]:

$$E = \frac{\mu_0}{4\pi c} \frac{\partial^2 M(t - r/c)}{\partial t^2} \frac{\sin \theta}{r} \hat{\phi}$$  \hspace{1cm} (3.14a) 

$$B = -\frac{\mu_0}{4\pi c^2} \frac{\partial^2 M(t - r/c)}{\partial t^2} \frac{\sin \theta}{r} \hat{\theta}$$  \hspace{1cm} (3.14b) 

$$\langle S \rangle = \frac{\mu_0}{16\pi^2 c^3} \left( \frac{\partial^2 M(t - r/c)}{\partial t^2} \right)^2 \frac{\sin^2 \theta}{r^2} \hat{r}$$  \hspace{1cm} (3.14c) 

with $E$ representing the electric field vector, $B$ representing the magnetic field vector, and $\langle S \rangle$ representing the time averaged (over a cycle of the radiation) Poynting (power density) vector. This is compared to the more common electric dipole:

$$E = -\frac{\mu_0}{4\pi} \frac{\partial^2 M(t - r/c)}{\partial t^2} \frac{\sin \theta}{r} \hat{\phi}$$  \hspace{1cm} (3.15a) 

$$B = -\frac{\mu_0}{4\pi c} \frac{\partial^2 M(t - r/c)}{\partial t^2} \frac{\sin \theta}{r} \hat{\theta}$$  \hspace{1cm} (3.15b) 

$$\langle S \rangle = \frac{\mu_0}{16\pi^2 c^3} \left( \frac{\partial^2 M(t - r/c)}{\partial t^2} \right)^2 \frac{\sin^2 \theta}{r^2} \hat{r}.$$  \hspace{1cm} (3.15c) 

This radiation pattern can be used to confirm the origin (electrical or magnetic) of the emitted signal, as even if the polarization (that produces the electric dipole) and magnetisation (that produces the magnetic dipole) are parallel, producing the same radiation pattern, the polarization of the emitted radiation is different. This can be simply recalled as the electric field always being parallel to the changing polarisation that produces it, similarly the magnetic field is parallel to the changing magnetisation that produces it.
3.4 Heat Capacity

In order to model the thermal transmission of energy between systems, a relationship between temperature change and energy input is required. Heat capacity is the property of a substance that specifies the quantity of energy required to change the temperature of that substance by a given amount. Heat capacity is defined as the quantity of heat (energy) required to raise the temperature (mean kinetic energy) of a substance by an infinitesimal amount:

\[ C = \frac{\delta Q}{\Delta T} \]

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V. \]  

(3.16)

The equipartition theorem requires that a substance will, at equilibrium, take up energy in all of its different degrees of freedom equally. Applying this in the context of non-equilibrium heating gives the result that the total heat capacity of a substance is the sum of the heat capacities of each of its components:

\[ C = \sum_{i=0}^{n} C_i. \]  

(3.17)

In the models considered in this thesis, there are typically three energy reservoirs, with three heat capacities, the electrons (kinetic energy of the electrons), \( C_e \), the spins (magnetic energy of the electrons), \( C_s \), and the lattice (energy of lattice phonons), \( C_l \);

\[ C_{tot} = C_e + C_s + C_l. \]  

(3.18)

Since the spins do not represent a separate physical object, and spin heat capacity only exists in magnetic substances, standard models of the spin heat capacity are not available. The model for magnetic heat capacity developed in this thesis is explained in section 4.5, and given explicitly in equation 4.79.

3.4.1 Lattice Heat Capacity (Debye Model)

The contribution of the atomic lattice to heat capacity is accurately described by the Debye Model[30]. The Debye model of lattice heat capacity is given in Equation 3.19, where \( N \) is the atomic concentration, the number density of the nuclei in macroscopic space, \( k_B \) is the Boltzmann constant, \( T_D \) is the Debye temperature,
and $x$ is the dummy variable of integration:

$$C_l(T) = 9Nk_B \left( \frac{T}{T_D} \right)^3 \int_0^{\frac{T}{T_D}} \frac{x^4e^x}{(e^x - 1)^2} \, dx. \quad (3.19)$$

At low temperatures ($T_l \sim 0$), the lattice heat capacity is proportional to $T_l^3$. As the temperature (and therefore kinetic energy) increases, more phonon modes become available, and the heat capacity increases, until at high temperatures ($T_l > T_D$), all phonon modes are available, and the value predicted by the Debye function approaches that of the classical Dulong-Petit law; $C_V = 3k_B N_A$ per mole.

### 3.4.2 Electron Kinetic Heat Capacity

Electrons which are not within $k_B T$ energy of the Fermi level cannot thermally interact and therefore do not contribute to the heat capacity of the material. The electronic heat capacity expression is the result of considering the heat capacity of those electrons within $k_B T$ of the Fermi level, with an idealised electronic density of states, as free particles\[30\]:

$$C_e = \frac{\pi^2 k_B T}{2E_F}. \quad (3.20)$$

In practice, an empirically derived constant $\gamma$ is used;

$$C_e = \gamma T, \quad (3.21)$$

with the implication,

$$\gamma \approx \frac{\pi^2 k_B}{2E_F}. \quad (3.22)$$

This is necessary due to the complex nature of the electronic density of states in real materials. In particular, there is a significant asymmetry between the spin sub-bands due to the exchange interaction, as well as singularities near the Fermi level\[2\].

### 3.5 Electron Relaxation

The Drude model of electrical conductivity\[30\] gives a relationship between the conductivity of a metal, $\sigma$, and the momentum relaxation time $\tau$, where $n$ is the
density of charge carriers, \( q \) is the charge of the carriers and \( m \) is the effective mass of the charge carrier[30];

\[
\sigma = \frac{nq^2 \tau}{m} \\
\tau = \frac{m \sigma}{nq^2},
\]

so for electrons as charge carriers;

\[
\tau_e = \frac{m_e \sigma}{q_e^2 n_e}.
\]

Values of \( \tau_e \) are typically a few femtoseconds. The Drude model suffers from the problem that it does not separate the effect of interactions between electrons, and interactions between electrons and the lattice. While these may be accounted for by the use of a (fictitious) effective charge carrier mass, the procedure has little predictive power in determining the mechanisms of electron energy loss, particularly for higher energy electrons. In order to properly distinguish between the various means by which electrons lose (or gain) energy, more detailed models are required.

### 3.5.1 Electron Thermalisation Time

Electron Thermalisation time is the characteristic time taken for the electron gas to return to a thermal distribution after interaction with the ultrafast laser pulse. Immediately after (and during) the ultrafast pulse the electron gas in the sample has a significantly non-thermal energy distribution, with each photon having transferred its full energy (1.5 eV for near infra-red photons) to an electron, and no energy to others. This results in a quantity of electrons with optical energies, and an energy distribution primarily dependent on the energies of the photons. These are distinct from those electrons which did not interact with a photon, have thermal energies and are thermally distributed.

A model for the electron-electron interaction time at optical energies is provided by Fann et al.[31], which was also demonstrated experimentally for Gold. According to Fermi liquid theory, under the random phase approximation, Pine and Nozieres give the lifetime of an excited electron in a degenerate system as[32];

\[
\tau_{ee} = \tau_0 \left( \frac{\epsilon_F}{\epsilon - \epsilon_F} \right)^2
\]

where \( \tau_{ee} \) is the characteristic electron-electron decay time (excited electron lifetime), \( \tau_0 \) is the mean electron-electron interaction time, \( \epsilon \) is the energy of the excited
3.5. Electron Relaxation

electron and $\epsilon_F$, the Fermi energy of the electrons. It can be seen that higher-
energy electrons decay faster, and therefore have shorter lives, than lower-energy
excited electrons.

Under the same conditions, the mean electron-electron interaction time can be
derived from the Lindhard dielectric equation[32];

$$\tau_0 = \frac{128}{\pi^2 \sqrt{3} \omega_P}$$

(3.26)

where $\omega_P$ is the plasma frequency of the electrons, and hence the metal.

3.5.2 Electron-Lattice Relaxation

While conduction electrons are loosely bound (i.e. nearly free) within the conduction
band, they still interact with phonons in the lattice. This coupling transfers energy
between the electrons and the lattice, and is most commonly encountered as the
(primary) source of electrical resistance in metals.

In the course of investigating non-equilibrium heating in non-magnetic sub-
stances, Allen[33] derived the following expression for the characteristic electron-
phonon relaxation time $\tau_{ep}$, in terms of temperature of the electrons $T_e$, the Debye
frequency of the lattice $\omega_D$, and a dimensionless parameter $\lambda_p$, representing the
strength of the electron-phonon interaction[33];

$$\tau_{ep} = \frac{2\pi k_B T_e}{3h\lambda_p \omega_D^2}.$$  (3.27)

The value of the parameter $\lambda_p$ is typically $\sim 0.5$, with trends between otherwise
similar materials being evident[34]. Aside from the empirical nature of $\lambda_p$, a problem
exists in that the electron temperature $T_e$ is a function of both time, and the electron-
phonon relaxation time $\tau_{ep}$. Derivations from Allen used various approximations for
the relevant electron temperature[33].

The Debye frequency is a characteristic maximum frequency of lattice vibrations (phonons) in the crystal lattice[35]. In this way it is related the the Debye
temperature and energy. The Debye frequency can be determined from the atomic
concentration $N$, and the speed of sound in the material $v_s$:

$$\omega_D = \left(\frac{3N}{4\pi}\right)^{1/3} v_s.$$  (3.28)
3.5.3 Spin-Lattice Relaxation

In an electron phonon interaction, there is a finite probability of the transfer of spin between an electron and the lattice. These events are known as Elliot-Yafet interactions. Elliot-Yafet interactions were thought to be rare in metals, with the spin-flip probability in Copper being of the order of 0.001. However \textit{ab-initio} calculations, and subsequent experiments have shown the probabilities to be much higher in ferromagnets, and higher at optical rather than thermal electron energies\cite{11}. Since each electron-lattice interaction has a chance of being a spin-flip event, the spin-lattice relaxation time $\tau_{sl}$ is related to the electron-lattice relaxation time\cite{14}:

$$\frac{1}{\tau_{sl}} = pb^2 \frac{1}{\tau_{el}}$$

(3.29)

where $p$ is a material specific constant ($1 < p < 10$) and $b^2$ is the spin-mixing parameter describing the spin-flip interaction probability. The constant of proportionality $pb^2$ is the spin-flip probability $\alpha_{EY}$;

$$pb^2 = \alpha_{EY}$$

$$\tau_{sl} = \frac{\tau_{el}}{\alpha_{EY}}.$$  

(3.30)

Values of $\alpha_{EY}$ are estimated to be of the order of 0.1\cite{4}.

3.5.4 Electron-Spin Relaxation

In models with a separate electron and spin temperature, the spin temperature refers to the mean energy required to produce the observed distribution of spin states, as distinct from the translational kinetic energy of electrons. Since magnetism is a result of the total angular momentum of the electrons, as opposed to the linear momentum of the electron temperature, and both momenta are separately conserved quantities which cannot be converted to to one another, direct transfer of energy between the electron and spin systems is not possible. Electron-spin relaxation may occur indirectly however, through spin-spin interactions\cite{10}, or through spin-lattice interactions\cite{11}, as discussed in section 3.5.3.
3.6 Hydrodynamic Model of the Photo-Dember Effect

In order to calibrate the detection ability of the apparatus used in this experiment (detailed in chapter 5), a model was used to predict the Terahertz output of the reference Indium Arsenide sample.

Indium Arsenide emits Terahertz radiation via the Photo-Dember effect. When a high fluence radiation pulse is incident on a semiconductor surface, and the photon energy is above the bandgap, large numbers of charge carriers (free electrons and holes) are created. These carriers diffuse from the surface into the bulk semiconductor. If there is a large disparity in the mobilities of these carriers, one species of charge carrier will diffuse into the material faster than the other. If this were to occur inside a semiconductor, no net effect would result, as the centre of the charge distribution would not change, but since the pulse is (necessarily) incident on the surface of a material, the carriers can only move away from (or parallel to) the surface. This means that, in a given time, the centre of charge for the more mobile carriers will move farther away from the surface than that of the less mobile carriers, creating a time varying electric dipole, which emits radiation. The parameters used in the model are detailed in table 3.1:

Table 3.1: Parameters used in the hydrodynamic model of the photo-Dember effect.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J(t)$</td>
<td>Current density as a function of time</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>The relative electric constant ($\epsilon$)</td>
</tr>
<tr>
<td>$\kappa_0$</td>
<td>The electric constant ($\epsilon_0$)</td>
</tr>
<tr>
<td>$m^*$</td>
<td>Reduced effective mass of the photoexcited carriers</td>
</tr>
<tr>
<td>$v_t$</td>
<td>Velocity difference between the photoexcited charges and holes</td>
</tr>
<tr>
<td>$\omega_{\text{max}}$</td>
<td>Maximum plasma frequency of carriers</td>
</tr>
<tr>
<td>$\omega_{\text{min}}$</td>
<td>Minimum plasma frequency of carriers</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Momentum relaxation rate of photoexcited electrons</td>
</tr>
</tbody>
</table>

The current density as a function of time ($J(t)$) is given by [36]:

$$J(t) = \frac{4\kappa\kappa_0 m^* v_t^2 e^{-\frac{\gamma t}{2}}}{\epsilon t} \sin \left( \frac{\omega_{\text{max}} + \omega_{\text{min}}}{2} t \right) \sin \left( \frac{\omega_{\text{max}} - \omega_{\text{min}}}{2} t \right). \quad (3.31)$$

Expressions for $\omega_{\text{max}}$ and $\omega_{\text{min}}$ are given in terms of $\omega_{\text{exc}}$, the plasma frequency of the photo-excited charge carriers and $\omega_{\text{eq}}$, the plasma frequency of the equilibrium
The reduced effective mass of the photoexcited carriers is given by:

\[ m^* = \left( m_e^{-1} + m_h^{-1} \right)^{-1} \]  

where \( m_e \) is the effective mass of the photoexcited electron and \( m_h \) is the heavy hole effective mass.

The electromagnetic power radiated by a changing current is proportional to its first derivative squared. Integrating the power, from \( t = 0 \) to \( t \to \infty \) gives the total energy emitted:

\[
P(t) = \frac{1}{6\pi\epsilon_0c^3} \left( \frac{dJ}{dt} \right)^2
\]

\[
W = \int_0^\infty \frac{1}{6\pi\epsilon_0c^3} \left( \frac{dJ}{dt} \right)^2 \, dt
\]

For low excitation densities, \( n_{exc} \ll n_{eq} \), therefore \( \omega_{exc} \gg \omega_{eq} \) and equation 3.31 simplifies to:

\[
J(t) = \frac{en_{exc} v_t^2}{\sqrt{\omega_{eq}^2 - \gamma^2/4}} e^{-\gamma t/2} \sin \left( \sqrt{\omega_{eq}^2 - \gamma^2/4} \, t \right)
\]

and substituting into equation 3.36:

\[
W = \frac{e^2}{12\pi\epsilon_0 c^3 \gamma} n_{exc}^2 v_t^4.
\]
Chapter 4

Model Development

In order to generate predictions from a simulated experiment, and to compare the models with the same assumptions in place, in this thesis the ultrafast demagnetisation models obtained from literature (detailed in section 2.5) were modified in this chapter, to be similar in form, and have the same parameters wherever the underlying physical concept was the same. It was also an aim to reduce or remove free or curve-fit parameters and replace them with values with a theoretical or independent empirical basis.

The models and their supporting components are described in this chapter, with their predictions for this thesis’ experiments in section 5.5, and theoretical results derived from the models in section 6.2.

The overall model predicting Terahertz output from the properties of the ultrafast pulse, and sample materials is complex. The model is therefore broken into sections, each modelling a component of the modelled experiment. The model components are presented in an approximately causal order, although there are some interdependencies between components.

The shared elements of the models are described in separate sections. The ultrafast pulse function $P(t)$ is described in section 4.1, with its associated laser coupling factor $L$ described in section 4.2. The core models describing the changing temperatures of material components after the pulse are contained in section 4.3. The coupling constants between the components, $G$, are described in section 4.4. The heat capacities of the material sub-components $C$, are described in section 4.5. The change of magnetisation as a function of temperature $M(T)$ is described in section 4.6, and the resultant emission of electromagnetic radiation described in section 4.7.

The models were implemented in MATLAB, and the source code is included in appendix B.
Chapter 4. Model Development

4.1 Ultrafast Pulse Model

In order to model the response of these models to ultrafast pulses, an expression for the ultrafast pulse $P(t)$ is required. As the penetration depth is a material specific property, the pulse function is kept as an areal power density, which is then divided by the penetration depth as a part of the laser coupling factor, detailed in section 4.2.

The ultrafast pulse is modelled as a monochromatic wave packet with a hyperbolic secant squared envelope$^{[37]}$, horizontally polarised and characterised by the following parameters:

Table 4.1: Ultrafast pulse model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Basic Properties</strong></td>
<td></td>
</tr>
<tr>
<td>Laser central (mean) wavelength</td>
<td>$\bar{\lambda}$</td>
</tr>
<tr>
<td>Laser power</td>
<td>$p$</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>$t_p$</td>
</tr>
<tr>
<td>Pulse repetition frequency</td>
<td>$f_p$</td>
</tr>
<tr>
<td>Laser beam diameter</td>
<td>$D$</td>
</tr>
<tr>
<td><strong>Derived Properties</strong></td>
<td></td>
</tr>
<tr>
<td>Beam area</td>
<td>$A$</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>$W_p$</td>
</tr>
<tr>
<td>Pulse fluence</td>
<td>$W_p/A$</td>
</tr>
<tr>
<td>Pulse electric field magnitude</td>
<td>$E(t)$</td>
</tr>
<tr>
<td>Pulse magnetic field magnitude</td>
<td>$B(t)$</td>
</tr>
<tr>
<td>Pulse power density</td>
<td>$S(t)$</td>
</tr>
<tr>
<td>Pulse function</td>
<td>$P(t)$</td>
</tr>
<tr>
<td>Photon energy</td>
<td>$\epsilon$</td>
</tr>
</tbody>
</table>

where laser power is the long-time average power, pulse duration is the FWHM duration of the power of each pulse and pulse repetition frequency is the rate at which ultrafast pulses are emitted. Beam area, pulse energy and photon energy are calculated as:

$$A = \pi \left( \frac{D}{2} \right)^2$$  \hspace{1cm} (4.1)

$$W_p = \frac{p}{f_p}$$  \hspace{1cm} (4.2)

$$\epsilon = \frac{hc}{\bar{\lambda}}.$$  \hspace{1cm} (4.3)
4.1. Ultrafast Pulse Model

The pulse model is constructed as the product of a known pulse energy, a normalised monochromatic wave, and a normalised hyperbolic secant squared wavelet envelope;

\[
S(t) = \frac{W_p}{A} \cdot 2 \cos^2 \left( \frac{2\pi ct}{\lambda} \right) \cdot \frac{\ln \left( 1 + \sqrt{2} \right)}{t_p} \cdot \text{sech}^2 \left( \frac{2 \ln \left( 1 + \sqrt{2} \right) \cdot t}{t_p} \right).
\]

Direct use of the power density function \(S(t)\) is problematic since a linearly polarised wave contains a time-varying power at twice the wave frequency. This high frequency component has no significance to the model, but it requires a much smaller step size when numerically solving the ultrafast demagnetisation models. Therefore the pulse function \(P(t)\) is distinguished from \(S(t)\) by removing the optical/infra-red frequency components, leaving only the lower-frequency, pulse train components. \(P(t)\) can be derived by integrating \(S(t)\) over a cycle of the normalised monochromatic wave, which by definition produces 1:

\[
\int_0^{\frac{T}{2}} 2 \cos^2 \left( \frac{2\pi ct}{\lambda} \right) \, dt = 1,
\]

giving,

\[
P(t) = \frac{W_p}{A} \cdot \frac{\ln \left( 1 + \sqrt{2} \right)}{T} \cdot \text{sech}^2 \left( \frac{2 \ln \left( 1 + \sqrt{2} \right) \cdot t}{T} \right) \tag{4.4}
\]

Since the pulse is a linearly polarised electromagnetic wave, propagating in free space, the electric and magnetic field components are related by\[19\]:

\[
P(t) = \langle S(t) \rangle = \frac{1}{\mu_0} E(t) \cdot B(t) \tag{4.5}
\]

\[
B(t) = \frac{1}{c} E(t). \tag{4.6}
\]

Therefore the electric and magnetic fields can be determined:

\[
E(t) = 2 \sqrt{\frac{\mu_0 c W_p}{A t_p}} \cos \left( \frac{2\pi ct}{\lambda} \right) \sqrt{\ln \left( 1 + \sqrt{2} \right)} \cdot \text{sech} \left( \frac{2 \ln \left( 1 + \sqrt{2} \right) \cdot t}{t_p} \right) \tag{4.7}
\]

\[
B(t) = 2 \sqrt{\frac{\mu_0 W_p}{c A t_p}} \cos \left( \frac{2\pi ct}{\lambda} \right) \sqrt{\ln \left( 1 + \sqrt{2} \right)} \cdot \text{sech} \left( \frac{2 \ln \left( 1 + \sqrt{2} \right) \cdot t}{t_p} \right). \tag{4.8}
\]

Only the pulse function (\(P(t)\)) component of the pulse model is used by the ultrafast demagnetisation models. The \(E\) and \(B\) results are produced for the sake of com-
Chapter 4. Model Development

Pleteness, and as an error checking opportunity. By design, the pulse is centred at $t = 0$ and has a duration (FWHM of power) of $t_p$. The pulse energy density ($W_p/A$) and total pulse energy ($W_p$) are also set by design, but can be confirmed as:

\[
\frac{W_p}{A} = \int_{-\infty}^{+\infty} S(t) \, dt \tag{4.9}
\]

\[
W_p = A \cdot \int_{-\infty}^{+\infty} S(t) \, dt. \tag{4.10}
\]

To demonstrate the model, two examples are produced, one of the focused pulse used experimentally in this thesis, the other of the pulse used by Beaurepaire et al. in their 2004 paper[7]. The examples are illustrated in figures 4.1 and 4.2 respectively. The parameters describing the pulses modelled in this thesis are given in table 4.2.

Table 4.2: Parameter values for modelled ultrafast pulses.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>620</td>
<td>800</td>
<td>790</td>
<td>790</td>
<td>$\times 10^{-9}$ m</td>
</tr>
<tr>
<td>$p$</td>
<td>0.25</td>
<td>200</td>
<td>400</td>
<td>400</td>
<td>$\times 10^{-3}$ W</td>
</tr>
<tr>
<td>$t_p$</td>
<td>60</td>
<td>100</td>
<td>10</td>
<td>10</td>
<td>$\times 10^{-15}$ s</td>
</tr>
<tr>
<td>$f_p$</td>
<td>5</td>
<td>1</td>
<td>7500</td>
<td>75 000</td>
<td>$\times 10^3$ Hz</td>
</tr>
<tr>
<td>$D$</td>
<td>30</td>
<td>5000</td>
<td>2000</td>
<td>50</td>
<td>$\times 10^{-6}$ m</td>
</tr>
<tr>
<td>$A$</td>
<td>0.7</td>
<td>19635</td>
<td>3142</td>
<td>1.96</td>
<td>$\times 10^{-9}$ m$^2$</td>
</tr>
<tr>
<td>$W_p$</td>
<td>50</td>
<td>200 000</td>
<td>5.3</td>
<td>5.3</td>
<td>$\times 10^{-9}$ J</td>
</tr>
<tr>
<td>$W_p/A$</td>
<td>70 736</td>
<td>10 186</td>
<td>1.7</td>
<td>2 716</td>
<td>$\times 10^{-3}$ J·m$^{-2}$</td>
</tr>
</tbody>
</table>
4.1. Ultrafast Pulse Model

Figure 4.1: Model of the ultrafast pulse used in this thesis. Note the similar peak power but much shorter duration than the pulse used by Beaurepaire et al. (figure 4.2). The large spectral broadening from 700 to 900 nm is due to the uncertainty principle (modelled via a Fourier transform) and this broadening is confirmed experimentally for this laser[38].
Figure 4.2: Model of the ultrafast pulse used by Beaurepaire et al. in their 2004 paper[7]. Note the similar peak power, but much greater length of the pulse, and hence pulse energy (distinct from power) density, compared to the one pulse in this thesis (figure 4.1). This is not strictly a model of the Beaurepaire pulse, but an extrapolation of the experimental pulse model to its parameters. As such the accuracy is uncertain for all components other than the power density plot, which is the component used in the model.
4.2 Ultrafast Pulse Coupling

While the properties of the ultrafast pulse are modelled in section 4.1 and the effects of the pulse on the material are modelled in section 4.3, the coupling of the ultrafast pulse to the materials is non-trivial, and depends on the properties of the pulse, the material, and experimental construction details.

The ultrafast demagnetisation models make the assumption that temperatures are homogeneous across the illuminated volume, and that thermal conductivity both within the volume, and across its boundaries is negligible. This was done to avoid introducing extra dimensions in the problem which would have drastically increased the complexity of the numerical solutions. Similarly the pulse coupling model approximates a uniform illumination of the sample volume by the pulse. The vertical \((z)\) component of the uniform illumination approximation is detailed in section 4.2.2. The horizontal \((\rho \text{ and } \phi)\) component of the uniform approximation is detailed in section 4.2.3.

The model also ignores conduction across the boundaries of the volume. There are energy transport mechanisms for all energy reservoirs, plasmons and ballistic transport for the electrons, phonons for the lattice and magnons for the spins. These assumptions are valid if the conduction effects are great enough to homogenise the temperatures within the volume, but low enough to not appreciably remove energy from the irradiated volume. These assumptions are more plausible for ultrathin films on insulating substrates, where transport into the bulk of the sample is inhibited due to the properties of the substrate and interface. Experiments on samples of all thicknesses have however been carried out with similar results, implying that the presence or absence of thermal transport is not a critical parameter to model.

To model these components, a laser coupling factor \(L\) is introduced. The laser coupling factor is designed as a constant of the experiment, and can therefore be introduced into the ultrafast demagnetisation models as a multiplicative constant applied to the pulse function.

\[
L = A \cdot \eta_z \eta_{\rho\phi} \cdot \cos(\theta_i) \cdot \frac{2}{d} \tag{4.11}
\]

The components of the laser coupling factor are described further (where necessary) in the following subsections. \(A\) is the absorptivity of the sample at the relevant wavelength, detailed in section 4.2.1. \(\eta_z\) is the depth coupling model efficiency, describing the proportion of pulse energy disregarded by assuming uniform beam penetration, detailed in section 4.2.2. \(\eta_{\rho\phi}\) is the profile coupling model efficiency, describing the proportion of pulse energy disregarded by assuming a uniform beam penetration.
cross section, detailed in section 4.2.3. The factor $\cos(\theta_i)$ describes the geometric spreading effect of the oblique incidence of laser light, where $\theta_i$ is the angle of incidence of the laser on the sample. Finally, the factor of $\frac{2}{d}$ represents division by half the penetration depth, the depth over which the uniform beam is modelled to penetrate, this component is described in section 4.2.2 and depicted in figure 4.3.

### 4.2.1 Absorption and Reflection

The coupling of the ultrafast pulse to the material depends both on the properties of the material, and on the polarization of the pulse. The reflectivity of p-polarised ($E$ field parallel the plane of incidence) light $R_p$, and and s-polarised ($E$ field perpendicular to the plane of incidence) light $R_s$, can be described in terms of the real component of the refractive index $n$, the imaginary component of the refractive index $k$, the angle of incidence $\theta_i$:

$$R_p = \frac{(n - \sec \theta_i)^2 + k^2}{(n + \sec \theta_i)^2 + k^2}$$

$$R_s = \frac{(n - \cos \theta_i)^2 + k^2}{(n + \cos \theta_i)^2 + k^2}$$

with it assumed that the material is within a medium with refractive index $\approx 1$, viz. air, and that $n^2 + k^2 \gg 1$ which is true for all the materials modelled. For linearly polarised light, with an arbitrary polarisation direction, the reflectivity can be determined in terms of the angle between the $E$ field and the plane of incidence, $\theta_p$:

$$R = R_s \sin^2 \theta_p + R_p \cos^2 \theta_p. \quad (4.15)$$

Conservation of energy requires that all of the beam be either transmitted, reflects or absorbed. In bulk materials, the transitivity $T = 0$ and in optically thick, yet still thin films, $T \approx 0$, therefore with $R$ being the reflectivity and $A$ the absorptivity:

$$1 = R + T + A \quad (4.16)$$

$$A = 1 - R \quad \text{for } T \rightarrow 0. \quad (4.17)$$

The modelled reflectivity for p-polarised light incident at 45° on Nickel, as used in both the examples (replicating Beaurepaire et. al) and experimentally was 0.5899, giving an absorptivity of 0.4101. This can be contrasted with the reflectivity of
s-polarised light in the same situation, modelled as 0.7597, showing the disparity in reflectance between p and s polarised light. This effect increases as the angle of incidence approaches Brewster’s angle (modelled as 78.688°, where $R_s = 0.9257$ and $R_p = 0.3403$). $R_p$ does not reach zero, due to the complex refractive index of the material.

While the temperature dependence of reflectivity for metals is well established\cite{40}, the ultrafast pulse induces a non-thermal temperature distribution, leaving the notion of temperature in the electron shell ill defined. Even if a thermalised temperature is assumed during the pulse, the temperature reflectivity coefficient for Nickel is only of the order of $10^{-4}$\cite{41}, and the change in electron temperature is of the order of $10^0$ (see figure 2.7), therefore the temperature will not have a significant effect. While very high fluences can cause large decreases in the reflectivity of a metal due to free plasma production at the surface of the metal\cite{42}, these fluences are far higher than seen in this thesis. This is reinforced by the fact that the number of photons in an ultrafast pulse is significantly lower than the free electron density on the surface of the metal, meaning that the photoexcited electrons are never a significant proportion of the free electron population. Therefore the dependence of reflectivity upon the electron temperature was assumed to be negligible, for the electron temperatures encountered ($T_e \leq 10^3$ K).

4.2.2 Coupling Depth

The proportion of pulse energy coupled to the material $\eta_z$ is given by the following expression, where $S(z)$ denotes the power density of the laser as a function of depth, the subscript \textit{ideal} denotes a realistic model, and the subscript \textit{simple} the simplified constant approximation:

$$\eta_z = \frac{\int_0^\infty S(z)_{\text{simple}} dz}{\int_0^\infty S(z)_{\text{ideal}} dz}.$$  \hspace{1cm} (4.18)

The penetration depth of the pulse into a material can be realistically modelled as an exponential falloff in the (power) density of light $S$, in terms of the absorption coefficient $\alpha$:

$$S(z)_{\text{ideal}} = S_0 e^{-\alpha z}.$$ \hspace{1cm} (4.19)

Taking the penetration depth to be the depth where the power density $S$ has diminished by a factor of $1/e^2$, and the electric and magnetic fields by a factor of $1/e$, the penetration depth $d = \frac{2}{\alpha}$ can be found in terms of the wavelength of the light
Chapter 4. Model Development

\( \lambda \), and the imaginary component of the complex refractive index \( k \) (which is also a function of the wavelength)\[39\]:

\[
d = 2 \frac{\lambda}{2\pi k} \quad \text{(4.20)}
\]

\[
S(z)_{\text{ideal}} = S_0 e^{\left( \frac{-z}{d} \right)} \quad \text{(4.21)}
\]

The penetration depth of near infra-red light into metals is typically tens of nanometres. Under 790 nm light, the calculated result was 48 nm for Nickel and 79 nm for Gadolinium.

As described previously, the pulse is modelled as being the average power over the first half of the penetration depth \( d \), being absorbed over half the penetration depth. With the penetration depth defined as the depth \( z \) by which power has decreased by a factor of \( 1/e^2 \):

\[
S(z)_{\text{simple}} = \int_0^{d/2} S(z)_{\text{ideal}} \, dz \quad 0 \leq z \leq \frac{d}{2} \quad \text{(4.22)}
\]

\[
= 2 S_0 \left( 1 - \frac{1}{e} \right) \quad \text{(4.23)}
\]

Substituting equations 4.21 and 4.23 into equation 4.18 yields:

\[
\eta_z = 2 \left( 1 - \frac{1}{e} \right) \quad \text{(4.24)}
\]

\[
\approx 0.68 \quad \text{(4.25)}
\]

The vertical component of the uniform model couples \( \approx 68\% \) of the pulse energy to the sample.

### 4.2.3 Coupling Profile

The proportion of pulse energy coupled to the material \( \eta_{\rho \phi} \) is given by the following expression, where \( S(\rho, \phi) \) denotes the power density of the laser as a function of radius and azimuth, the subscript \( \text{ideal} \) denotes a realistic model, and the subscript \( \text{approx} \) the simplified constant approximation;

\[
\eta_{\rho \phi} = \frac{S(\rho, \phi)_{\text{simple}}}{S(\rho, \phi)_{\text{ideal}}} \quad \text{(4.26)}
\]

While the pulse power density is approximated as being constant across the beam diameter, the actual variation is Gaussian. This variation is modelled using a normalised Gaussian function, with a standard deviation \( \sigma \) of half the beam radius.
\( \rho_R \). In cylindrical polar coordinates:

\[
S(\rho, \phi)_{\text{ideal}} = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{1}{2} \left( \frac{\rho}{\sigma} \right)^2 \right) \tag{4.27}
\]

\[
= \frac{1}{\rho_R \sqrt{\frac{2}{\pi}}} \exp \left( -2 \left( \frac{\rho}{\rho_R} \right)^2 \right) \tag{4.28}
\]

where \( \rho \) the distance from the beam centre, and \( \rho_R \) is the beam radius, defined as the distance (in the \( \hat{\rho} \) direction) at which power has decreased by \( 1/e^2 \).

The simplified model on the other hand assumes that the absorbed power is constant throughout a cylindrical volume. The laser power density is modelled as a constant over the beam radius \( \rho_R \), such that the total power is equal to \( S_0 \):

\[
S(\rho, \phi)_{\text{simple}} = \frac{1}{2\rho_R} \quad 0 \leq \rho \leq \rho_R. \tag{4.29}
\]

Substituting equations 4.28 and 4.29 into equation 4.26 yields:

\[
\eta_{\rho\phi} = 1. \tag{4.30}
\]

The horizontal component of the uniform model couples all of the pulse energy to the sample.

These assumptions result in significant overestimates in the energy absorbed in the deeper and outer sections (high \( \rho \) and \( z \)) of the cylinder defined by \( \rho_R \) and \( d \). It is expected that this is compensated for by larger underestimates in the energy absorbed in the central and surface sections (low \( \rho \) and \( z \)) of the illuminated cylinder. The degree to which the compensation occurs depends on the degree of non-linearity of Terahertz emission with respect to pulse power density, which is explored in section 6.2.2.
Figure 4.3: Pulse coupling approximations. The blue lines show the realistic model of the spatial variations in power density. The green lines show the simplified model. The figures are normalised to give the total power of the realistic model (blue) as 1.

The left figure shows the power density as a cross section over the beam radius, in units of the beam radius $\rho R$. The areas beneath both curves are equal.

The right figure shows the power density as a function of the penetration depth, in units of the penetration depth. The area beneath the green curve (simplified model) is \( \approx 68\% \) of the blue curve (realistic model).

### 4.3 Ultrafast Demagnetisation Models

All of the models are systems of ordinary differential equations describing the transfer of energy between systems. At normal (not-ultrafast, $> 1$ ns) timescales, these systems are tightly coupled, and equilibrium is maintained. However an ultrafast pulse has a high enough peak power, and acts over a short enough timescale, that differences between the temperatures of the constituent parts of a material can be modelled and observed.

Important differences in the models are the system to which the ultrafast pulse couples, and the system whose temperature change correlates with demagnetisation. Some models published do not explicitly include pulse functions, and may model them as delta functions, or model the system as relaxing from a disturbed state. While this assists in producing analytical solutions, it complicates producing a shared framework for numerically solving and comparing models. In this thesis, models are therefore modified to include pulse functions coupled to the appropriate reservoir. Models also include different assumptions about heat capacities, which are replaced by the shared models described in section 4.5. The modified models in this thesis consist of a system of coupled differential equations. These equations are numerically integrated using a variable order backwards difference method, to
produce an approximation of the temperatures of the components of the materials, as a function of time.

All of the models are less complex than they appear. Each term $G_{ab}(T_a - T_b)$ appears in two equations with equal magnitude, but opposite sign. This represents energy transfer between the two reservoirs, proportional to the temperature difference, in the same manner as regular thermal conductivity. The pulse function $P(t)$ represents the input of energy into the system which then returns to equilibrium over time. Magnetisation is generally modelled as a function of the spin temperature, using the relation found in equation 4.81.

The form of the pulse function $P(t)$ has been modified from some uses in the literature, so that $P(t)$ was the (short-time averaged) magnitude of the Poynting vector of the laser, i.e. its (2 dimensional) power density. The material and experiment specific coupling is included in the laser coupling factor $L$, detailed in section 4.2. The final pulse function component, included in each model is:

$$\text{Pulse}(t) = LP(t).$$ (4.31)

The complete pulse function component (as distinct from the pulse power density $P(t)$) now describes the three dimensional energy density transferred by the pulse, as a function of time, in units J·m$^{-3}$·s$^{-1}$.

As a check on the validity of the models, result sets were produced for each model with the conditions of the Beaurepaire et al. 1996 paper[2]. This experiment used a sample constructed of 100 nm of MgF$_2$ coating over 22 nm of Ni. The Magnesium Difluoride layer complicates the coupling of the pulse to the Nickel as it functions as an anti-reflective coating, increasing the amount of pulse energy that is delivered to the Nickel. On the other hand, the Nickel layer is substantially thinner than the penetration depth of red (620 nm) light into Nickel. Using the model described in section 4.2, it was determined that $\approx 1/3$ of the laser light is transmitted through the Nickel layer, and hence not absorbed. As an approximation, it was assumed that these conflicting effects cancelled out.

### 4.3.1 Two Temperature Model

The Two Temperature Model described in section 2.5.1 was altered to explicitly include a lattice reservoir (subscript $p \rightarrow l$) and a pulse function (equation 4.31). The pulse function couples directly to the electron shell. The Two Temperature Model neglects to distinguish between the kinetic and magnetic energy of the electrons, but according to the dipole approximation of the laser field, a direct coupling of the laser
Chapter 4. Model Development

to the spin system is not possible, due to conservation of angular momentum[10]. Therefore the electron reservoir in the Two Temperature Model was treated as being a combined kinetic and magnetic reservoir, denoted by subscript capital $E$. Any result obtained from the combined electronic temperature will be smaller due to the greater heat capacity of the combined electron system, rather than the kinetic or magnetic portion alone.

\[
\frac{dT_E}{dt} = \frac{G_{El}(T_i - T_E) + LP(t)}{C_E(T_E)} \quad (4.32a)
\]

\[
\frac{dT_i}{dt} = \frac{G_{El}(T_E - T_i)}{C_l(T_i)} \quad (4.32b)
\]

where $T_E$ is the combined electronic temperature, $C_E$ is the total electronic specific heat and $G_{El}$ is the combined electron-lattice coupling constant:

\[
C_E(T_E) = C_e(T_E) + C_s(T_E) \quad (4.33)
\]

\[
T_E = T_e = T_s. \quad (4.34)
\]

The magnetisation is a function of the combined electron temperature:

\[
M(T_E).
\]

The Two Temperature Model produces extremely rapid demagnetisation, as a result of the direct coupling of the laser pulse to the spin system. This is important due to the rapid demagnetisation, and therefore large magnetic dipole emission this would cause. This effect is greater when shorter laser pulses are used, as the increase in temperature is in general even more rapid. This can be seen by comparing demagnetisation from the 100 fs pulse here in figure 4.4b to the two temperature model predictions for the similar power density, 10 fs laser shown in figure 5.4, for the same material model.

To quantitatively show the differences between considering the electron reservoir as either purely electronic, purely magnetic, or as the sum of the two, the heat capacities and coupling constants for each alternative are tabulated in table 4.3. The combined reservoirs have significantly greater heat capacities, and effectively function as a three temperature model, but with infinite coupling between the electron and spin reservoirs ($G_{es} = \infty$, $\tau_{es} = 0$). This produces more reasonable results than either the purely electronic heat capacity, which is far too low, or the purely magnetic heat capacity, which is too variable. The combined model remains problematic as the direct coupling of the pulse to the demagnetisation reservoir, produces results
4.3. Ultrafast Demagnetisation Models

(a) Two Temperature Model temperatures. Note that the profile of the electron temperature rise is that of the pulse, showing the direct coupling to the electron temperature. This is not an issue in non-magnetic materials, however when this temperature is used as the basis for magnetisation, implausible results are predicted.

(b) Two Temperature Model magnetisation. According to the two temperature model, roughly half of the magnetisation is lost over $\sim 75$ fs. Notable is the asymmetry in the demagnetisation-remagnetisation cycle, with fast near linear demagnetisation, and slow, but also near linear recovery of magnetisation.

Figure 4.4: Example of the Two Temperature Model, calculated with material parameters for Nickel, and laser parameters for the laser used by Beaurepaire et al. in their 2004 paper[7].
not supported by experiment, including in this thesis.

Table 4.3: Values of possible parameters for the Two Temperature Model. Values are calculated using the methods described in section 4.4. Note that the Heat capacities near the Curie temperature are far from slowly changing (see figure 4.8, 4.9), as is required for the constant relaxation time to be an accurate approximation. Heat capacities have the units J·m\(^{-3}\)·K\(^{-1}\) and coupling constants W·m\(^{-3}\)·K\(^{-1}\).

<table>
<thead>
<tr>
<th>Spin Temperature</th>
<th>Nickel (C_E(\times 10^5))</th>
<th>G(_{El})((\times 10^{17}))</th>
<th>Gadolinium (C_E(\times 10^5))</th>
<th>G(_{El})((\times 10^{16}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic</td>
<td>3.371</td>
<td>4.364</td>
<td>1.194</td>
<td>0.583</td>
</tr>
<tr>
<td>Magnetic</td>
<td>2.439</td>
<td>3.239</td>
<td>0.236</td>
<td>2.745</td>
</tr>
<tr>
<td>Combined</td>
<td>5.811</td>
<td>7.055</td>
<td>1.430</td>
<td>3.230</td>
</tr>
</tbody>
</table>

4.3.2 Three Temperature Model

The Three Temperature Model has been minimally modified from that of the literature (section 2.5.2). The heat capacities are now accurate functions of their respective temperatures, and the Pulse function was changed as described by equation 4.31. The heat capacity terms are also moved to the right hand side of the equation system, from their positions in the Beaurepaire et al. paper from 1996[2], to match both the other models, and the form from which a differential equation system is typically solved:

\[
\begin{align*}
\frac{dT_e}{dt} &= G_{es}(T_e - T_s) + G_{el}(T_e - T_l) + L P(t) \frac{C_e(T_e)}{C_e(T_e)} \\
\frac{dT_s}{dt} &= G_{es}(T_s - T_e) + G_{sl}(T_s - T_l) \frac{C_s(T_s)}{C_s(T_s)} \\
\frac{dT_l}{dt} &= G_{el}(T_l - T_e) + G_{sl}(T_l - T_s) \frac{C_l(T_l)}{C_l(T_l)}.
\end{align*}
\]

The magnetisation is a function of spin temperature:

\[M(T_s).\]

The values of the coupling constants \(G_{es}, G_{el} \) and \(G_{sl}\) are given in table 4.4 and their derivation described in section 4.4. Without curve fit values for \(C_e(T), G_{es} \) and \(G_{el}\), the Three Temperature model fails to predict the observed change in temperature profiles. Comparing the temperature profiles in figure 4.5a, to experimental data from Beaurepaire et al. in figure 2.7 and modelling by Zhang et al. in figure 2.16, leads to the conclusion that the experimental value for electronic heat capacity
(a) Three Temperature Model temperatures. This version of the model fails to reproduce the results of Beaurepaire et al., shown in figure 2.7. This is due to both the use of differing spin coupling relationships and the use of the smaller, macroscopically valid, value of the electronic heat capacity. Comparison with the models by Zhang et al.[8] in figure 2.16c implies that the flatness of the spin temperature profile can be attributed to the smaller electronic heat capacity, and the smaller magnitude of the spin temperature profile attributed the the symmetric coupling.

(b) Three Temperature Model magnetisation. While the temperature profiles do not reproduce the results of Beaurepaire et al. from 1996, the demagnetisation curve does however qualitatively reproduce the Terahertz producing demagnetisation published by Beaurepaire et al. in 2004, shown at figure 2.9, which was undertaken in similar conditions, but used THz-TDS rather than the TR-MOKE used in 1996.

Figure 4.5: Example of the Three Temperature Model, calculated with material parameters for Nickel, and laser parameters for the laser used by Beaurepaire et al. in their 2004 paper[7].
does not properly account for the electronic heat capacity in this case, and leads to overestimates in the temperature of the electron system.

It also appears that the ratio $G_{es}/G_{el}$ is important in determining the degree of demagnetisation that occurs. In the simple model of spin-flip energy transfer used in this thesis (section 4.4) the apparently separate electron-lattice, electron-spin and spin-lattice interactions are modelled as the outcomes of an electron-phonon interaction, whereby the energy of a hot electron is distributed between the lattice or spin system, dependent on the spin-slip probability. This process is necessarily two way, since a high energy phonon-electron interaction should also be able to give kinetic energy to an electron, or inelastically change its spin state. In any interaction with the spin system, a phonon must be present and angular momentum must be transferred between the spins and the phonon. Whether this interaction involves a gain or loss of energy by the spin system must depend on the relative energies of the electron and phonon concerned. Since every electron interaction requires a phonon present, every electron-spin interaction is necessarily also an electron-lattice interaction. This does not require that energy transfer to the spin system be less than transfer to the lattice, as the frequency of interaction events is independent of the energy transfer in each. The energy exchanged with the spin system in an interaction is a relatively large, discrete quantity (the exchange energy), and the electron kinetic energies are semi-continuous in distribution, therefore, in general, electron spin interactions (when they occur) will involve a significant transfer to the lattice. This implies a ratio $G_{es}/G_{el} \sim 1$, in contrast with the larger ratio of $G_{es}/G_{el} = 30$ that was fit by Beaurepaire et al.. This is complicated by the difference in heat capacity models used, with the spin heat capacity values used in this thesis being larger than those used by Beaurepaire et al.[2], and the electronic heat capacities being smaller, reducing the ability of the electrons to raise the temperature of the spins, and the ability of the lattice to lower it.

The other possibility is that $G_{es}$ is actually the sum of other effects in addition to spin-flip interactions such as spin-orbit coupling mediated interactions[10]. The problem with incorporating this into the model is that spin-orbit coupling mediated electron-spin coupling is almost certainly not a thermal-like process where the rate of energy transfer is proportional to temperature difference. Predictions limit spin-orbit coupling mediated interactions to the presence of the laser field, and hence the pulse, or limit the degree of magnetisation reduction to half[10]. In any case the issue is raised as to whether spin-coupling can be treated thermally at all, or whether the magnetisation dynamics are better handled by an explicit magnetisation term. This would take the form of a function of electron and lattice temperatures, amongst
4.3. Ultrafast Demagnetisation Models

This is the approach taken by the microscopic three temperature model, detailed in section 4.3.4.

4.3.3 Non-Thermal Electron Model

The Non-Thermal Electron Model (NTEM) was developed from that presented by Zhang et al.\cite{8} and described in section 2.5.3. The ultrafast pulse function is transformed as described in equation 4.31, and divided by the photon energy $\epsilon$, to give the photon number density. In the temperature equations, the non-thermal relaxation parameters are changed to $\alpha$, $\beta$ and $\gamma$ for consistency. The relaxation constants are also multiplied by the photon energy to convert from the number density of photons in equation 4.36a to energy densities required in the numerator of the right-hand side of the other equations. The term $N$ denotes the non-thermal electron density. Therefore the quantity in equation 4.36a has the units $({\text{m}}^{-3} \cdot {\text{s}}^{-1})$, while the remaining equations remain in terms of temperature rate of change (${\text{K}} \cdot {\text{s}}^{-1}$).

\[
\frac{dN}{dt} = -\alpha N - \beta N - \gamma N + \frac{LP(t)}{\epsilon} \quad (4.36a)
\]

\[
\frac{dT_e}{dt} = \frac{G_{es}(T_e - T_s) + G_{al}(T_e - T_l) + \epsilon\alpha N}{C_e(T_e)} \quad (4.36b)
\]

\[
\frac{dT_s}{dt} = \frac{G_{es}(T_s - T_e) + G_{al}(T_s - T_l) + \epsilon\beta N}{C_s(T_s)} \quad (4.36c)
\]

\[
\frac{dT_l}{dt} = \frac{G_{el}(T_l - T_e) + G_{sl}(T_l - T_s) + \epsilon\gamma N}{C_l(T_l)} \quad (4.36d)
\]

where $\epsilon$ is the photon energy, and with magnetisation a function of spin temperature:

\[M(T_s).\]

The values of the coupling constants $G_{es}$, $G_{el}$ and $G_{sl}$ are given in table 4.4 and their derivation described in section 4.4.

Values for the parameters $\alpha$, $\beta$ and $\gamma$ can be approximated by relating them to their physical meaning. After the pulse, $P(t) = 0$, and $\alpha$, $\beta$ and $\gamma$ function as decay constants for the non-thermal population. Denoting the time for the non-thermal population to decay as $\tau_{ee}$:

\[
\frac{dN}{dt} = -\alpha N - \beta N - \gamma N \quad (4.37)
\]

\[N = N_0 \exp - (\alpha + \beta + \gamma) t \quad (4.38)\]

\[N = N_0 \exp - \frac{t}{\tau_{ee}} \quad (4.39)\]
In this model, a non-thermal (optical) electron can decay (thermalise) by three mechanisms, a thermalising interaction with another electron, at a rate described by $\alpha$, an interaction with a lattice phonon, creating an optical phonon, at a rate described by $\gamma$, and an inelastic spin-flip interaction with a phonon, at a rate described by $\beta$.

The electron-electron decay constant $\alpha$ can be approximated from Fermi-Liquid Theory\[32\], by equating the excited electron decay time, $\tau_{ee}$, and the time for the non-thermal population to decay, $\tau_N$ (given by equation 3.25):

$$\alpha = \frac{1}{\tau_{ee}} - \beta - \gamma.$$  \hspace{1cm} (4.41)

The methods used to derive approximations for the parameters $\beta$ and $\gamma$ are based on those used to approximate the values of the coupling constants $G_{es}$ and $G_{el}$ respectively, as contained in section 4.4. At optical energies, coupling between the electrons and the lattice occurs at a higher rate. Classically, this is described by the optical resistivity $\rho_o$, being distinguished from the regular, or dc resistivity, denoted here as $\rho_{th}$. The subscript $th$ signifies that the electrons are at thermal, as opposed to optical energies, and does not refer to the thermal transfer of energy. Koopmans et al. also describe an increase in the spin flip probability at optical frequencies\[4\], denoted here by $\alpha_{sf}$. These parameters allow an approximation for the values of $\beta$ and $\gamma$, based upon those of the regular coupling constants.

Each non-thermal electron carries energy $\epsilon$, the photon energy, in excess of the regular thermal energy. Therefore each thermalisation of a non-thermal electron delivers energy $\epsilon$ (the energy of the pulse photons) from the non-thermal system to the thermal systems. By examining the NTEM equations (equations 4.36), it can be seen that the role of a coupling constant in the equation is equivalent to that of a non-thermal decay parameter, multiplied by the photon energy. Since the non-thermal electrons are still electrons, albeit at higher energies, the following (qualitative) similarities, or functional equivalencies, can be determined:

$$G_{es} \sim \epsilon \beta$$ \hspace{1cm} (4.42)

$$G_{el} \sim \epsilon \gamma.$$ \hspace{1cm} (4.43)

The parameters $\beta$ and $\gamma$, describe the interaction between a non-thermal electron, and a phonon. The rate at which electrons interact with the lattice is enhanced at optical frequencies, as is the proportion of spin flips. The degree of electron-phonon interaction enhancement is modelled using the ratio of electrical resistivity at optical
to thermal energies $\rho_o/\rho_{th}$. The proportion of electron-phonon interactions resulting in a spin-flip interaction at optical energies is denoted by $\alpha_{sfo}$. Therefore, taking equations 4.69 and 4.70, introducing a factor of $\rho_o/\rho_{th}$, and replacing $\alpha_{sf}$ with $\alpha_{sfo}$:

$$\epsilon\beta = \frac{\rho_o}{\rho_{th}} \alpha_{sfo} G_{El} \tag{4.44}$$

$$\epsilon\gamma = \frac{\rho_o}{\rho_{th}} (1 - \alpha_{sfo}) G_{El}. \tag{4.45}$$

Substituting these equations into equation 4.41, produces a final expression for $\alpha$:

$$\epsilon\alpha = \frac{1}{\epsilon \tau_{ee}} - \frac{\rho_o}{\rho_{th}} G_{El}. \tag{4.46}$$

The non-thermal electron model still suffers from the same difficulty in modelling Table 4.4: Calculated values of NTEM parameters. There is a wide variation in the predicted decay constants, and the resultant decay pathways.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Gd</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>8.881</td>
<td>8.877</td>
<td>8.685</td>
<td>7.914</td>
<td>$\times 10^{13} \text{ m}^{-3} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.511</td>
<td>6.531</td>
<td>4.345</td>
<td>0.616</td>
<td>$\times 10^{11} \text{ m}^{-3} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.666</td>
<td>2.012</td>
<td>1.497</td>
<td>0.144</td>
<td>$\times 10^{12} \text{ m}^{-3} \cdot \text{s}^{-1}$</td>
</tr>
</tbody>
</table>

electron-spin and spin-lattice interactions as the three temperature model. This is partially mitigated however as the $\beta$ parameter allows another position for non-thermal electron-spin coupling, such as laser-field based spin-orbit coupling, to be included.
(a) Non-Thermal Electron Model temperatures. The results are similar to those of the three temperature model, with the exception that the electron temperature rise is not as sharp. This is due to the pulse coupling indirectly to the electron temperature. While the non-thermal population exists, there is enhanced coupling to the spin system, due to larger spin-flip probabilities at optical energies. Once the non-thermal population has subsided, the model proceeds identically, but with slightly different starting values, to the Three Temperature model. This is to be expected from the structure of the differential equation system.

(b) Non-thermal Electron Model magnetisation as a function of time. Since the spin temperature profile is similar, but slightly higher, than that of the three temperature model, so the demagnetisation is similar, but slightly greater.

Figure 4.6: Example of the Non-Thermal Electron Model, calculated with material parameters for Nickel, and laser parameters for the laser used by Beaurepaire et al. in their 2004 paper[7].
4.3.4 Microscopic Three Temperature Model

The Microscopic Three Temperature Model (M3TM) was first proposed by Koopmans et al. in 2010\cite{4}, and is described in section 2.5.4. The M3TM was altered by removing the electron thermal conductivity cooling term, as it had little effect on the demagnetisation dynamics, and long term cooling (which the term modelled) is outside the scope of the other models. The pulse function was transformed as described in equation 4.31, and the phonon reservoir was renamed to the lattice reservoir, in line with the other models:

\[
\frac{dT_e}{dt} = \frac{G_{el}(T_i - T_e) + LP(t)}{C_e(T_e)} \quad (4.47a)
\]

\[
\frac{dT_i}{dt} = \frac{G_{el}(T_e - T_i)}{C_i(T_i)} \quad (4.47b)
\]

\[
\frac{dm}{dt} = R \frac{T_i}{T_c} \left(1 - m \coth \left(\frac{mT_c}{T_0}\right)\right). \quad (4.47c)
\]

where \(R\) is a material specific parameter given by:

\[
R = \frac{8a_{sl}G_{el}k_B T_c^2}{N(\mu_{sat}/\mu_B)E_D}. \quad (2.10)
\]

In order to provide the correct initial conditions for the differential equation system, a value of \(m\), at \(t = 0\) and therefore \(T = T_0\), was required, this is denoted here as \(m_{T_0}\). It was necessary to solve equation 4.47c for an equilibrium solution. Letting,

\[
\frac{dm}{dt} = 0 \quad (4.48)
\]

\[
T_i = T_e = T_0, \quad (4.49)
\]

and substituting into equation 4.47c:

\[
1 = m_{T_0} \coth \left(\frac{m_{T_0}T_C}{T_0}\right)
\]

\[
m_{T_0} = \tanh \left(\frac{m_{T_0}T_C}{T_0}\right), \quad (4.50)
\]

which was solved numerically.

While this produces the correct equilibrium solution, this solution is still in terms of relative magnetisation. Multiplying the relative magnetisation by the saturation magnetisation used elsewhere \((M_0)\) produced initial values of magnetisation \((M_{M3TM}(t = 0))\) similar to, but different from the other models. This is due to inbuilt assumptions about the magnetisation as a function on temperature in the
Chapter 4. Model Development

M3TM. To compensate for this, the initial magnetisation was normalised to the value used by the other models:

\[ M_{M3TM}(t) = \frac{M(T_0)}{m(T_0)} m(t) \]  

(4.51)

where \( M(T_0) \) uses the magnetisation function from equation 4.81. This normalises the magnetisation as a function of temperature with the experimental values used in other models.

The equilibrium magnetisation as a function of temperature in the microscopic three temperature model is a Langevin function as opposed to the Brillouin function used by the shared model. The function used in this model also does not include the contribution of the \( H \) field. These differences are small for ordinary values of \( H \), and temperatures away from \( T_c \), however the features are visible in the comparison between magnetisations for different materials, illustrated in figure 4.11.

The value of the coupling constant \( G_{El} \) is given in table 4.4, and its derivation in section 4.4. While there is no explicit spin reservoir in the three temperature model, references to the electron reservoir in the M3TM (with lower case \( e \) subscript) are to the kinetic component of the electrons only, as the spin/magnetic component is subsumed within the explicit magnetisation function.

The values of \( R \) used in this thesis are calculated from the material parameters listed in table A.2 and the laser parameters listed in table 4.2, and are tabulated in table 4.5. The \( R \) values calculated here are for the focused experimental laser. While Iron, Cobalt and Nickel have very similar values, the \( R \) value for Gadolinium is \( \approx 50 \) times less. This implies that demagnetisation is \( \approx 50 \) times slower in Gadolinium than the other ferromagnets listed, before the effects of electron and lattice temperature dynamics are taken into account. While changing the laser model does affect the values of the \( R \) parameter, the general distribution of the transition metal values being similar, and Gadolinium being 1-2 orders of magnitude slower remains.

Table 4.5: Calculated values of the M3TM \( R \) parameter. Via their dependence on \( G_{El} \), these values depend on the laser model used. The values tabulated here are for the focused experimental laser, with parameters listed in table 4.2.

<table>
<thead>
<tr>
<th>Material</th>
<th>( R ) (( s^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>1.3063 ( \times 10^{12} )</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1.4316 ( \times 10^{12} )</td>
</tr>
<tr>
<td>Nickel</td>
<td>1.5856 ( \times 10^{12} )</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>3.6486 ( \times 10^{10} )</td>
</tr>
</tbody>
</table>
4.3. Ultrafast Demagnetisation Models

The electron and lattice temperatures predicted by the M3TM are very similar to the other models, reflecting the similar mathematical structure. The magnetisation is qualitatively similar, reflecting the similarities between the Langevin like magnetisation function used in the M3TM, and the Brillouin based magnetisation function used elsewhere, the Langevin function being Brillouin function in the limit as $J \to \infty$. The predicted magnitude of the demagnetisation however, is much greater in the M3TM.
(a) Microscopic Three Temperature Model Temperatures. Despite the name, the M3TM features only two explicit temperatures, the spin temperature concept of the 3TM has been replaced by a direct expression for the magnetisation as a function of the electron and lattice temperatures. Note the similarities to the 3TM (figure 4.5), without the spin temperature.

(b) Microscopic Three Temperature Model Magnetisation. While the temperature profiles are similar, the demagnetisation and remagnetisation is much more pronounced than in the 3TM (figure 4.5).

Figure 4.7: Example of the Microscopic Three Temperature Model, calculated with material parameters for Nickel, and laser parameters for the laser used by Beaurepaire et al. in their 2004 paper[7].
4.4 Reservoir Coupling Models

The reservoir coupling models describe the strength of the coupling between the energy reservoirs defined by each ultrafast demagnetisation model. These models contain parameters $G_{xy}$ with subscripts representing the reservoirs they couple between. The $G$ parameters have the units $W \cdot m^{-3} \cdot K^{-1}$.

In two-component models the coupling constants can be derived from the relaxation time of the system. Under the assumption that heat capacities are constant, and the pulse function is zero (i.e. the pulse has already occurred and the system is relaxing without outside input) an exact solution for the characteristic relaxation time can be found. With respect to the pulse, this assumption amounts to approximating the pulse as a delta function, which is valid when the pulse duration is much shorter than the relaxation time. With respect to the heat capacities, the approximation as constant is valid for the lattice above the Debye temperature. For the electron temperature, the assumption is never strictly valid, although this effect is lessened by the small magnitude and rate of change of the electron temperature. For spin temperatures, the assumption is approximately valid while significantly less than the Curie temperature, valid while greater than it, and invalid while approaching the Curie temperature from below.

Since the pulse has a finite length in time, the characteristic decay time can only be approximated from the centre of the pulse, which occurs before the maximum of the electron temperature (which can be seen to occur almost at the end of the pulse). This effect will tend to increase the nominal decay time, making the approximation for the decay time smaller, and the coupling constant larger. The heat capacity assumptions are all of the form of assuming heat capacity is in fact constant when it is generally slowly increasing (except for the singularity in the spin heat capacity, where heat capacity is rapidly increasing, and therefore an even worse approximation). These effects would tend to increase the value of the coupling constant, and decrease the decay time. These effects can be partially compensated for by calculating the coupling constants using the heat capacities at a higher, compromise temperature, or using the average heat capacity, over the range of temperatures encountered. The latter approach was used in this thesis, as described in section 4.4.3

4.4.1 Total Electron-Lattice Coupling

The approximate solution for $G_{El}$ can be found by subtracting the two differential equations comprising the two-temperature model (4.32a and 4.32a) and finding the
characteristic decay time ($\tau_{El}$) for their difference ($T_e - T_l$):

$$\frac{1}{\tau_{El}} = G_{El} \frac{C_E + C_l}{C_E C_l}$$  \hspace{1cm} (4.52)

$$G_{El} = \frac{1}{\tau_{El}} \frac{C_E + C_l}{C_E C_l}$$  \hspace{1cm} (4.53)

$$G_{El} = \frac{1}{\tau_{El}} \frac{(C_e + C_s) C_l}{C_e + C_s + C_l}$$  \hspace{1cm} (4.54)

where the subscript $E$ refers to a combined electron component of the material, as used elsewhere;

$$C_E = C_e + C_s$$  \hspace{1cm} (4.55)

$$T_E = T_e = T_s.$$  \hspace{1cm} (4.56)

This is an approximation based on the assumption of constant heat capacities (which is compensated for in section 4.4.3, and constant coupling constants, which is assumed (and questioned) in these models.

### 4.4.2 Total Electron-Lattice Relaxation Time

The value of $\tau_{El}$ is taken from the electron-lattice relaxation model of Allen[33], introduced in section 3.5.2. This model features a temperature component which can be taken to be that of the electrons, the lattice, or a compromise temperature. It was decided that the appropriate temperature to use would be the equilibrium temperature, denoted by $T_{eq}$ and defined as the temperature of the system at equilibrium, after the pulse. This is determined by the pulse energy $E_p$, the initial temperature $T_0$ and the total heat capacity as a function of temperature $C(T)$:

$$T_{eq} = T_e(t \rightarrow \infty) = T_s(t \rightarrow \infty) = T_l(t \rightarrow \infty)$$  \hspace{1cm} (4.57)

$$E_p = \int_{T_0}^{T_{eq}} C(T) \ dT.$$  \hspace{1cm} (4.58)

Since the antiderivative of the heat capacity is the internal energy $U(T)$:

$$E_p = U(T_{eq}) - U(T_0)$$  \hspace{1cm} (4.59)

$$U(T_{eq}) = U(T_0) + E_p.$$  \hspace{1cm} (4.60)

Since the internal energy function is single valued, an inverse function $U^{-1}$ can be defined, relating the internal energy to the appropriate temperature, and allowing
4.4. Reservoir Coupling Models

the calculation of the equilibrium temperature:

\[ T = U^{-1}(U(T)) \] (4.61)

\[ T_{eq} = U^{-1}(U(T_0) + E_p) \] (4.62)

which then allows an approximation for the combined electron lattice relaxation
time using equation 3.27:

\[ \tau_{El} \approx \frac{2\pi k_B T_{eq}}{3\hbar \lambda_p \omega_D^2}. \] (4.63)

4.4.3 Heat Capacities and Coupling

Also required for the calculation of a constant coupling constant are approximations
for the heat capacities. The heat capacities were approximated as being the mean
of their actual value, over the temperature range of the relaxation. This calculation
is straightforward for the lattice, with the mean heat capacity \( \bar{C}_l \) given by:

\[ \bar{C}_l = \frac{\int_{T_0}^{T_{eq}} C_l(T) \, dT}{T_{eq} - T_0}. \] (4.64)

Calculating an approximation for the electronic heat capacity is not as straightfor-
ward, as the initial temperature from which the electron reservoir relaxes is difficult
to determine. This value was (over) estimated using a similar technique to that
used to determine the equilibrium temperature \( T_{eq} \). The maximum electron tem-
perature \( T_{E\text{Max}} \) was defined as the temperature attained by the combined electron
system \( (T_E) \), if the total energy of the pulse is deposited into it, before any coupling
takes place. This is an overestimate of the maximum temperature obtained. For a
real pulse of finite length, energy and temperature are lost by the electron system
from the beginning of its heating by the laser pulse, rather than the end, as in this
approximation. Denoting \( U_E(T_E) \) as the internal energy of the combined electron
system, as a function of its temperature, and \( U_E^{-1}(U_E) \) as its inverse:

\[ T_{E\text{Max}} = U_E^{-1}(U_E(T_0) + E_p). \] (4.65)

Mean heat capacity values can be determined similarly, reversing the bounds of
integration to produce a positive result:

\[ \bar{C}_E = \frac{\int_{T_{eq}}^{T_{E\text{Max}}} C_E(T) \, dT}{T_E - T_{eq}}. \] (4.66)
which yields a final expression for the combined electron-lattice coupling constant of:

\[ G_{El} \approx \frac{1}{\tau_{El}} \frac{\tilde{C}_E \tilde{C}_l}{C_E + C_l} \]  (4.67)

\[ G_{El} \approx \frac{3h\lambda_D^2}{2\pi k_B T_\text{eq}} \frac{\tilde{C}_E \tilde{C}_l}{C_E + C_l} \]  (4.68)

which is a constant depending only on the initial conditions of the simulation.

### 4.4.4 Reservoir Coupling Constants

It now remains to extend this concept to models with separate electron kinetic and magnetic reservoirs. The only confirmed mechanism involved in ultrafast demagnetisation is an inelastic spin-flip electron-lattice interaction\[4\]. These interactions involve all three reservoirs. Every electron-lattice interaction has a probability \( \alpha_{sf} \) of being a spin-flip interaction. Since each spin-flip interaction requires an energy input of the order of the exchange energy, which is of similar magnitude to a phonon energy, it is assumed that spin flip interactions are perfectly inelastic, *i.e.* that a spin flip interaction transfers energy entirely to the spin system, instead of the lattice. Since this is the only mechanism by which energy can be transferred to and from the spin system, and the mechanism is symmetric, the coupling constants between the spins and electrons, and the spins and the lattice are modelled as equal. The coupling constants are modelled as:

\[ G_{el} = (1 - \alpha_{sf}) G_{El} \]  (4.69)

\[ G_{es} = \alpha_{sf} G_{El} \]  (4.70)

\[ G_{sl} = \alpha_{sf} G_{El} \]  (4.71)

where \( G_{El} \) is the electron-lattice coupling constant in a two-temperature system, as used in section 4.3.1. The parameters together describe a system in which a majority of the energy (assuming \( \alpha_{sf} \leq 1/2 \)) initially in the spin system, transfers from the electrons to the lattice, but a fraction \( \alpha_{sf} \) is temporarily diverted to the spin system.

### 4.5 Heat Capacity Models

The heat capacity models describe the relationship between the internal energy and temperature of the materials, as described in section 3.4. Since the materials used
4.5. Heat Capacity Models

Table 4.6: Calculated values of coupling constants. Larger constants denote stronger coupling and therefore imply shorter relaxation times, although heat capacity also has an effect. \( G_{es} \) and \( G_{sl} \) are modelled as equal for theoretical reasons, as discussed in section 4.4.4 and expressed in equations 4.70 and 4.71.

<table>
<thead>
<tr>
<th>Coupling Constant</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Gd</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_{El} )</td>
<td>9.538</td>
<td>8.605</td>
<td>13.488</td>
<td>0.355</td>
<td>( \times 10^{17} \text{ W} \cdot \text{m}^{-3} \cdot \text{K}^{-1} )</td>
</tr>
<tr>
<td>( G_{el} )</td>
<td>8.395</td>
<td>8.132</td>
<td>11.802</td>
<td>0.248</td>
<td>( \times 10^{17} \text{ W} \cdot \text{m}^{-3} \cdot \text{K}^{-1} )</td>
</tr>
<tr>
<td>( G_{es} )</td>
<td>1.145</td>
<td>0.473</td>
<td>1.686</td>
<td>0.106</td>
<td>( \times 10^{17} \text{ W} \cdot \text{m}^{-3} \cdot \text{K}^{-1} )</td>
</tr>
<tr>
<td>( G_{sl} )</td>
<td>1.145</td>
<td>0.473</td>
<td>1.686</td>
<td>0.106</td>
<td>( \times 10^{17} \text{ W} \cdot \text{m}^{-3} \cdot \text{K}^{-1} )</td>
</tr>
</tbody>
</table>

are solids, their temperature expansion coefficients are small (compared to liquids and especially gases), and therefore the work done by a thermally expanding material is negligible. It is therefore assumed that:

\[
C_P \approx C_V \approx C. \quad (4.72)
\]

In all models the heat capacities are defined as volumetric heat capacities, with units of \( \text{J} \cdot \text{K}^{-1} \cdot \text{m}^{-3} \).

The electronic heat capacity model was taken directly from the literature[30]:

\[
C_e = \gamma T \quad (3.21)
\]

with experimental values of gamma sourced from literature as described in table A.2. As mentioned in section 3.4.2, these experimental values are a rough empirical approximation, as the density of states is quite complex and directly measuring the electronic heat capacity is difficult. Direct measurement is also complicated by the fact that electrons contribute a significant part of total, macroscopic, heat capacity only at low temperatures. At these temperatures, the electron energy distribution, and hence the portion of the density of states available for electrons to occupy, is significantly different to that at room and higher temperatures.

The electronic heat capacity forms a linear and increasing component of the heat capacity. However, except at low temperatures, where the lattice heat capacity is approximately cubic, and the magnetic heat capacity is negligible, it never forms a large component of the total heat capacity of a material. It is however important as the electrons are the only component of the material that the pulse directly interacts with, and the electron heat capacity directly influences the temperature attained by the electron system, and hence the rate of energy transfer to the other systems.

The lattice heat capacity was modelled using the Debye model[30]:

71
Chapter 4. Model Development

\[ C_l(T) = 9Nk_B \left( \frac{T}{T_D} \right)^3 \int_0^{T_D} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \]  
(3.19)

with values for the Debye temperature sourced from literature, as detailed in table A.2, as opposed to calculated from other material parameters. For most solid materials at room temperature, lattice phonons are the main store of internal energy within a material, and this is generally the case in these models. For magnetic materials, this remains true for all temperatures except near the Curie temperature, where the magnetic heat capacity is briefly significant, and even dominant (see figure 4.9).

The spin (magnetic) heat capacity was modelled by relating the stored energy in the magnetisation of the material, to the magnetisation as a function of temperature. This allows an expression to be found connecting the magnetic internal energy and temperature of the material, and therefore a magnetic heat capacity. A dipole of moment \( \mathbf{m} \) in a magnetic field \( \mathbf{B} \) has the potential energy \( u \);

\[ u = -\mathbf{m} \cdot \mathbf{B}. \]  
(4.73)

The dipole moment density in a material is the magnetisation \( \mathbf{M} \). The specific internal energy of a material \( U \), can be obtained from the following relationship;

\[ U = -\frac{1}{2} \int_V \mathbf{M} \cdot \mathbf{B} \, dV \]  
(4.74)

where the factor of \( \frac{1}{2} \) is to avoid double counting the dipole interactions. In the Curie-Weiss model of ferromagnetism, magnetisation is the result of the internal field \( \mathbf{H}_{\text{int}} \). In a saturated ferromagnet, \( \mathbf{M} \) is parallel to \( \mathbf{H} \), therefore;

\[ \mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{H}_{\text{int}}) \]  
(3.4)

\[ U = -\frac{\mu_0}{2} \mathbf{M} \cdot (\mathbf{H} + \mathbf{H}_{\text{int}}) \]  
(4.75)

\[ U = -\frac{\mu_0}{2} \mathbf{M}(H + H_{\text{int}}). \]  
(4.76)

However while the magnetisation is a function of temperature, the strength of the internal field is not, since the thermal energy input required for each dipole to overcome the exchange interaction does not vary with temperature. Therefore, using equation 3.16;

\[ U(T) = -\frac{\mu_0}{2} (\mathbf{H} + \lambda \mathbf{M}(T = 0)) \mathbf{M}(T) \]  
(4.77)

\[ \frac{\partial U}{\partial T} = -\frac{\mu_0}{2} (\mathbf{H} + \lambda \mathbf{M}_0) \frac{\partial \mathbf{M}}{\partial T} \]  
(4.78)
4.5. Heat Capacity Models

\[ C_s = -\frac{\mu_0}{2} \left( H + \lambda M_0 \right) \frac{\partial M}{\partial T}. \]  

The spin heat capacity serves a dual role in the models in which it appears. Firstly it serves the direct role in determining the relationship between the energy and temperature of the spin system, and hence the rate of heat transfer to and from it. The less direct effect is that the magnetic heat capacity determines, along with the magnetisation as a function of temperature, the relationship between the spin system energy and the magnetisation, controlling the degree and rate of demagnetisation. By basing the model directly upon magnetic potential energy, rather than a phenomenological model, conservation of energy can be maintained, neglecting the small portion lost as magnetic dipole radiation.

The heat capacity of the material was taken to be the sum of the three sub-components, as described in section 3.4:

\[ C_{\text{tot}} = C_e + C_s + C_l \]  

\[ C_{\text{tot}} = \gamma T - \frac{\mu_0}{2} \left( H + \lambda M_0 \right) \frac{\partial M}{\partial T} + 9Nk_B \left( \frac{T}{T_D} \right)^3 \int_0^{T_D} \frac{x^4e^x}{(e^x - 1)^2} \, dx. \]  

The heat capacity models are illustrated in figures 4.8 for Nickel and 4.9 for Gadolinium, the materials used experimentally in this thesis. The output of the heat capacity functions, both combined and separately, correspond well to those in literature[43][44], with the exception of the height of the singularity at \( T = T_C \). This is attributed to both experimental difficulties in measuring a near-singularity, and theoretical deficiencies in the mean-field model, which breaks down to an extent at the Curie Temperature.

Due to the large lattice component relative to the electronic component, the heat capacity of Nickel at or above normal temperatures, and away from the Curie temperature is a relatively constant \( 4 \times 10^6 \, \text{J} \cdot \text{m}^{-3} \cdot \text{K}^{-1} \), close to the empirically measured, macroscopic, heat capacity of Nickel. The model also reproduces the doubly-inflected heat capacity curve of Gadolinium, changing from concave up, to down, then up, over the 0 to 200 K range, while remaining quasi-linear over a large scale. This is due to the large magnetic heat capacity, and relatively low lattice heat capacity of Gadolinium, each, in turn, becoming the dominant component over a short range of temperatures.
Figure 4.8: Heat capacity model for Nickel, produced from equation 4.80. The Curie temperature of Nickel at 627 K is clearly visible as the peak in the spin heat capacity.

Figure 4.9: Heat capacity model for Gadolinium, produced from equation 4.80. The Curie temperature of Gadolinium at 292 K is clearly visible as the peak in the spin heat capacity.
4.6 Magnetisation as a Function of Temperature

Starting from the mean-field theory expression for magnetisation as a function of temperature:

\[ M = N g J \mu_B B_J \left( \frac{N g J \mu_B \mu_0 (H + \lambda M)}{k_B T} \right) \]  

substituting the value of \( \lambda \) from equation 3.7 and the experimental value of the saturation magnetisation at 0 K \( (M_0) \), expressed as a function of the experimental atomic magnetic moment:

\[ \lambda = \frac{3k_B T_C}{N g^2 \mu_B^2 \mu_0 J (J + 1)} \]  

\[ M_0 = N \mu_{at} \mu_B \]  

gives the expression:

\[ M(T) = M_0 B_J \left( \frac{M_0 \mu_0 H}{k_B N T} + \frac{3J}{J + 1} \frac{M T_C}{M_0 T} \right) \]  

\[ 0 = B_J \left( \frac{M_0 \mu_0 H}{k_B N T} + \frac{3J}{J + 1} \frac{M T_C}{M_0 T} \right) - \frac{M}{M_0}. \]  

Since this has no closed form solution, the solutions (roots) of equation 4.82 were approximated numerically, from an initial approximation of \( M = M_0 (T_c - T) \).

The applied magnetic field \( (H) \) used experimentally was \( \frac{0.14}{\mu_0} T \), i.e. the H field generated by a 0.14 Tesla B field in free space. Qualitatively this produces the curved transition where \( T \approx T_c \). Having qualitative accuracy when \( T \approx T_c \) is important to help prevent non-physical results arising from discontinuities in the derivatives of \( M(T) \) where complete demagnetisation is predicted.

The magnetisation as a function of temperature models are illustrated in figure 4.10. On close inspection the effect of different values of \( J \) can be seen, with the Magnetisation curve for Ni being rounder (slower demagnetisation initially, faster as \( T \to T_C \)) than the curve for Fe, which has otherwise similar proportions. The main effect of increasing \( H \) is to increase the Magnetisation for \( T > T_C \), removing the sharp corner at \( T = T_C \).

The modelled magnetisation as a function of time curves are produced by numerically solving the magnetisation function (equation 4.81) with the temperature provided by the spin system; \( T_s \) for the three temperature and non-thermal electron models, and \( T_E \) for the two temperature model. The magnetisation predicted by the microscopic three temperature model is taken to be the normalised result given by
Chapter 4. Model Development

Figure 4.10: Magnetisation as a function of temperature for elemental ferromagnets, produced from equation 4.82, with parameters from table A.2. The H field used for the model was $0.14\mu_0T$.

equation 4.51. The difference in the final magnetisation is due to the difference in the magnetisation model used internally by the microscopic three temperature model. The differences between the models are small for low $H$ fields and temperatures, but increase as $T \rightarrow T_C$.

An example of the magnetisation function applied to the ultrafast demagnetisation models is provided in figure 4.11. The curves shown are the predictions of each of the ultrafast demagnetisation models given in section 4.3, with the magnetisation function (equation 4.81) applied to the appropriate temperature component. The magnetisation curve provided for the M3TM is provided directly from the model, and not derived from equation 4.81, but is included here for comparison. The material parameters are for Nickel, and the laser parameters for the laser used by Beaurepaire et al. in their 2004 paper[7]. This provides a virtual recreation of the Beaurepaire et al. experiment.

The deviation of the two temperature model is clear, with both a larger degree of demagnetisation, and a far shorter characteristic time. This is especially relevant when electromagnetic emissions are calculated. As mentioned in their respective sections, the degree of demagnetisation reported in the literature could not be reproduced in the three temperature, and non-thermal electron models, without either the invention (or deduction) of an exclusively electron-spin coupling term, or the modification of the models to support non-thermal style coupling of the spin system. The microscopic three temperature model takes the latter approach, and gives results of similar characteristic time, but more experimentally accurate mag-
4.7 Electromagnetic Emission Model

Figure 4.11: Magnetisation curves produced by each ultrafast demagnetisation model. Calculated using material parameters for Nickel, and laser parameters for the laser used by Beaurepaire et al. in their 2004 paper[7].

nitude, without theoretical contortions. The characteristic times for the latter three demagnetisations are all broadly consistent with literature.

4.7 Electromagnetic Emission Model

Taking equation 3.14c and disregarding the retarded time \((t - r/c \rightarrow t)\), and the vector components, the electric field emitted by the demagnetising sample is given by:

\[
E(t, r, \theta) = \frac{\mu_0}{4\pi c} \frac{\partial^2 M}{\partial t^2} \frac{\sin \theta}{r}
\]

(4.83)

Where \(M\) is the magnetisation function \(M(H, T)\) at equation 4.81, with the \(H\) field a constant of the experiment. The flux density \(S\), is integrated over the whole sphere \(S\), to produce the total power output \(\mathcal{P}\):

\[
S(t, r, \theta) = \frac{1}{\mu_0 c} E(t, r, \theta)^2
\]

\[
\mathcal{P}(t) = \oint_S \frac{1}{\mu_0 c} E(t, r, \theta)^2 \, dS
\]

\[
= \int_0^{2\pi} \int_0^\pi \frac{1}{\mu_0 c} \frac{\mu_0^2}{16\pi^2 c^2} \left( \frac{\partial^2 M}{\partial t^2} \right) \frac{\sin^2 \theta}{r^2} \frac{\sin \theta}{r} d\theta \, d\phi
\]

\[
= \frac{\mu_0}{6\pi c^3} \left( \frac{\partial^2 M}{\partial t^2} \right)
\]

(4.84)
A power spectrum $P(f)$, is then produced, taking care that the Fourier transform is properly scaled to be energy preserving, where the $\mathcal{F}$ operator denotes the (discrete) Fourier transform:

$$E(f) = \mathcal{F}(E(t)) \quad (4.86)$$

$$P(f) = \frac{8\pi}{3\mu_0 c} E(f)^* E(f).$$

Since $E(t)$ is real valued, $E(f)$ is a real valued, even function. Using this property, the power from negative frequencies (which is a meaningless distinction in this context) can be combined with the positive, and the domain restricted to positive frequencies:

$$P(f) = \frac{16\pi}{3\mu_0 c} (E(f))^2 \quad (f \geq 0). \quad (4.87)$$

This value is a power emission density over the simulated time. It is then multiplied by the irradiated volume to produce the power output, then multiplied by the pulse repetition frequency to produce the final power output figure.

The range over which the solutions are solved for is determined by the results required. In order to obtain frequency domain results down to 0.1 THz, the sampling theorem requires that the time domain result be long enough to contain at least a full wavelength, i.e. the span of time domain results must be at least 10 ps. This was typically implemented by beginning that integration at -1 ps and ending at 9 ps. The step size was limited by the requirement of the Fast Fourier Transform algorithm that time domain points be equally spaced, and the need to properly capture a 10 fs long pulse function, the step size was therefore set at 1 fs.

For some results, where resolution in the 0.1-1 THz range was important, the upper limit of the time domain was extended to provide the required resolution. The upper limit of frequency is determined by the time domain step size. A step size of 1 fs gives a maximum frequency of 500 THz, far above what is necessary theoretically, or detectable experimentally.

An example of the electromagnetic emissions component of the models is provided in figures 4.12 and 4.13, showing the time domain signal and power spectra respectively. The curves shown are the predictions of each of the ultrafast demagnetisation models given in section 4.3. The material parameters are for Nickel, and the laser parameters for the laser used by Beaurepaire et al. in their 2004 paper[7].
This provides a virtual recreation of the Beaurepaire et al. experiment.

In figure 4.12, the predictions of the two temperature model are again significantly different from the other models, this time being orders of magnitude greater. The asymmetry in the impulses is due to the faster demagnetisation, then slower remagnetisation, yielding a larger downward spike from the demagnetisation, and a slower upward spike from the remagnetisation.

In figure 4.13, the effects of the direct coupling of the pulse to the spin system are visible here as the two temperature model’s far higher magnitude and frequency emission. The three temperature model has the lowest output, with the otherwise similar non-thermal electron models output being increased due to enhanced pulse-spin coupling during the lifetime of the non-thermal electron population. This also has the effect of increasing the frequency of the emitted radiation, due to the greater rate of spin-temperature, and hence magnetisation, change. This microscopic three temperature model produces output much higher than the three temperature model, but with essentially the same frequency dependence.

### 4.8 Reference Emitter Modelling

In order to calibrate the experimental apparatus, a reference emitter with an independently modelled power output was used, as described in section 5.3. The output
Figure 4.13: Power Spectrum produced by each ultrafast demagnetisation model, with material parameters for Nickel, and laser parameters for the laser used by Beaurepaire et al. in their 2004 paper[7].

of the reference Indium Arsenide emitter was calculated using the Hydrodynamic model. Combining the values of parameters given by Reklaitis[36], with the appropriate laser parameters, the total electromagnetic energy output from the InAs reference emitter $W_{\text{InAs}}$ is given by:

$$W = \frac{\varepsilon^2}{12\pi\varepsilon_0 c^3 \gamma} \eta^2_{\text{exc}} v_t^4$$  \hspace{1cm} (3.38)

$$W_{\text{InAS}} = 2.0405 \times 10^{-13} \text{ J.} \hspace{1cm} (4.88)$$

Due to internal reflection considerations at the surface of the sample, as detailed in section 5.3, only a small proportion (0.0013 from equation 5.9) of the Terahertz radiation generated ever leaves the sample. Therefore the effective conversion efficiency, $\eta$, from pulse energy incident of the sample $W_{\text{pulse}} = 5.3\text{nJ}$, to Terahertz emitted $W_{\text{InAS}}$, is given by:

$$\eta = \frac{W_{\text{InAS}}}{W_{\text{pulse}}} \times 0.0013$$  \hspace{1cm} (4.89)

$$= 4.9736 \times 10^{-8}$$  \hspace{1cm} (4.90)

giving a continuous power output $P_{\text{InAs}}$ of:

$$P_{\text{InAS}} = \eta \ P_{\text{laser}}$$

$$= 1.9894 \times 10^{-8} \text{ W} \hspace{1cm} (4.91)$$
which is consistent with estimates of output power of the order of nanowatts.
Chapter 5

Experimental Methods

In this chapter the experimental apparatus, processes and procedures are described, along with refinements and justifications, culminating in the results predicted, for these experiments, by the models contained in chapter 4.

5.1 Terahertz Time Domain Spectroscopy

The Terahertz Time-Domain Spectroscopy (THz-TDS) system is driven by a 532 nm, 5 W continuous wave laser[45]. This laser drives an optical mode-locking apparatus[46] that converts the 532 nm continuous wave laser light into 790 nm near infra-red (NIR), 10 fs duration pulses, at a pulse repetition frequency of 75 MHz. The ultrafast pulsed laser has much lower continuous wave power (400 mW) than the 532 nm laser, but much higher peak power (within each pulse). The peak power during each pulse reaches 530 kW while the total energy in each pulse is only 5 nJ. The pulses are horizontally polarised. The ultrafast pulses, while referred to as NIR, are still visible as red, due to both the high intensity of the pulses, and the frequency spread of the pulse, as modelled in figure 4.1.

The beam (of pulses) is then split into two parts. A small (< 10%) portion is diverted into a delay line, referred to as the reference beam. The remainder, referred to as the pump beam continues to the optical chopper. The chopper is a perforated disc that is driven to interrupt the beam at a controllable frequency. This frequency is transmitted to the lock-in amplifier and is used to isolate the signal from noise.

For these ultrafast demagnetisation experiments, high fluence (areal pulse energy density) is required. The pump beam was therefore focused onto the sample by a 10 cm focal length lens, mounted on a translating stage. The stage was adjusted to minimise the focal spot diameter, which was estimated as < 100 µm.
Figure 5.1: Diagram of THz-TDS apparatus in the quasireflection geometry. Note that neither the pump beam, nor the emitted THz radiation reach the photodiodes. Detection is achieved by the THz emission modulating the time-delayed reference beam, as they co-propagate in the ZnTe crystal. For clarity, mirrors, irises and polarizing filters which do not effect the laser or Terahertz radiation, and serve only to align the beam, or to reject noise, have been omitted. Also omitted are connections from the chopper lock-in amplifier, providing the amplifier with the chopper frequency, and the control cable from the control computer to the delay stage, which allows the delay to be altered, and the time-domain signal sampled.
5.1. Terahertz Time Domain Spectroscopy

The sample was mounted on an adjustable sample mount with a rare earth magnet, which is rotatable in the sample plane. The magnet strength was measured as 0.14 T. This magnetic field was sufficient to saturate the magnetisation of all of the samples used.

The beam spot (on the sample) is also located at the focus of a set of parabolic mirrors. The mirrors are made of Gold, for infra-red reflectivity and corrosion resistance, are 5 cm in diameter, and have a focal length of 10 cm. Point source Terahertz emissions travel spherically from the illuminated sample to the first parabolic mirror. Between the first and second mirrors, waves travel as planes. The plane wavefronts are then focused by the second mirror to a point used for transmission spectroscopy experiments. In these experiments this space is unused. The third mirror is located at twice the focal length (20 cm) from the second, and takes the now diverging spherical wavefront and reflects it into a plane wave. The fourth mirror takes the plane wave and focuses it into the electro-optic (ZnTe) detector crystal.

Mounted close to the fourth mirror is a small, semi-transparent, flat, diagonal mirror that takes the (NIR) reference beam from the delay line and directs it onto the ZnTe detector crystal. This mirror partially occludes the converging Terahertz wave from the sample.

The electro-optic detector crystal in this instance is a 1 mm thick Zinc Telluride crystal. This crystal exhibits the Pockels Effect; incident lower energy electromagnetic radiation changes the refractive index of the material for higher energy photons. The detector crystal is cut on such an axis, that without incident Terahertz radiation, NIR photons pass through without a change of polarisation, however with incident Terahertz radiation, the polarisation of the NIR beam will be rotated by an amount proportional to the intensity of the incident Terahertz radiation.

In the absence of Terahertz radiation from the sample, the reference beam will emerge from the Electro-Optical crystal still horizontally polarised. The beam then passes through a quarter wave plate, which transforms the horizontally polarised beam into a circularly polarised beam. If the Electro-Optical crystal rotated the polarisation of the reference beam, then after the quarter wave plate, the polarisation will be slightly elliptical rather than circular.

The beam then passes through a Wollaston prism, which separates the circularly polarised beam into two diverging linearly polarised beams. If the polarisation of the beam was circular before entering the prism, the two beams will have equal power. If the incident beam was elliptically polarised before entering the prism, the two linearly polarised beams will carry unequal power.

The beams emerging from the Wollaston prism then are absorbed by a balanced
pair of Silicon photodiodes. These photodiodes are coupled to a pre-amplifier, which amplifies any difference in the current emitted from the photodiodes. This signal is then sent to the lock-in amplifier.

The lock-in amplifier takes the signal from the photodiodes and compares it to the signal from the beam chopper. The amplifier extracts and amplifies the components of the photodiode signal that are modulated at the chopper frequency, removing noise not related to the signal. The signal from the lock-in amplifier is then digitised and sent to the control computer, which records the result.

The control program controls the delay stage through which the reference beam passes. For each delay line step the amplified photodiode signal is integrated (by the Lock-In Amplifier) for a configurable time. During this time, for each ultrafast pulse, electrons produced by the reference beam illuminating each of the photodiodes form a current. The difference between these currents is then sent to the pre-amplifier, then to the lock-in amplifier and recorded. The integration time and delay stage time can be controlled independently. Setting the integration time shorter than the step time is wasteful as signals received go unrecorded. Setting the integration time longer than the step time will cause time domain smearing of the signal, with results from multiple steps being integrated together.

The photodiode current is proportional to the intensity of Terahertz radiation emitted by the sample, and the delay stage position can be converted into a delay time by multiplying by $\frac{2}{c}$, since the time taken is a round trip at the speed of light ($c$). A plot is then produced of photodiode current against the delay time, which is a representation of the Terahertz signal in the time domain. A Fourier transform is then used to convert the time domain signal into a frequency domain signal and power spectrum. The end effect of THz-TDS is to provide a time and frequency domain representation of Terahertz radiation, without the electronic components of the system operating at the frequencies of either the Terahertz radiation, or the ultrafast pulse.

Several components of the system place limits on the range and resolution of detection. The laser pulse duration provides a minimum time domain resolution, and the pulse repetition frequency a minimum frequency domain limit. The Zinc Telluride crystal has an upper limit of its first optical phonon mode, when incident Terahertz radiation will be absorbed, at 5.31 THz\[47\]. Before this limit is reached however, response will be severely diminished due to the mismatch in the group velocity of Terahertz and NIR light in the relatively thick crystal\[38\]. Since the reference pulse must be physically coincident with the Terahertz electric field inside the ZnTe crystal, this group velocity mismatch causes the reference pulse to be ro-
tated by Terahertz radiation from different time delays, smearing the time-domain signal, and equivalently attenuating higher frequencies. For a given EO crystal, the magnitude of the effect is proportional to its width, since the time mismatch increases linearly as the NIR and THz propagate at different speeds through the crystal. There is a tradeoff however since the magnitude of the rotation is also proportional to the time spent in the EO crystal, by the NIR reference pulse, coincident with the THz field. This effect causes thicker EO crystals to have greater sensitivity, but smaller bandwidth.

Several limits of the system are set by the length of the delay stage, with the maximum round trip length being 60 cm, or 20 nanoseconds. Resolution in the time domain is limited by the minimum step size of 7 \( \mu \text{m} \) (14\( \mu \text{m} \) round trip) to 4.8 fs. The time domain limits transfer to frequency domain limits via the sampling theorem, the time domain resolution providing a frequency upper limit, the total path length covered providing the lower frequency limit, and the number of samples taken determining the frequency resolution.

5.2 Samples

Three different samples were used experimentally, in an attempt to capture a cross section of materials and structure. Testing multiple materials also provided an opportunity to identify material or structural dependencies of ultrafast demagnetisation phenomena.

5.2.1 Bulk Nickel

The bulk Nickel sample is 99.98% Nickel. The sample measures 25 \( \times \) 25 \( \times \) 0.5 mm. The tested surface was polished and free of visible marks. Nickel was chosen as a material due to its relatively low Curie Temperature of 631 K[30] and its prominence in the literature of ultrafast demagnetisation. Bulk Nickel has the advantage that the material is isotropic, both magnetically and thermally, in contrast to the thin film sample below. Bulk Nickel was first used by Hohlfield et al. in 1997 confirming the existence of ultrafast demagnetisation by magnetisation-dependent second harmonic generation[18].

5.2.2 Nickel Thin Film

The Nickel thin film sample is composed of Nickel on a crystalline silica (SiO\(_2\)) substrate. The film was created by pulsed laser deposition from a Nickel target, onto
a silica substrate. The sample is polycrystalline, with an axis aligned perpendicular to the substrate. The thickness was measured via optical transmittivity to be $\approx 100$ nm. The thin film differs from the bulk by having an aligned crystal axis, perpendicular to the substrate, but since magnetisation is parallel to the plane of the unaligned axes, the sample will behave as polycrystalline. Thinner Nickel thin films were used by Beaurepaire et al. in the 1996 publication proposing the three temperature model[2] and in the 2004 publication demonstrating Terahertz emission by ultrafast demagnetisation[7].

Thin films often differ from bulk structures in their macroscopic properties. It has be observed that thin ferromagnetic films have lower saturation magnetic moments than thicker films and bulk materials[48]. This effect arises if the film is thinner than 25 Å, which is not the case experimentally. This effect would also have flow on effects to the magnetic (spin) heat capacity, according to the model described in section 4.5.

5.2.3 Bulk Gadolinium

The bulk Gadolinium sample is a 1 mm diameter grain of polycrystalline Gadolinium, embedded in epoxy resin. Gadolinium differs from Nickel by having a much lower Curie temperature, given by various sources as between 290 and 297 K[30], and a much higher atomic dipole moment of 7.63 Bohr magnetons[30]. The effects of the higher dipole moment can be seen by its enormous saturation magnetisation at 0 K (see figure 4.10). Also notable is the magnitude of the magnetocaloric effect in Gadolinium[49] demonstrating a strong connection between the magnetisation, heat capacity and applied magnetic field. Bulk Gadolinium was used by Vaterlaus et al. in the 1991 publication proposing non-equilibrium spin temperatures[1].

5.3 Quantitative Calibration

Before each session of data collection, a sample data set was taken using an Indium Arsenide reference emitter. Detection efficiency was estimated by comparing the theoretical output of the reference emitter with the received signal. This gives an effective efficiency for the detection apparatus. This factor is then applied to the ultrafast demagnetisation measurements. With $S(t)$ representing the power emitted by the sample, $V(t)$ representing the time-domain signal measuring in the experiment, amplified and recorded by the detection apparatus, $g$ being geometrical factors representing the portion of total power emitted that is captured by the
5.3. Quantitative Calibration

apparatus, which may differ between emitters, and \( \eta \) representing the detection efficiency for the THz-TDS apparatus, the calibration procedure is described by:

\[
V_{\text{InAs}}(t) = \eta G_{\text{InAs}} S_{\text{InAs}}(t)
\]

\[
\eta = \frac{1}{g_{\text{InAs}} V_{\text{InAs}}(t)}.
\]

The calibration equation is then:

\[
V_{\text{MD}}(t) = \eta g_{\text{MD}} S_{\text{MD}}(t)
\]

\[
= \frac{g_{\text{MD}} S_{\text{InAs}}(t)}{g_{\text{InAs}} V_{\text{InAs}}(t)} S_{\text{MD}}(t).
\]

\( V_{\text{InAs}}(t) \) is provided by the reference scan, \( S_{\text{InAs}}(t) \) by the hydrodynamic model (3.36), \( g_{\text{InAs}} \) is the geometric factor for an electric dipole perpendicular to the sample plane. \( g_{\text{MD}} \) is the geometric factor for a magnetic dipole, vertical, in the sample plane (perpendicular to the optics table). This allows a relationship between the theoretical model, and the measured result, and for comparisons to be made between them.

The geometric factor can be calculated by considering the dipole radiation pattern. The distribution of power in emitted radiation is the same for both electric and magnetic dipoles (relative to the dipole), where \( P_0 \) is the total power emitted over the sphere:

\[
S(r, \theta, \phi) = \frac{3P_0 \sin^2 \theta}{8\pi r^2}.
\]

(5.1)

However the electric and magnetic dipoles are oriented differently, the electric dipole in the reference InAs sample is perpendicular to the sample plane, whereas the magnetic dipole is oriented vertically in the sample plane (figures 5.2 and 5.3). The parabolic mirror can be modelled as a parabola with the focus at the origin, and a semi-latus rectum \( l \) of 10 cm. This surface is described by the equation:

\[
r = \frac{l}{1 + \cos \theta},
\]

(5.2)

where \( \phi \) does not appear as the parabola is cylindrically symmetric.

While the radiation pattern within the bulk Indium Arsenide is that of an electric dipole, the Terahertz radiation generated by the ultrafast pulse via the photo-Dember effect undergoes refraction at the surface. The refractive index for Indium Arsenide at THz frequencies is \( \approx 3.5 \)[50]. The refraction at the surface is given by Snell’s law, with \( \theta_e \) being the external angle of incidence, \( \theta_i \) the internal angle of
Chapter 5. Experimental Methods

incidence, \( n_{\text{InAs}} = 3.5 \) and \( n_{\text{air}} = 1 \):

\[
\frac{\sin \theta_e}{\sin \theta_i} = \frac{n_{\text{InAs}}}{n_{\text{air}}}
\]

\[
\sin \theta_e = n_{\text{InAs}} \sin \theta_i. \tag{5.4}
\]

This causes most of the radiation produced to be totally internally reflected:

\[
\theta_c = \sin^{-1} \left( \frac{n_{\text{air}}}{n_{\text{InAs}}} \right) \tag{5.5}
\]

\[
\approx 16.6^\circ \tag{5.6}
\]

where \( \theta_c \) is the critical angle of total internal reflection. Therefore the total power that leaves the sample is:

\[
P_{\text{InAs}} = \int_0^{2\pi} \int_0^{\theta_c} \frac{3P_0 \sin^2 \theta}{8\pi r^2} r^2 \sin \theta \, d\theta \, d\phi \tag{5.7}
\]

\[
= \frac{3P_0}{4} \left[ \frac{1}{3} \cos^3 \theta - \cos \theta \right]_{\theta = \theta_c} \tag{5.8}
\]

\[
\approx 0.0013 \cdot P_0. \tag{5.9}
\]

This is only a small fraction of the total power produced.

While these three constructs have simple descriptions in spherical polar coordinates, they are all symmetric about differing axes. A global coordinate system is defined with the origin at the point where the beam intersects the sample, which is also the focus of the parabola. The x-axis points from the sample to the laser. The laser is therefore travelling in the \(-\hat{x}\) direction, the magnetisation is in the \(\hat{z}\) direction, and the parabolic mirrors are in the \(\hat{y}\) direction. By rotating the coordinate systems of the electric dipole and parabolic collector expressions it is possible to align all three coordinate systems, then, by integrating the power over the surface of the parabolic mirror, determine the proportion of each radiation pattern collected.

The Magnetic Dipole equation is already in the proper coordinate system and requires only transformation into Cartesian coordinates:

\[
r \rightarrow \sqrt{x^2 + y^2 + z^2},
\]

\[
\theta \rightarrow \cos^{-1} \left( \frac{z}{r} \right),
\]

\[
\phi \rightarrow \tan^{-1} \left( \frac{y}{x} \right)
\]

substituting these into equation 5.1, leaving \( r \) unconverted where convenient, gives:
5.3. Quantitative Calibration

Figure 5.2: The radiation pattern of a magnetic dipole, oriented in the $\hat{z}$ direction. The section collected by the THz-TDS apparatus is along the $y$-axis, slightly towards the right of the viewer. The normalised powers in this region are $\approx 1$, since on the equator of the radiation pattern, $\theta = \pi/2$, $\sin^2 \theta = 1$.

Figure 5.3: The radiation pattern of a electric dipole, oriented perpendicular the sample plane, with refraction effects. The section collected by the THz-TDS apparatus is along the $y$-axis, slightly towards the right of the viewer. The normalised powers in this region are $\approx 0.005$, since at $45^\circ$ from the pole of the radiation pattern, taking into account the refractive index of Indium Arsenide $n_{\text{InAs}} = 3.5$, $\theta = \pi/(4 \cdot 3.5)$, $\sin^2 \theta = 0.00495$. 
Chapter 5. Experimental Methods

\[ S_{MD} = \frac{3S_0}{8\pi} \frac{1 - \cos^2 \theta}{r^2} \]

\[ S_{MD} = \frac{3S_0}{8\pi} \left( \frac{1}{r^2} - \frac{z^2}{r^4} \right). \]  

(5.10)

The electric dipole is oriented out of the sample plane, along a vector \((-1, 1, 0)\) \(i.e.\) requiring a clockwise rotation of 90 degrees around the vector \((1,1,0)\). In addition the refraction (5.4) must be taken into account. This transformation can be effected by the following substitution, where \(n_{\text{InAs}} = 3.5\) is the refractive index in Indium Arsenide at Terahertz frequencies[50]:

\[
\begin{align*}
x &\rightarrow \frac{1}{2} x - \frac{1}{2} y - \frac{1}{\sqrt{2}} z, \\
y &\rightarrow -\frac{1}{2} x + \frac{1}{2} y - \frac{1}{\sqrt{2}} z, \\
z &\rightarrow \frac{1}{\sqrt{2}} x + \frac{1}{\sqrt{2}} y.
\end{align*}
\]

Simultaneously converting to Cartesian coordinates, leaving \(r\) unconverted where convenient:

\[
\begin{align*}
r &\rightarrow \sqrt{x^2 + y^2 + z^2}, \\
\theta &\rightarrow n_{\text{InAs}} \cos^{-1} \left( \frac{\frac{1}{\sqrt{2}} x + \frac{1}{\sqrt{2}} y}{r} \right), \\
\phi &\rightarrow \tan^{-1} \left( \frac{-\frac{1}{2} x + \frac{1}{2} y - \frac{1}{\sqrt{2}} z}{\frac{1}{2} x - \frac{1}{2} y - \frac{1}{\sqrt{2}} z} \right).
\end{align*}
\]

Then substituting these into equation 5.1:

\[ S_{\text{InAs}} = \frac{3P_0}{8\pi} \frac{1}{r^2} \left( \sin^2 \left( n_{\text{InAs}} \cos^{-1} \left( \frac{\frac{1}{\sqrt{2}} x + \frac{1}{\sqrt{2}} y}{r} \right) \right) \right). \]  

(5.11)

The parabolic mirror requires that its axis of symmetry be rotated from the \(\hat{z}\) direction to the \(-\hat{x}\) direction, \(i.e.\) rotating 90 degrees anticlockwise about the y-axis. This transformation can be effected by the following substitution:

\[
\begin{align*}
x &\rightarrow -z, \\
y &\rightarrow y, \\
z &\rightarrow -x
\end{align*}
\]
Simultaneously converting to Cartesian coordinates, leaving $r$ unconverted where convenient:

\[ r \rightarrow \sqrt{x^2 + y^2 + z^2}, \]
\[ \theta \rightarrow \cos^{-1}\left(\frac{-x}{r}\right), \]
\[ \phi \rightarrow \tan^{-1}\left(\frac{y}{-z}\right). \]

Substituting into equation 5.2:

\[ r = \frac{l}{1 + \left(\frac{z}{l}\right)}, \]
\[ r = l - z, \quad (5.12) \]
\[ y = \sqrt{(l - z)^2 - x^2 - z^2}. \quad (5.13) \]

The extent of the mirror is described by a cylinder about the y-axis of radius $\rho_m$, with the mirror being the portion on the positive y-axis:

\[ \rho_m^2 = x^2 + z^2 \quad \text{for} \quad y > 0. \quad (5.14) \]

For the magnetic dipole, the portion of the radiation pattern collected by the apparatus is given by integrating the power incident upon the mirror surface, over the extent of the mirror:

\[
g_{\text{MD}} = \int_{-\rho_m}^{\rho_m} \int_{-\sqrt{\rho_m^2 - x^2}}^{\sqrt{\rho_m^2 - x^2}} \frac{3P_0}{8\pi} \left(\frac{1}{(l - z)^2} - \frac{z^2}{(l - z)^4}\right) dz \ dx \tag{5.15} \]

and similarly for the electric dipole out of the sample plane:

\[
g_{\text{InAs}} = \int_{-\rho_m}^{\rho_m} \int_{-\sqrt{\rho_m^2 - x^2}}^{\sqrt{\rho_m^2 - x^2}} \frac{3P_0}{8\pi} \frac{1}{(l - z)^2} \left(\sin^2\left(n_{\text{InAs}} \cos^{-1}\left(\frac{1}{\sqrt{2}} x + \sqrt{\frac{(l - z)^2 - x^2 - z^2}{2}} \right)\right)\right) dz \ dx \tag{5.16} \]

In these experiments, the value of $l$ was 10 cm (for a parabolic mirror 10 cm from the source) and the value of $\rho_m$ was 2.5 cm (for a 5 cm diameter mirror).
5.4 Signal to Noise Ratio Improvement

Since the Terahertz emissions being sought were very small, multiple techniques were used to increase the sensitivity of the apparatus. All techniques are based on the principle that when summed actual signals will add linearly, whereas uncorrelated noise will only increase by a factor of $\sqrt{n}$.

5.4.1 Integration Time

Increasing the time-constant of the lock-in amplifier, and increasing the step time for the delay line, has the effect of integrating (exponentially smoothing) the results for each data point over time, averaging each data point over more emitted Terahertz pulses. Since the signal component of the pulse (ideally) does not change from pulse to pulse, these components will increase linearly with integration time. Assuming the background noise is random and uncorrelated, the noise components will only increase as the square root of the integration time. This should increase the signal to noise ratio by a factor of the square root of the integration time. This technique is limited by diminishing returns, and the maximum time the laser could maintain a mode-lock. This was usually a maximum of 8 hours.

5.4.2 Reversal of Magnetic Field Direction

The sign (but not the magnitude) of the emitted signal depends of the direction of the magnetization. Reversing the magnetizing field ($H$) will reverse the magnetisation ($M$), which will reverse the polarity of the signal. Subtracting these signals should produce double the Terahertz signal, but since the random noise signals are uncorrelated (either with the magnetic field, or each other), their magnitude will increase by only $\sqrt{2}$. This also has the effect of cancelling systematic error in the experiment. Denoting the received signals as $V$, the pure Terahertz signal as $T$, the noise as $N$, the systematic error as $E$, with subscripts referring the the direction of the $M$ (and $B$, and $H$) field:

$$V_{up}(t) = T_{up}(t) + N_{up} + E_{up}(t)$$

with the signal to noise ratio given by:

$$\frac{T_{up}}{V_{up} - T_{up}} = \frac{T_{up}}{N_{up} + E_{up}}.$$ (5.17)
5.4. Signal to Noise Ratio Improvement

Similarly for the down direction;

\[ \frac{T_{\text{down}}}{V_{\text{down}} - T_{\text{down}}} = \frac{T_{\text{down}}}{N_{\text{down}} + E_{\text{down}}}. \]

All samples used are magnetically soft, and \( H \) is greater than required to saturate the material. Therefore the magnetization will be a single valued, odd, function of magnetising field;

\[ M(H) = M_0 \]
\[ M(-H) = -M_0. \]

The signal received is proportional to the electromagnetic radiation emitted, which itself is proportional to the second derivative of the magnetisation with respect to time;

\[ T_{\text{up}}(t) \propto \frac{\partial^2 M}{\partial t^2} \]
\[ T_{\text{down}}(t) \propto \frac{\partial^2 (-M)}{\partial t^2} \]
\[ \propto -\frac{\partial^2 (M)}{\partial t^2} \]
\[ = -T_{\text{up}}(t) \]
\[ T_{\text{up}}(t) - T_{\text{down}}(t) = 2T. \quad (5.18) \]

Since \( N \) represents random uncorrelated noise;

\[ N_{\text{up}} \pm N_{\text{down}} = \sqrt{2}N \quad (5.19) \]

and where \( E \) is an additive systematic error, such as a stray voltage or current, it is independent of the magnetisation, therefore

\[ E_{\text{up}} = E_{\text{down}}. \quad (5.20) \]

Subtracting the magnetisation reversed signal will provide a signal to noise ratio improvement of at least \( \sqrt{2} \);

\[ V_{\text{up}} - V_{\text{down}} = 2T + \sqrt{2}N \quad (5.21) \]

\[ \frac{T_{\text{up}}(t) - T_{\text{down}}(t)}{(V_{\text{up}} - V_{\text{down}}) - (T_{\text{up}}(t) - T_{\text{down}}(t))} = \frac{2T}{\sqrt{2}N}. \]
which is a $\sqrt{2}$ improvement in signal to noise ratio, or greater if there is systematic error present.

### 5.4.3 Combination of Multiple Scans

Multiple scans with the same parameters may be combined to produce a similar effect to increasing the time constant, without the difficulty of maintaining mode-locking for long periods of time. This introduces the problem of keeping the experimental conditions totally unchanged between runs. Minor errors in positioning have the effect of changing the position of zero path difference, moving the signals in the time domain. Adding the signals in the time domain would therefore have the effect of smearing out detail.

The alternate approach is to produce a power spectrum from each scan separately, then combine the results together. Since the noise components in the frequency domain are functions of the noise components in the time domain, they are functions of random variables, and therefore random variables, which will, when averaged, decrease as the $\sqrt{N}$. Since the time domain signal both starts and ends with small, inconsequential values i.e noise, windowing before the Fourier transform is not necessary. This is an implementation of the method of averaged periodograms, also known as Bartlett’s method.

### 5.5 Predictions for THz-TDS Experiments

#### 5.5.1 Predicted Demagnetisation

To compare the predictive power of the competing models, predictions of demagnetisation were made for the laser pulse and samples used in the experiments in this thesis. For the Microscopic Three Temperature Model, these predictions are the solution for its explicit magnetisation function (equation 4.47c), for the experimental conditions modelled in these experiments. For the other models the equation 4.81 was used to determine magnetisation as a function of the relevant temperature for the model.

The predictions for the demagnetisation of Nickel are given in figure 5.4. The parameters for the laser are those contained in table 4.2; 10 fs pulses of 5.3 nJ at 790 nm. The material properties are listed in table A.2. The initial temperature was 300 K and the magnetizing field was $0.14/\mu_0$ T. The near vertical drop in magnetisation
5.5. Predictions for THz-TDS Experiments

![Graph showing demagnetization predictions for Nickel.](image)

Figure 5.4: Predicted demagnetisation of Nickel, as predicted by the various models of ultrafast demagnetisation, under the experimental conditions used in this thesis. The 3TM and NTEM predictions are near coincident.

from the two temperature model is due to the direct coupling of the pulse to the demagnetising temperature, this effect is wholly unrealistic and increases as laser pulse durations are reduced from scales near the demagnetisation times of hundreds of femtoseconds, down to ten or less femtoseconds. The predictions of the other models follow those of the example model in figure 4.11, with the timescales of the demagnetisation being similar, but the magnitude of the demagnetisation being roughly double in the modified three temperature model.

The predictions for the demagnetisation of Gadolinium are given in figure 5.5. The parameters for the laser are those contained in table 4.2; 10 fs pulses of 5.3 nJ at 790 nm. The material properties are listed in table A.2. The initial temperature was 300 K and the magnetizing field was $0.14/\mu_0$T. The predictions for Gadolinium are much different to those of Nickel, with Gadolinium undergoing a ferromagnetic to paramagnetic phase transition at approximately the initial temperature, and therefore having a decreasing magnetic heat capacity. For the 2TM, the sample is almost completely demagnetised by heating it nearly to the Curie temperature. The 3TM and NTEM proceed identically, with the curve upward due to the aforementioned decreasing heat capacity, which decreases faster than the rate of heating of the spins by the electrons. The M3TM proceeds similarly, but with a lower degree of demagnetisation, possibly due to differences in the handling of the applied magnetic field, which is an important factor in the magnetisation in the vicinity of $T_C$. 

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Figure 5.5: Predicted demagnetisation of Gadolinium, as predicted by the various models of ultrafast demagnetisation, under the experimental conditions used in this thesis. The 3TM and NTEM predictions are near coincident.

5.5.2 Predicted Electromagnetic Emissions

Based on the predicted demagnetisation curves derived from equation 4.81, and plotted in figures 5.4 and 5.5, the magnetic dipole emissions can be calculated using the magnetic dipole emission equation in section 4.7.

Figure 5.6 show the predicted electromagnetic emissions for Nickel, as predicted by the various models of ultrafast demagnetisation, under the experimental conditions used in this thesis.

The rapid changes in magnetisation from a 10 fs laser can be contrasted with those modelled for a 100 fs laser shown in 4.12. There is asymmetry in the pulses due to the faster demagnetisation than remagnetisation. In the two temperature model, these processes occur at high enough rates for significant emission to occur from remagnetisation, this is not the case in other models. Since the demagnetisation times are exceedingly short, the power spectra are very broad. While difficult to determine on a logarithmic scale, the peak frequencies for the three temperature and modified three temperature models are 4 THz, and 6 THz for the non-thermal model. The frequency peak for the two temperature model is unrealistically high. Predictions of emission magnitude are in broad agreement for the three temperature and non-thermal models and the modified three temperature predictions are an order of magnitude higher, but otherwise similar.

Figure 5.7 shows the predicted electromagnetic emissions for Gadolinium, as predicted by the various models of ultrafast demagnetisation, under the experimental
5.5. Predictions for THz-TDS Experiments

(a) Modelled time domain signal for Nickel, as predicted by the various models of ultrafast demagnetisation, under the experimental conditions used in this thesis.

(b) Modelled power spectrum for Nickel, as predicted by the various models of ultrafast demagnetisation, under the experimental conditions used in this thesis.

Figure 5.6: Predicted results for Nickel samples.
conditions used in this thesis. The asymmetry of the two temperature model pulse (however unrealistic its magnitude) is diminished due to the fact that the change in magnetisation occurs near equally from demagnetisation and remagnetisation. The results for the other models are similar to Nickel, with the exception that the modified three temperature predictions are smaller than those of the three temperature and non-thermal model. Despite the significant differences in the temperature profiles and magnetisation curves, the predicted emissions from Gadolinium are quantitatively and qualitatively similar to those for Nickel, with the exception that the predictions for the modified three temperature model are now lower than the predictions of the non-thermal electron model. That magnitude similarity is likely a coincidence, however the frequency similarity is probably due to effects dependent of the laser.

An interesting difference between the predicted results for both Nickel and Gadolinium, is that the power spectrum for the non-thermal electron model increases at high frequencies for Nickel, but remains essentially equal to the 3TM for Gadolinium.
5.5. Predictions for THz-TDS Experiments

(a) Modelled time domain signal for Gadolinium, as predicted by the various models of ultrafast demagnetisation, under the experimental conditions used in this thesis.

(b) Modelled power spectrum for Gadolinium, as predicted by the various models of ultrafast demagnetisation, under the experimental conditions used in this thesis.

Figure 5.7: Predicted results for Gadolinium samples.
Chapter 6

Results and Discussion

In this chapter the experimental and theoretical results are presented. For each experimental result a brief description of the particular method used, the results, and their implications is provided. For the theoretical results, the implications of the models, taking into account the experimental results are presented and discussed.

6.1 Experimental Results

Each set of experimental results is comprised of a time domain signal as recorded from the lock-in amplifier, and a frequency domain power spectrum, produced from the Fourier transform of the time domain signal. The time domain signal is a recording of the voltage signal produced by the lock-in amplifier, for each path difference step. The signal produced by the lock-in amplifier is derived by extracting those components of the signal from pre-amplifier, which are modulated at the frequency of, and in phase with, the chopper. The signal output by the pre-amplifier is amplified in voltage, but not in current, from the direct signal from the photodiode pair. This is done to allow the ultra-low impedance signal produced by the photodiode to be transmitted via coaxial cable and received by the lock-in amplifier.

The vertical axis of the time-domain results is a representation of the electric field strength incident on the electro-optic detector. While some sort of calibration could be applied to the time domain signal as it is to the frequency domain signal, no useful physical interpretation could be found as there is no notion of the total rate at which an electric field is produced by a sample, except in terms of the power emitted, information which is contained in the power spectrum. Therefore the scale of the vertical axis is arbitrary.
The horizontal axis of the time-domain results is denominated in path difference, expressed in light-picoseconds (i.e. the time distance travelled by light in 1 picosecond; \(\approx 300 \mu m\)). This is a compromise between presenting the result directly as a time difference (i.e. in seconds, representing the reconstructed emitted waveform), which would obfuscate the manner in which the measurements were taken, and giving the results in terms of path length difference, which would interfere with interpreting the results as a time domain representation. The zero point on the axis is arbitrary, as the point of zero path difference is very sensitive to sample placement and optical alignment, and is of no physical significance.

The vertical axis of the frequency domain results are an estimate of the power produced at each frequency. This takes into account both the geometry of the detection apparatus, and the pulse repetition frequency. The detector geometry is significant in that only a small section of the spherical wavefront is collected by the detector, as modelled in section 5.3, and figures 5.2 and 5.3. The pulse repetition frequency is significant in that many pulses are emitted each second, both of light by the NIR laser, and of Terahertz radiation by the emitter. This means that the power output figures for the emitters are directly comparable to the long-term average power output of the laser used (400 mW).

A positive result in the time domain would appear as an impulse or spike, without substantial ringing following. A positive result in the frequency domain would appear as a broad peak (according to the predictions in section 5.5). This wide peak would be hard to distinguish from a uniform rise in the noise floor, however the appearance of water vapour absorption lines in the power spectrum will indicate detection of broadband Terahertz radiation. Table 6.1 lists the absorption lines of water vapour in air at Terahertz Frequencies. The strength of each absorption line is a function of atmospheric humidity and pressure, variables which were not recorded or controlled for, therefore only their locations (in frequency space) can be usefully provided. An indicative result is provided for the reference Indium Arsenide photodember emitter in section 6.1.1. The frequency domain results in figure 6.1b also show the absorption lines of water vapour in air. The raw time domain results are depicted in blue, with other colours being used when the result set contains more than one time domain signal. The time domain results are, when clarity is unaffected, augmented by a smoothed red curve. This curve is the result of the signals convolution with a normalised Gaussian, with a full-width half-maximum of 0.25 ps-c, or 75 \(\mu m\). The width of this convolution is arbitrary as the line is intended only as a guide to the eye.

The raw power spectra are denoted by a thin, blue line. Water vapour absorption
6.1. Experimental Results

Table 6.1: Water Vapour Absorption Lines at Terahertz Frequencies, for frequencies below 2.5 THz. The lines are marked as vertical red lines with the experimental results in this chapter.

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</tbody>
</table>

lines from table 6.1 are added in red. These lines have equal apparent widths of 5 GHz on the plot, slightly larger than in reality (typically $\sim 1$ GHz[53]). An interpolated green curve is added to assist in the analysis of signals with very limited frequency resolution. The interpolated curve is formed by extending the time domain signal with its final value to a length of 10 000 samples (effectively zero-extension, but compensating for the dc offset of the signal). This extended time-domain signal is then processed regularly via Fourier transform. This adds no information to the signal, as the Terahertz emission between pulses is zero, but provides a view of the power spectra that does not include the sharp corners of the original. The interpolated curve appears somewhat asymmetric, with sharper lower peaks than upper peaks. This is an artifact of the logarithmic vertical scale, and on a linear scale the peaks are sinusoidal, as would be expected.

6.1.1 Reference Sample

This is an indicative reference scan of the Indium Arsenide Reference emitter. The actual reference scan was different for each experimental session, however no large differences were encountered. It consisted of 2500 data points taken 0.0480 light picoseconds (14.4 $\mu$m) apart. Each data point was integrated over for 100 ms. The time domain signal is presented in figure 6.1a and a power spectrum in figure 6.1b.

Comparison of local minima in the power spectrum, with the absorption lines presented in table 6.1 shows prominent absorption lines at 0.56, 0.75, 1.1-1.2 and 1.4 Terahertz, as well as a smaller line at 0.9 Terahertz. Also visible on closer inspection are local minima that correspond to Terahertz absorption, even where no signal appears to exist (e.g. 1.5-1.8 THz). This is attributed to a long tail of higher
frequency, broadband, Terahertz radiation emitted, which is of similar magnitude to the background noise. Since a flat broadband signal is hard to distinguish from the noise floor, water vapour absorption lines provide a means by which the presence of a low level, broadband signal can be inferred.

Also notable is the Fabry-Perot interference signal at 191 ps. This impulse is due a potion of the NIR pulse reflecting back, while the rest of the pulse exits the Zinc Telluride crystal, and continues to the waveplate. A portion of the reflected component is similarly reflected from the other side of the crystal and then proceeds normally to the detector. This results in a signal that is delayed by twice the travel time though the crystal. In this case the delay time is $\approx 20$ ps, implying a crystal transit time of 10 ps. The refractive index of Zinc Telluride at 790 nm wavelength is $2.85[54]$, this implies a crystal thickness $d$ of:

$$d = \text{speed} \times \text{time}$$

$$= \frac{c}{2.85} \times \frac{20^{-11}}{2} \text{m}$$

$$= 1.05 \times 10^{-3} \text{m}$$

$$\approx 1 \text{ mm}$$

matching the crystal thickness of 1 mm, with the error likely arising from inaccurate measurement of the delay time.

The total power emitted during this scan is estimated at $1.5303 \times 10^{-16} \text{W}$ and the total power emitted between 0.1 and 5 THz is estimated at $1.5154 \times 10^{-16} \text{W}$. 
(a) Time domain signal from Indium Arsenide. The Terahertz pulse is clearly visible at \(~170\) ps path difference. A secondary pulse due to Fabry-Perot interference is visible at \(~191\) ps path difference.

(b) Power Spectrum from Indium Arsenide. Absorption lines of water vapour in air are clearly visible up to 1.5 THz, where the signal to noise ratio reaches 1. The ripple visible at high amplitude is a frequency domain artifact of the Fabry-Perot signal in the time domain.

Figure 6.1: Reference results from Indium Arsenide.
Chapter 6. Results and Discussion

6.1.2 Bulk Nickel

To test the predictions for bulk Nickel, contained in figure 5.6, a scan was taken of 1600 data points taken 0.0240 light picoseconds (7.2 µm) apart. Each data point was integrated over for 300 ms. The time domain signal is presented in figure 6.2a and a power spectrum in figure 6.2b.

The scan shows a noise floor of $\sim 10^{-22}$ W·THz$^{-1}$. There is a relative low in the frequency domain at $\sim 1$ THz, but it does not appear to be significant.
6.1. Experimental Results

(a) Time domain signal from bulk Nickel. There is a possible signal at 154 ps, however there is no corresponding signal in the power-spectrum, indicating the transient is spurious.

(b) Power spectrum from bulk Nickel. While some minima align with absorption lines, many do not, any present signal has been overpowered by noise.

Figure 6.2: Experimental results from bulk Nickel.
6.1.3 Bulk Gadolinium

To test the predictions for bulk Gadolinium, contained in figure 5.7 a scan was taken of 1600 data points taken 0.0240 light picoseconds (7.2 µm) apart. Each data point was integrated over for 300 ms. The time domain signal is presented in figure 6.3a and a power spectrum in figure 6.3b.

The scan shows a noise floor of $\sim 10^{-22} \text{ W} \cdot \text{THz}^{-1}$, and no discernible signal in either time or frequency domain. This is consistent with the possibility that the Terahertz emission was the result of thermal demagnetisation which may have been essentially complete for Gadolinium at room temperature. ($290 \leq T_c \leq 300$) K for Gadolinium, the same as the air-conditioned room temperature of 20 °C (293 K).
(a) Time domain signal from bulk Gadolinium. A possible signal is evident at 157 ps, however there is no corresponding signal in the power-spectrum, indicating the transient is spurious.

(b) Power spectrum from Bulk Gadolinium. While some minima align with absorption lines, many do not, any present signal has been overpowered by noise.

Figure 6.3: Experimental results from Bulk Gadolinium.
Chapter 6. Results and Discussion

6.1.4 Nickel Thin Film

To test the predictions for thin film Nickel, contained in figure 5.6, a scan was taken of 1300 data points taken 0.0480 light picoseconds (14.4 µm) apart. Each data point was integrated over for 100 ms. The time domain signal is presented in figure 6.4a and a power spectrum in figure 6.4b. The data from this scan is also used in combination with other like sets in section 6.1.5.

The scan shows a noise floor of \( \sim 10^{-21} \text{ W} \cdot \text{THz}^{-1} \). While there are promising candidates for correlations with absorption lines in the power spectrum, there is no likely signal in the time domain. This relative increase in power at low frequency is probably due to the long term drift in the time domain signal.
(a) Time domain signal from Nickel thin film. There is no discernible, probable location for a signal.

(b) Power spectrum from Nickel thin film. While some absorption lines do correlate well, particularly at 0.9 and 1.4 THz, the degree on corelations is not significantly better than random chance.

Figure 6.4: Experimental results from Nickel thin film.
6.1.5 Multiple Scan Combination with Nickel Thin Film

This scan was produced from the combination of seven scans, each with an identical experimental setup. The scans were transformed into frequency space by a Fourier transform and then the mean taken. A power spectrum was then produced from the averaged scan. The time domain signals are presented in figure 6.5a and a power spectrum of their average in figure 6.5b. The first (of the seven) scans was used as the result for thin film Nickel in section 6.1.4.

The average was performed to minimise the effects of long term amplitude drift in the signals, which can be clearly seen in the time domain, and of slight time offsets due to changes in path difference due to experimental error. These effects would obscure a signal if averaging was performed in the time domain, however in the frequency domain, long term drift is converted into aperiodic ($\omega = 0$) signals which are easily disregarded, and time offsets become phase offsets, which are suppressed when converting to a power spectrum.

Each scan consisted of 1300 data points taken 0.0480 light picoseconds apart (14.4 $\mu$m), with each point integrated for 100 ms, with each scan taking 130 seconds.

This scan shows a noise floor of $\sim 10^{-21}$ W · THz$^{-1}$, which is an increase in noise level from previous scans. The summation of 7 results should have provided a decrease in relative noise of:

$$\sqrt{7} \approx 2.645 \approx 10^{0.422}$$

slightly less than half an order of magnitude, however then scans averaged also had the shortest integration times (100 ms) and were therefore the noisiest. The reduction in the apparent noise, without reduction in the magnitude of the signal, supports the concept of low level broadband Terahertz emission, but the absence of water vapour absorption lines makes that unlikely.
6.1. Experimental Results

(a) Time domain signal from multiple scans of Nickel thin film. While all scans are similar, long term drifts and offsets are evident, illustrating the difficulty in maintaining consistent measurements over long time spans.

(b) Power Spectrum from combined multiple scans of Nickel thin film. While the power spectrum is much smoother than other results, the noise floor has not been substantially lowered. While some minima align with absorption lines, many do not, any present signal has been overpowered by noise.

Figure 6.5: Experimental results from combined multiple scans of Nickel thin film.
Chapter 6. Results and Discussion

6.1.6 Magnetisation Reversed Bulk Nickel

This scan was produced from the combination of two similar scans of Nickel thin film. Each scan consisted of 1600 data points taken 0.0240 light picoseconds (7.2 µm) apart. Each data point was integrated over for 300 ms, with each scan taking 8 minutes. The time domain signals are presented in figure 6.6a and a power spectrum of their difference in figure 6.6b.

One scan was taken with the the magnet in a South pole up (H up) position, and the other in a North pole up (H down) position. The first scan was then subtracted from the second, and then the difference scan was processed normally. The purpose of this was to attempt to cancel error while increasing the strength of the signal. Reversing the magnet (and therefore magnetisation and demagnetisation) direction changes the polarity of the emitted signal, taking the difference of these signals should yield a signal of twice the magnitude, while cancelling or reducing errors. Since this operation is performed in the time-domain however, the possibility of the time domain signals blurring due to path difference drift cannot be excluded.

This scan shows a noise floor of \( \sim 10^{-22} \text{ W} \cdot \text{THz}^{-1} \). The magnetisation reversal technique should have increased the signal to noise ratio by a factor of \( \sqrt{2} \).

The time-domain signals at 146 ps are promising, having the same duration and magnitude, but opposite sign, precisely as expected. Unfortunately this is not reflected in the power spectrum, with the correlation between power minima and water vapour peaks remaining poor.
6.1. Experimental Results

(a) Time domain signals from magnetisation-reversed bulk Nickel. The smoothed signals are provided in light blue and green to associate them with their respective raw signal. A probable signal is visible at 146 ps, being a peak visible in both signals, with similar shape, but inverted magnitude, as would be expected from the magnetisation reversal (see section 5.4.2).

(b) Power spectrum for magnetisation-reversed difference signal from bulk Nickel. The degree of correlation between minima in the signal and absorption lines is better than the previous experiments (figures 6.2 and 6.3). There is still no signal visible over the background noise however.

Figure 6.6: Experimental results from magnetisation reversal of bulk Nickel.
Chapter 6. Results and Discussion

6.1.7 Long Duration Nickel Thin Film

In an effort to increase the signal to noise ratio, the integration time of each data point was increased drastically, from 300 ms to 10 s, a 33 fold increase, with the aim to produce a $\sqrt{33} \approx 3.7$ fold decrease in the amplitude noise. This had the obvious side effect of a large increase in the time taken to scan over a given path length, which also exposed the time domain signal to drifts due to diurnal variations such as temperature, air pressure, sunlight angles and levels and building vibrations. While controls are implemented for all of these variations, none of them are perfect. The time domain signals are presented in figure 6.7a and their combined power spectrum in figure 6.7b.

The power spectrum is the combination 2 separate scans. Each scan was taken of thin-film Nickel. They consisted of 1400 data points taken 0.0048 light picoseconds (1.44 $\mu$m) apart. Each data point was integrated over for 10 s, with each scan therefore taking nearly four hours. The limitation on the length of these scans was the propensity of the laser to fall out of mode lock after a period of several hours. This occurred in the second scan slightly after the 1400th data point, therefore the data set was truncated there. The first scan originally consisted of 1500 data points but was truncated to 1400 prior to data processing so that the two scans could be directly compared, since differing numbers of points in the time-domain series would have produced differently spaced frequency domain points (as a result of the fast Fourier transform algorithm), greatly complicating the analysis.

This scan shows a noise floor of $\sim 10^{-22}$ W · THz$^{-1}$. There is a possible signal in the area of 0.5 - 2 THz, with local minima in this range showing reasonable correlation with water vapour absorption lines. While it is possible that a THz signal lies in this area, the combination of low noise (requiring long integration times) and high frequency resolution (requiring large path differences) could not be obtained due to experimental limitations.
6.1. Experimental Results

(a) Terahertz emission from long duration scans with Nickel thin film. Large deviations can be seen at ∼172 ps, however they do not precisely correlate between the scans. These spikes have a width of the order of 100s of fs which is inconsistent with the predictions of the two-temperature model, but broadly consistent with the others.

(b) Power spectrum from long duration scans with Nickel thin film. Poor frequency resolution is due to the short path difference covered by the scan, however a prominent local minima is visible at ∼0.75 THz. Correlation with individual absorption lines are difficult due to the poor frequency resolution.

Figure 6.7: Experimental results from long duration scans with Nickel thin film.
6.1.8 Congruence of Models with Results

While no certain detection of Terahertz was made, it is likely that the absorption lines indicate that a broadband Terahertz signal, with an amplitude of the same magnitude as the noise was present. While this makes detailed examination difficult, it does allow for reasonably rigorous upper limits to be determined on the Terahertz power emitted, with the expectation that the actual result was within an order of magnitude below that.

While the models produced similar predictions for experimental conditions, and for the conditions of the Beaurepaire et al. 2004 experiment (compare figures 5.6 and 4.13), the results produced were markedly different. The principal source of the difference was the much greater level of noise in the experimental results than those of Beaurepaire et al. (compare figures 6.7 and 2.9). This can be accounted for by considering the effects of noise and the pulse repetition frequency. While the predictions of Terahertz power output were similar (excepting those of the Two-Temperature Model), the Beaurepaire et al. 2004 results were produced from a laser with a pulse frequency of 5 kHz, in contrast to the 75 MHz used here experimentally. Considering each time domain data point as the sum of a number of ultrafast demagnetisation events, the Terahertz signals sum linearly with the pulse repetition frequency, while the random noise would sum as the square root of the pulse repetition frequency (analogously to the technique described in section 5.4.3). If the noise received by both apparatus is assumed as equal, the higher pulse frequency experimental results would feature a noise level \( \sqrt{15000} \approx 122.5 \approx 10^2 \) times higher, for the same signal level. This is an increase in the noise floor, and decrease in the signal to noise ratio of 2 orders of magnitude, which accounts for the difficulty experienced in signal detection.

The signal to noise ratio of the signal reported by Beaurepaire et al., in figure 2.9, is of the order of \( 10^1 \). The effect of higher pulse repetition frequencies on noise would have completely swamped any signal, leaving a signal to noise ratio of the order of \( 10^{-1} \). This implies that with the laser used in this experiment, the detection apparatus would have experienced similar difficulties in detecting any signal. Similarly with the laser used by Beaurepaire et al., a \( 10^2 \) improvement in the signal to noise ratio could be expected from the detection apparatus used experimentally. This is much greater than the effect of any experimental technique used to increase SNR in this thesis. Since no definitive signal was detected, the magnitude of the signal that would have been received by the detection apparatus used experimentally cannot be calculated. If it is assumed however, that the upper bound of \( \sim 10^{-22} \text{ W} \cdot \text{THz}^{-1} \) represents a signal with an SNR of the order of 1, improvements by the use of the
Beaurepaire *et al.* laser would result in a detected signal of $\sim 10^{-20} \text{ W} \cdot \text{THz}^{-1}$. A regular scan, featuring a noise floor of $\sim 10^{-21} \text{ W} \cdot \text{THz}^{-1}$, as shown in figure 6.1a, would then yield a similar result to that of Beaurepaire *et al.*, shown in figure 2.9.

### 6.1.9 Evaluation of Models

By comparing the predictions illustrated in section 5.5 to the results in section 6.1, the most appropriate model appears to be the Microscopic Three Temperature Model. While its predictions are not greatly different, its agreement (with the parameters used in this thesis) with results from the literature is better. In addition its predictions of relatively lower output for Gadolinium, and relatively higher output for Nickel, are more consistent (i.e. farther within the error bounds) with the experimental results.

The Two Temperature Model produces clearly different predictions to the other models (see figures 5.6 and 5.7). These predictions are inconsistent with the experimental results observed. It also has theoretical difficulties in accounting for transfers of angular momentum, discussed in section 4.3.1 and elsewhere by Zhang *et al.*[10] amongst others. In combination, these are sufficient to state that the Two Temperature Model cannot properly describe Terahertz production via Ultrafast Demagnetisation.

The Three Temperature Model and Non-Thermal Electron Model are similar in their structure (see sections 4.3.2 and 4.3.3) and predictions (see figure 5.5). The extension of the Non-Thermal Electron model to include enhanced coupling of non-thermal electrons both to the spin reservoir and the lattice has good theoretical and experimental basis[14][4], however the effect of this extension is relatively small, and the predictions for both models are consistent with the results observed, i.e. they are both below the noise floor. It is therefore not possible to determine whether the extension of the Three Temperature Model to include non-thermal components is necessary, sufficient or warranted. Both models are however theoretically plausible and consistent with experiment, and as such remain viable explanations of Terahertz production via Ultrafast Demagnetisation.

A shared issue of both the Three Temperature Model and Non-Thermal Electron Model is that there is no evidence that the spin reservoir should, or should not, be treated thermally. Conduction-band electrons and lattice phonons are identical (quasi)-particles, with semi-continuous energy distributions, and can be certainly treated thermally. The spin reservoir, as a two-level system of identical particles, can also be treated thermally, and said to have a temperature. There is no direct evidence however, that the spin system is coupled thermally to the electrons and
lattice, i.e. it is not certain that energy transfer between systems is proportional to their temperature difference. The Microscopic Three Temperature Model addresses this concern by removing the notion of the spin reservoir as a thermal reservoir, and directly modelling the magnetisation. This allows for a (mathematically) arbitrary coupling to either be curve-fit to results, or derived from another theoretical mechanism. This practical advantage, along with the slightly better fit to experimental results, is the basis for the selection of the Microscopic Three Temperature Model as the preferred model.

6.2 Theoretical Results

Since the Microscopic Three Temperature Model was judged to be the most appropriate of the models examined, and Nickel was the main material tested in this thesis, as well as the primary material found in literature, simulations were performed using the Microscopic Three Temperature Model on Nickel, using the focused laser used in this experiment.

The aim of these simulations was to estimate the effects of adjustable parameters on the modelled, and ideally experimental outcomes, with a view to maximising the utility of ultrafast demagnetisation as a Terahertz source. In the practical world, most design decisions are tradeoffs between a number of partially exclusive parameters, and while it is easy to decide that more power in should produce more power out, it is more useful to look at how the system can be optimised. Therefore simulations undertaken involve deducing the dependence of EM output, primarily Terahertz output between 0.1 and 5 THz, on pairs of linked parameters.

6.2.1 Pulse Duration Effects

It can be seen by comparing the predictions of these experiments (figure 5.6), to the simulations with the laser used by Beaurepaire et al. in 2004[7] (figure 4.13), that pulse duration has a (loosely) inverse relationship to the peak frequency emitted. Simulating a series of experiments with the laser parameters used experimentally on a Nickel sample, the (modelled) effect of changing the pulse duration, while maintaining the pulse energy (simulating dispersion) can be examined.

This set of simulations involved increasing the laser pulse duration \( t_p \) from 10 fs to 100 fs, the typical spread of laser pulses used experimentally, in steps of 10 fs. This was done while maintaining pulse energy \( W_p \), and therefore reducing the pulse
power $P_p$ by a factor of 10 over the set of simulations. These are plotted in figure 6.8, and described by:

$$P_{tp}(f) = P(tp, P_p, f)$$  \hspace{1cm} (6.5)$$

with the pulse energy $W_p$ held constant;

$$tpP_p = W_p = 5.33 \times 10^{-9} \text{ J.}$$  \hspace{1cm} (6.6)$$

Each curve in figure 6.8 represents the power spectrum produced from the M3TM

Figure 6.8: Modelled effects of pulse dispersion on ultrafast demagnetisation. The uppermost spectrum is modelled on a 10 fs pulse, with each spectrum beneath being 10 fs longer than the one above. Each pulse has the same energy, therefore longer pulses have lower pulse power. The frequency peak decreases noticeably from $\approx 4$ to $\approx 1.5$ THz, as the pulses lengthen, the rate being greatest at lower pulse durations. While for shorter pulse durations most of the power is emitted at higher frequencies, a decrease in pulse duration never results in a decrease in power at any frequency.

for a particular pulse duration. It can be clearly seen that stretching or compressing a pulse, without otherwise changing its energy, has a large effect on the magnitude, shape and peak frequency of the power spectrum. While shorter pulses produce higher peak frequencies, they also produce more power at every frequency. This is analogous to spectrum of black body radiation, where higher temperatures produce peak emission at higher frequencies, but also continue to increase emission at all frequencies.
Chapter 6. Results and Discussion

To estimate the efficiency changes as a result of the changing pulse duration, each power spectrum $P_{tp}(f)$ was integrated over all frequencies, producing an estimate of the power output. This is plotted as figure 6.9a, and described by:

$$P_{EM}(t_p) = \int_0^\infty P(t_p, P_p, f) \, df$$

(6.7)

with the pulse energy $W_p$ held constant, as described by equation 6.6. Restricting the integration domain to the broader Terahertz region defined as 0.1 to 5 THz, produces figure 6.9b, described by:

$$P_{THz}(t_p) = \int_{0.1 \, \text{THz}}^{5 \, \text{THz}} P(t_p, P_p, f) \, df$$

(6.8)

again with the pulse energy $W_p$ held constant, as described by equation 6.6. The gradient of the line fit in figure 6.9a is -1.069, on a log-log. This gradient of $\approx 1$ implies that the total power emitted is inversely proportional to the pulse duration;

$$P_{EM} \propto \frac{1}{t_p}.$$  

(6.9)

This relationship cannot hold in reality for all pulse durations however, as the power emitted ($P_{EM}$) cannot exceed the laser power input ($p$) unless there is another source of energy not as yet identified (and which the model does not contain, and therefore cannot be reflected here). The relationship also contrasts strongly with the Terahertz power emitted, as shown by figure 6.9b. While this relationship is linear, it is on a linear scale, with gradient $-5.3 \times 10^{-24}$. Diminishing returns from the reduction of pulse duration are also evident at the lower end of the pulse durations. These results differ from those in figure 6.9a as a result of the moving frequency peak. While for every frequency, shorter pulse durations produce more power, the vast majority of this increase is produced at higher frequencies (hence shifting the emission peak). This reduces the effect of shorter pulses on Terahertz emission from hyperbolic, as it is for the full spectrum, to linear, with even the linear trend failing at pulse durations shorter than 10 fs. Disregarding this diminishing return, the relationship between Terahertz power emitted, $P_{THz}$ and pulse duration, $t_p$, for constant pulse energy, predicted by the M3TM is;

$$P_{THz} \propto -t_p$$

(6.10)

$$P_{THz} = at_p + b$$

(6.11)

where,
6.2. Theoretical Results

(a) Modelled relationship between pulse duration and emitted electromagnetic power. The circles are the results of integrating the previous power spectra (figure 6.8) over all frequencies. The line is a least squares fit, noting the log-log scale.

(b) Modelled relationship between pulse duration and emitted power for Terahertz (0.1-5 THz) frequencies. The circles are the results of integrating the previous power spectra (figure 6.8) over Terahertz frequencies. The line is a least squares fit.

Figure 6.9: Modelled relationship between pulse duration and emitted power.
This trend can be seen to be already failing by 10 fs pulse durations. The relationship must also diverge asymptotically at long pulse durations, as negative power emission is not physically meaningful in this context.

### 6.2.2 Pulse Focus Effects

Unlike the pulse energy or pulse duration, focusing of the pulse can be performed quickly and easily using a lens. Focusing the pulse reduces the irradiated volume, but increases the energy density (fluence) and power density (flux) of the pulse. While the power emitted by the more densely irradiated volume will be higher, the total power emitted is integrated over the irradiated volume, and so presents a decreasing factor.

In this comparison, the beam diameter $D$ was decreased from 2000 µm to 20 µm, in logarithmically spaced steps, while holding the pulse energy $W_p$ constant, therefore reducing the pulse energy density (fluence) $W_p/A$, from 16.975 J·m$^{-2}$ to $1.6975 \times 10^{-3}$ J·m$^{-2}$. Each power spectrum is reproduced in figure 6.10 and described by:

$$P_D(f) = P\left(D, \frac{W_p}{A}, f\right)$$

(6.14)

with $d$ the (constant) penetration depth and with the pulse energy $W_p$ held constant;

$$\pi \left(\frac{D}{2}\right)^2 d \cdot \frac{W_p}{A} = W_p = 5.33 \times 10^{-9} \text{ J.}$$

(6.15)

Each curve on figure 6.10 represents a power spectrum produced for a given beam diameter, but with the beam power density adjusted, so as to give the same beam power for all curves, effectively losslessly focusing the laser. It is clear from the even spacing of the curves that the frequency of radiation emitted from ultrafast demagnetisation does not depend on the long-term average power of the laser (in general, barring possible effects due to complete demagnetisation at high powers). The salient point however is that for all lines, the input power is the same, but the outputs still increase with greater focus. This shows that the ultrafast demagnetisation process is more efficient with more focused lasers. This relationship is examined and quantified below.
6.2. Theoretical Results

Figure 6.10: Modelled effects of laser focusing on ultrafast demagnetisation. The power spectrum for 2000 µm beam width, is the smallest, and 20 µm the largest. A 100 fold decrease in beam diameter leads to a greater than 100 fold increase in spectral power density.

To estimate the efficiency changes as a result of the changing beam diameter, each power spectrum $P_D(f)$ (as featured in figure 6.10) was integrated over all frequencies, producing an estimate of the energy output for each pulse. This is plotted as figure 6.11a, and described by:

$$P_{EM}(D) = \int_0^\infty P(D, f) \, df$$

with the pulse energy held constant, as described by equation 6.15. Restricting the integration domain to the broader Terahertz region, defined here as 0.1 to 5 THz, produces figure 6.11b, described by:

$$P_{THz}(D) = \int_{0.1 \, \text{THz}}^{5 \, \text{THz}} P(D, f) \, df$$

also with the pulse energy held constant, as described by equation 6.15. These results are plotted on a log-log scale in figure 6.11b. In both subfigures, a line is fit, and the gradient of this line used as the basis for a monomial approximation of the dependence of electromagnetic emission, from ultrafast demagnetisation, as a function of laser power density. The gradient of the line in figure 6.11a is -2.052 and the gradient of the line in figure 6.11a is -2.153. The similarity in these gradients is a reflection of the similarities between the power spectra from figure 6.10. These gradients imply that the relationships between Terahertz power emitted, $P_{THz}$, beam...
(a) Modelled relationship between laser focus and emitted electromagnetic power. The circles are the results of integrating the previous power spectra (figure 6.10) over all frequencies. The line is a least-squares fit.

(b) Modelled relationship between laser focus and emitted Terahertz power. The circles are the results of integrating the previous power spectra (figure 6.10) from 0.1 to 5 THz. The line is a least-squares fit.

Figure 6.11: Modelled relationship between laser focus and emitted energy per pulse.
6.2. Theoretical Results

diameter (for constant pulse energy), $D$, and pulse energy density, $W/A$, as predicted by the M3TM, can be approximated by;

\begin{align}
P_{\text{THz}} & \propto \frac{1}{D^2} \\
\text{(6.18)} \\
P_{\text{THz}} & \propto \frac{1}{A}. \\
\text{(6.19)}
\end{align}

Since the long-term average power is kept constant, by virtue of the pulse energy and pulse repetition frequency being kept constant, equation 6.19 shows that the efficiency of Terahertz production is inversely proportional to the area of the beam. This provides an avenue for increasing the efficiency of ultrafast demagnetisation by focusing the beam, and therefore increasing the pulse energy density. The limits to this process are explored in section 6.2.3.

6.2.3 Pulse Energy Effects

The use of ultrafast laser amplifiers allows high repetition frequency, low pulse energy beams, to be converted into lower repetition frequency, higher pulse energy beams. To examine the effectiveness of amplification or pulse coalescing of ultrafast pulsed lasers on ultrafast demagnetisation as a Terahertz source, a simulated comparison between high repetition frequency, low pulse energy beams, and low pulse repetition frequency, high pulse energy beams was made. This does not however take into account the effect of noise on signal detection, as the modelling of detector noise is beyond the scope of the models.

In this comparison the pulse energy $W_p$ was increased from 5 nJ to 5 mJ, in exponentially spaced steps, while holding the long-term average power $p$ constant, and therefore reducing the pulse repetition frequency $f_p$, from 75 MHz to 75 kHz. In order to compensate for the decreased number of pulses, care was taken to ensure the power spectrum was multiplied by the appropriate pulse repetition frequency. Each power spectrum is reproduced in figure 6.8, and described by:

\begin{align}
P_W(f) &= f_p \cdot P(W_p, f_p, f) \\
\text{(6.20)}
\end{align}

with the long-term average power $p$, held constant;

\begin{align}
W_p f_p &= p = 4 \times 10^{-1} \text{ W}. \\
\text{(6.21)}
\end{align}

Each curve in figure 6.12 shows the power spectrum from a different pulse energy, but with the pulse repetition frequency adjusted to maintain the long-term average
Chapter 6. Results and Discussion

Figure 6.12: Modelled effects of pulse energy on ultrafast demagnetisation. Input pulse energies decrease from 100 nJ to 5 nJ in steps of 5 nJ, while the pulse repetition frequency was reduced, so as to keep long-term average power constant. Linear increases in pulse energy (but constant long-term average power) lead to sub-linear increases in emitted power density. This effect is more easily visible in figures 6.13a and 6.13b.

To estimate the efficiency changes as a result of exchanging pulse energy for pulse repetition frequency, each power spectrum $P_W(f)$ was integrated over all frequencies, producing an estimate of the energy output for each pulse. This is plotted as figure 6.13a, and described by:

$$P_{EM}(W_p) = \int_0^\infty P(W_p, f_p, f) \, df$$

(6.22)

with the long-term average power $p$, held constant, as described by equation 6.21. Restricting the integration domain to the broader Terahertz region defined as 0.1 to 5 THz, produces figure 6.13b, described by:

$$P_{THz}(W_p) = \int_{0.1 \text{ THz}}^{5 \text{ THz}} P(W_p, f_p, f) \, df$$

(6.23)

again with the long-term average power $p$, held constant, as described by equation 6.21. Both plots in figure 6.13 display very similar characteristics. The log-log...
6.2. Theoretical Results

(a) Modelled relationship between pulse energy and emitted electromagnetic power. The circles are the results of integrating the previous power spectra (figure 6.12) over all frequencies. The line is a least-squares quadratic curve fit, on a log-log scale.

Figure 6.13: Modelled relationship between pulse energy and emitted power.

(b) Modelled relationship between pulse energy and emitted power for Terahertz frequencies. The circles are the results of integrating the previous power spectra (figure 6.12) from 0.1 to 5 THz frequencies. The line is a least-squares quadratic curve fit, on a log-log scale.

Figure 6.13: Modelled relationship between pulse energy and emitted power.
Chapter 6. Results and Discussion

A quadratic trend is complex to analyse, and has little real significance, as there is no realistic prospect of the other (decreasing) half of the parabola being valid. Notable is the near flatness of the curve for the highest energy pulses showing little effect from increased pulse energies, consistent with the material being completely demagnetised for the higher pulse energies. At the limit of low pulse energies, the gradient is approximately 1 (on a log-log scale) implying a linear relationship between pulse energy, and hence energy density and power output. This is consistent with the results derived in section 6.2.2. Since the long-term average power input has been kept constant, the increase in power from larger pulses also represents an increase in Terahertz production efficiency.

6.2.4 Material and Temperature

In an effort to optimise the production of Terahertz radiation via ultrafast demagnetisation, the selection of materials and conditions must be considered. Taking each elemental ferromagnet, and plotting the modelled energy output as a function of the initial temperature, figure 6.14a is produced. The curves produced are described by:

\[
P_{EM}(T_0) = \int_{0}^{\infty} P(f, T_0) \, df
\]  

with \( P_{EM} \) representing the emitted electromagnetic power, and \( T_0 \) representing the initial temperature and temperature of the outside environment. Restricting the radiation considered the greater Terahertz region, defined as 0.1 THz to 5 THz, figure 6.14b is produced, and described by:

\[
P_{THz}(T_0) = \int_{0.1 \, \text{THz}}^{5 \, \text{THz}} P(f, T_0) \, df.  
\]  

The curves for total EM radiation and Terahertz radiation are very similar for each material, differing only in their magnitude. This reflects the shape (but not the magnitude) of the power spectrum being unaffected by the initial temperature (or material), and depending primarily on the pulse durations (see figure 6.10). The curves for each material are also similar, differing only in magnitude, and the location of their peak. Each curve rises smoothly to a peak, somewhat below its Curie temperature, then decreases sharply, dropping to zero at the Curie temperature. This is due to output being maximised when a pulse completely demagnetises a sample, but provide no further energy. Once the sample has been demagnetised, extra energy input is wasted. For any pulse, output is maximised by producing the
6.2. Theoretical Results

(a) Modelled comparison of EM energy output between elemental ferromagnets as a function of initial temperature. The curves finish where the initial temperature reaches the Curie temperature for the material and the power output drops to zero, and becomes undefined on a logarithmic scale.

(b) Modelled comparison of Terahertz energy output between elemental ferromagnets as a function of initial temperature. The curves finish where the initial temperature reaches the Curie temperature for the material and the power output drops to zero, and becomes undefined on a logarithmic scale.

Figure 6.14: Modelled comparisons of ultrafast demagnetisation as a function of initial temperature between elemental ferromagnets.
greatest change in magnetisation possible. Examining the models of magnetisation as a function of energy, as seen in figure 4.10, the greatest change in magnetisation is present in the temperature range just below the Curie temperature. While the heat capacity of a magnetic material also peaks at the Curie temperature, the taking up of energy by the spin-system is a goal, not an impediment. Combining these effects, it can be seen that change in magnetisation in maximised when the material is heated such that it is completely demagnetised, but no further. This effect leads to the peak output being below the Curie temperature, by an amount dependent on the pulse energy. This can be illustrated by plotting the data from figure 6.14b with the x-axis in units of the materials Curie Temperature. This is shown in figure 6.15. The curves differ primarily in their magnitude, but differences are visible in the precise location of the peak output temperature.

![Figure 6.15: Modelled comparison of Terahertz energy output between elemental ferromagnets as a function of initial temperature in units of Curie temperature. Peak output for the modelled laser is achieved at temperatures of \( \approx 0.8T_c \).](image)

### 6.2.5 Optimising Terahertz Output

By examination of the predictions of the M3TM, a number of means of optimising the Terahertz production from ultrafast magnetisation processes have been identified. The material best suited to the production of Terahertz radiation was Gadolinium, due to its high magnetic moment per atom, lower heat capacity, and low Curie temperature. The initial temperature would best be adjusted so that the peak spin-temperature achieved equals the Curie temperature, or in the case of the
M3TM, the electron temperature is maintained long enough to achieve complete demagnetisation. For Gadolinium this may be problematic as this requires an initial temperature significantly below room temperature. As an alternative, Nickel may be used at moderate temperatures, and Iron at higher temperatures, but with an order of magnitude loss of output.

For laser selection, optimal Terahertz output is achieved once again when complete demagnetisation is reached. Once the sample is demagnetised, greater input of energy from laser pulses are wasted, and may lead to sample damage[2]. Pulse duration has a significant effect on the frequency of the output radiation, with shorter pulse durations producing higher frequency radiation, but still providing an output enhancing effect.

While higher pulse repetition frequencies contributed to low signal to noise ratios in the experiments, this is a shortcoming of the detection system and does not reflect a fundamental limitation. Conversely, when limited by complete demagnetisation, a higher pulse repetition frequency will allow Terahertz emitting demagnetisation cycles to occur at a higher rate, increasing output. This effect is limited by the time required for the material to remagnetise, which is itself a function of the ability of the bulk of the material to conduct away the heat delivered by the laser pulse. Another related limit is once again the prospect of sample damage at high fluence, as raised by Beaurepaire et al.[2]. While the source of this damage was not isolated, the relevant experiment used low pulse repetition frequency, high fluence pulses, with a (very) thin film sample, on an insulating substrate. These conditions combine to cause a worst-case scenario of both high peak temperatures, and low thermal conductivity, leading to high equilibrium temperatures.
Chapter 7

Conclusions

In regards to the objective of obtaining quantitative models and measurements of Terahertz emission by ultrafast demagnetisation, significant progress was made in creating models and inferring a physical basis for otherwise phenomenological parameters. The quasi-null result provides only an upper limit on the Terahertz radiation produced through ultrafast demagnetisation but that is still sufficient to contradict the predictions made by all versions of the Two Temperature Model. In addition this upper limit is quite close to the predictions made by the remaining models.

In regards to quantifying the production of Terahertz radiation from ultrafast demagnetisation using lower energy, shorter, ultrafast pulses, the experiment was only partially successful. While further techniques may have been able to increase the signal to noise ratio, it appears that while pulse energy density is the key factor in achieving demagnetisation, high pulse repetition frequencies cannot fully compensate for this, due to cumulative noise effects. Furthermore the detection of Terahertz radiation generated from short ultrafast pulses is problematic due the the extreme bandwidth predicted.

For the Two Temperature Model, any reasonable interpretation is inconsistent with the results presented here. If the spins reservoir is understood as a purely magnetic reservoir, which conservation of angular momentum dictates cannot be directly coupled to, demagnetisation is extremely rapid and far more efficient than any other model, this was not observed. If the spin reservoir is understood to be an purely kinetic reservoir, then the specific heat of that reservoir is still too low, and demagnetisation would proceed far too rapidly. Even if the reservoir is understood as a combined kinetic and magnetic reservoir, the direct coupling of the laser pulse the the magnetic reservoir produces an enormous rate of demagnetisation, and hence a Terahertz power output that would have been (easily) detectable.
Chapter 7. Conclusions

For the Non-Thermal electron model, the duration and manner of electron thermalisation determines both the time and degree to which it diverges from Three Temperature Model like behaviour. Taking the thermalisation time to be longer, or taking its coupling to the spin system to be weak, as for thermal electrons, the model behaves similarly to the Three Temperature Model, with results similarly compatible with experiment. While the theoretical basis for the model appears to be superior to that of the Three Temperature Model, the expansion of the model does not appear to increase its predictive power.

The results for Gadolinium provide some support for the Microscopic Three Temperature Model over the original Three Temperature Model, however this may also be attributable to the Gadolinium being above its Curie temperature while in the beamline, as opposed to at room temperature.

Since the null result provided no solid insight to favour either the Three Temperature Model, or the Microscopic Three Temperature Model, nothing in the results contradicts the assumption made, that, while ultrafast demagnetisation may have complicated and quantum mechanical mechanisms, the resultant magnetic effects are the same as normal, equilibrium, thermal demagnetisation, just in a non-equilibrium setting. Indeed it is possible that upon closer examination, these two concepts may be equivalent. That is, that the Elliot-Yafet mechanism described by Koopmans et al.[11] is a microscopic description of the regular mechanisms of thermal demagnetisation.

The most likely proposition however is that the link between the apparent spin temperature (the equilibrium temperature corresponding to the magnetisation as a function of temperature), and the electron and lattice temperatures, is only very approximately thermal, making the concept of spin temperature dubiously useful. Instead non-thermal models of electron-spin energy transfer, not based on temperature difference, may need to be developed. This approach is best allowed for by the Microscopic Three Temperature Model and is the basis for its use as the preferred model in the theoretical components of the thesis.

With regard to the future direction of the research, the models provide many interesting and testable predictions. The theoretical results derived from the models in this thesis, particularly sections 6.2.1 and 6.2.4 provide good opportunities to validate or disprove the models, and increase the understanding of ultrafast demagnetisation as a Terahertz source.
References


References


References


References


Appendix A

Constants and Material Specific Values

The values of the physical constants used are those recommended by the United States National Institute of Standards and Technology’s, Committee on Data for Science and Technology (CODATA)\cite{CODATA}.

Table A.1: Physical constants as used in this thesis. All values provided by, or calculated solely from, values provided by CODATA\cite{CODATA}.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltzmann Constant</td>
<td>$k_B$</td>
<td>1.380 648 8(13) $\times 10^{-23}$ J · K$^{-1}$</td>
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</tr>
<tr>
<td>Planck Constant</td>
<td>$h$</td>
<td>6.626 069 57(29) $\times 10^{-34}$ J · s</td>
<td></td>
</tr>
<tr>
<td>Reduced Planck Constant</td>
<td>$\hbar$</td>
<td>1.054 571 726(47) $\times 10^{-34}$ J · s</td>
<td></td>
</tr>
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<td>Electron Mass</td>
<td>$m_e$</td>
<td>9.109 382 91(40) $\times 10^{-31}$ kg</td>
<td></td>
</tr>
<tr>
<td>Avogadro Constant</td>
<td>$N_A$</td>
<td>6.022 141 29(27) $\times 10^{23}$ mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Bohr Magneton</td>
<td>$\mu_B$</td>
<td>9.274 009 68(20) $\times 10^{-23}$ J · T$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Atomic Mass Unit</td>
<td>$u$</td>
<td>1.660 538 921(73) $\times 10^{-27}$ kg</td>
<td></td>
</tr>
<tr>
<td>Speed of Light</td>
<td>$c$</td>
<td>2.997 924 58 $\times 10^{8}$ m · s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Electric Constant</td>
<td>$\epsilon_0$</td>
<td>8.185 418 788 7 $\times 10^{-12}$ F · m$^{-1}$</td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>Quantity</td>
<td>Symbol</td>
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</tr>
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<td></td>
<td>Co</td>
<td>8.78e-26</td>
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<tr>
<td></td>
<td>Ni</td>
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<td>Curie Temperature</td>
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<td>K</td>
</tr>
<tr>
<td>Debye Temperature</td>
<td>Td</td>
<td>1.85e3</td>
<td>K</td>
</tr>
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<td>Electronic Heat Capacity</td>
<td>Cγ</td>
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<td>J·K⁻²·m⁻³</td>
</tr>
<tr>
<td></td>
<td>λp</td>
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<td></td>
</tr>
<tr>
<td>Fermi Energy</td>
<td>εF</td>
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<td>J</td>
</tr>
<tr>
<td>Fermi Energy</td>
<td>MF</td>
<td>1.7784e-18</td>
<td>J</td>
</tr>
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<td>Mass Density</td>
<td>ρ</td>
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<td>kg·m⁻³</td>
</tr>
<tr>
<td>Speed of Sound</td>
<td>v</td>
<td>4.91e3</td>
<td>m·s⁻¹</td>
</tr>
<tr>
<td>Total Angular Momentum</td>
<td>J</td>
<td>4.33e-34</td>
<td></td>
</tr>
<tr>
<td>Total Angular Momentum</td>
<td>JT</td>
<td>4.33e-34</td>
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</tr>
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<td>Thermal Spin Flip Probability</td>
<td>fσT</td>
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<td></td>
</tr>
<tr>
<td>Optical Spin Flip Probability</td>
<td>fσO</td>
<td>0.185e4</td>
<td></td>
</tr>
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<td>Optical Resistivity (≈ 1.55 eV)</td>
<td>ρo</td>
<td>1.81e-7</td>
<td>Ω·m</td>
</tr>
<tr>
<td>Electrical Resistivity (nearly)</td>
<td>ρθ</td>
<td>0.81e-6</td>
<td>Ω·m</td>
</tr>
<tr>
<td>Imaginary Refractive Index</td>
<td>k2</td>
<td>4.35e-4</td>
<td></td>
</tr>
<tr>
<td>Real Refractive Index</td>
<td>n2</td>
<td>2.46e-2</td>
<td></td>
</tr>
<tr>
<td>Optical Resistivity</td>
<td>ρo</td>
<td>1.81e-7</td>
<td>Ω·m</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>ρθ</td>
<td>0.81e-6</td>
<td>Ω·m</td>
</tr>
<tr>
<td>Speed of Sound</td>
<td>v</td>
<td>4.91e3</td>
<td>m·s⁻¹</td>
</tr>
<tr>
<td>Total Angular Momentum</td>
<td>J</td>
<td>4.33e-34</td>
<td></td>
</tr>
<tr>
<td>Total Angular Momentum</td>
<td>JT</td>
<td>4.33e-34</td>
<td></td>
</tr>
<tr>
<td>Thermal Spin Flip Probability</td>
<td>fσT</td>
<td>0.12e4</td>
<td></td>
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<tr>
<td>Optical Spin Flip Probability</td>
<td>fσO</td>
<td>0.185e4</td>
<td></td>
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<tr>
<td>Optical Resistivity (≈ 1.55 eV)</td>
<td>ρo</td>
<td>1.81e-7</td>
<td>Ω·m</td>
</tr>
<tr>
<td>Electrical Resistivity (nearly)</td>
<td>ρθ</td>
<td>0.81e-6</td>
<td>Ω·m</td>
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<tr>
<td>Imaginary Refractive Index</td>
<td>k2</td>
<td>4.35e-4</td>
<td></td>
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<tr>
<td>Real Refractive Index</td>
<td>n2</td>
<td>2.46e-2</td>
<td></td>
</tr>
</tbody>
</table>
Appendix B

Model Source Code

B.1 Model Scripts

These MATLAB scripts implement the models developed in chapter 4 and are used as the basis for the modelled results presented in this thesis.

B.1.1 Ultrafast Pulse Model

This script implements the ultrafast pulse model described in section 4.1 using the laser parameter header files shown in section B.2.1.

```matlab
function [S,E,B] = Pulse(t,constants,laser)

pi = constants.Pi;
c = constants.SpeedOfLight;
mu0 = constants.MagneticConstant;

lambda = laser.MeanWavelength;
T = laser.PulseLength;
A = laser.BeamArea;
W = laser.PulseEnergy;

w = 2*pi*c/lambda;

S = (W/A)*(log(sqrt(2)+1)/T)*sech(t/T*2*log(sqrt(2)+1))^2;
E = sqrt(2*mu0*c*W/A)*cos(w*t)*sqrt(log(sqrt(2)+1)/T)*sech(t/T*2*log(sqrt(2)+1));
B = sqrt(2*mu0*W/(c*A))*cos(w*t)*sqrt(log(sqrt(2)+1)/T)*sech(t/T*2*log(sqrt(2)+1));

end
```
Appendix B. Model Source Code

B.1.2 Ultrafast Pulse Coupling Model

These scripts together implement the pulse coupling model from section 4.2.

Laser Coupling Constant

This script calculates the laser coupling constant $L$ as described by equation 4.11.

```matlab
1 function [L] = LaserCoupling (constants, laser, material)
2 d = PenetrationDepth (laser, material);
3 R = Reflectivity (laser, material);
4
5 zValue = 1 - 1/exp(1);
6 phiRhoValue = 1;
7 A0Ivalue = cos (laser.A0I);
8
9 L = (1 - R) * zValue * phiRhoValue * A0Ivalue / (d / 2);
10 end
```

B.1.3 Reflectivity.m

This script implements the reflectivity functions as described in section 4.2.1, by equations 4.12, 4.13 and 4.15.

```matlab
1 function [R, Rp, Rs] = Reflectivity (laser, material)
2 n = real (material.RefractiveIndex);
3 k = imag (material.RefractiveIndex);
4
5 phi = laser.A0I;
6 theta = laser.PolarisationAngle;
7
8 Rp = ((n - sec (phi)).^2 + k^2)./(n + sec (phi)).^2 + k^2);
9 Rs = ((n - cos (phi)).^2 + k^2)./(n + cos (phi)).^2 + k^2);
10
11 R = Rp.*cos(theta).^2 + Rs.*sin(theta).^2;
12 end
```

B.1.4 PenetrationDepth.m

This script calculates the penetration depth of the simulated pulse into the simulated material, as described in section 4.2.

```matlab
1 function [d] = PenetrationDepth (laser, material)
2 k = imag (material.RefractiveIndex);
3 ```
B.1.5 Ultrafast Demagnetisation Model Scripts

These scripts contain the declaration and integration of the systems of ordinary
differential equations that make up each model. The Two and Three Temperature
models, elsewhere abbreviated to 2TM and 3TM respectively are contained within
to as TwoTM.m and ThreeTM.m respectively as MATLAB does not permit function
names to begin with a number.

TwoTM.m

This script implements the Two Temperature Model from section 4.3.1.

```matlab
function [t,T,M,E,B,S,f,P,V] = TwoTM(tMin,tMax,tStep,material,
    laser,T0,H)
    constants = Constants();

    Gel = GFn(laser,material,T0,H);
    L = LaserCoupling(constants,laser,material);

    initCond = [T0;T0];
    t = tMin:tStep:tMax;

    function dT = ode(t,T)
        dT = zeros(2,1);
        dT(1) = (Gel*(T(2)-T(1)) + L*Pulse(t,constants,laser))/ (Ce(T(1),constants,material)+Cs(T(1),H,constants,material)) ;
        dT(2) = (Gel*(T(1)-T(2))) / Cl(T(2),constants,material);
    end

    options = odeset('Reltol',1e-6,'MaxStep',1e-14);
    [t,T] = ode113(@ode,t,initCond,options);
    M = Magnetisation(T(:,1),H,material);
    [E,B,S] = MagneticDipole(t,M);
    [f,P] = PowerSpectrum(t,E);
    V = laser.BeamArea*(PenetrationDepth(laser,material)/2);
end
```

ThreeTM.m

This script implements the Three Temperature Model from section 4.3.2.
Appendix B. Model Source Code

function [t,T,M,E,B,S,f,P,V] = ThreeTM(tMin,tMax,tStep,material,laser,T0,H)
constants = Constants();

[GEl,Gel,Ges,Gsl] = GFn(laser,material,T0,H);
L = LaserCoupling(constants,laser,material);

initCond = [T0;T0;T0];
t = tMin:tStep:tMax;

function dT = ode(t,T)
    dT = zeros(3,1);
    dT(1) = (Gel*(T(2) - T(1)) + Ges*(T(3) - T(1)) + L* Pulse(t,constants,laser))/ Ce(T(1),constants,material);
    dT(2) = (Gel*(T(1) - T(2)) + Gsl*(T(3) - T(2)))/ Cl(T(2),constants,material);
    dT(3) = (Ges*(T(1) - T(3)) + Gsl*(T(2) - T(3)))/ Cs(T(3),H,constants,material);
end

options = odeset('RelTol',1e-6,'MaxStep',1e-14);
[t,T] = ode113(@ode,t,initCond,options);
M = Magnetisation(T(:,3),H,material);
[E,B,S] = MagneticDipole(t,M);
[f,P] = PowerSpectrum(t,E);
V = laser.BeanArea*(PenetrationDepth(laser,material)/2);
end

NTEM.m

This script implements the Non-Thermal Electron Model from section 4.3.3.

function [t,T,M,E,B,S,f,P,V] = NTEM(tMin,tMax,tStep,material,laser,T0,H)
constants = Constants();
asfo = material.SpinFlipProbabilityOpt;

[GEl,Gel,Ges,Gsl,tauEl] = GFn(laser,material,T0,H);
tauee = TauEE(laser,material);

beta = asfo*(material.ResistivityOpt/material.Resistivity)/tauEl;
gamma = (1-asfo)*(material.ResistivityOpt/material.Resistivity)/tauEl;
alpha = 1/tauee;
L = LaserCoupling(constants,laser,material);
E = laser.PhotonEnergy;

initCond = [T0;T0;T0;0];
t = tMin:tStep:tMax;
function dT = ode(t,T)  
    dT = zeros(4,1);  
    dT(1) = (Gel*(T(2)-T(1)) + Ges*(T(3)-T(1)) + E*alpha*T(4)) / Ce(T(1),constants,material);  
    dT(2) = (Gel*(T(1)-T(2)) + Gsl*(T(3)-T(2)) + E*gamma*T(4)) / Cl(T(2),constants,material);  
    dT(3) = (Ges*(T(1)-T(3)) + Gsl*(T(2)-T(3)) + E*beta*T(4)) / Cs(T(3),H,constants,material);  
    dT(4) = -alpha*T(4) - beta*T(4) - gamma*T(4) + L*Pulse(t, constants,laser)/E;  
end

options = odeset('Reltol',1e-6,'MaxStep',1e-14);  
[t,T] = ode113(@ode,t,initCond,options);  
M = Magnetisation(T(:,3),H,material);  
[E,B,S] = MagneticDipole(t,M);  
[f,P] = PowerSpectrum(t,E);  
V = laser.BeamArea*(PenetrationDepth(laser,material)/2);

dtwnetrationDepth

M3TM.m

This script implements the Microscopic Three Temperature Model from section 4.3.4. The parameter cothE is used to prevent the argument of the hyperbolic cotangent function from reaching zero and becoming undefined, while being small enough to not affect the value of the function elsewhere.

function [t,T,M,E,B,S,f,P,V] = M3TM(tMin,tMax,tStep,material, laser,T0,H)  
    constants = Constants();  
    [GE1,Gel] = GFn(laser,material,T0,H);  
    kB = constants.BoltzmannConstant;  
    asf = material.SpinFlipProbability;  
    mu = material.MagneticMoment;  
    N = material.AtomicConcentration;  
    Tc = material.CurieTemperature;  
    TD = material.DebyeTemperature;  
    L = LaserCoupling(constants,laser,material);  
    R = (8*asf*Gel*kB*Tc^2)/(mu*N*(kB*TD)^2);  
    cothE = 1e-9;  
    function y = mzero(m)  
        y = (m*coth(m*Tc/T0)+cothE) - 1;  
    end  
    M0 = fzero(@(mzero,1);
Appendix B. Model Source Code

23 \texttt{initCond = [T0;T0;M0];}
24 t = tMin:tStep:tMax;
25
26 \textbf{function} \ dT = ode(t,T) \ 
27 \quad \texttt{dT} = \texttt{zeros}(3,1);
28 \quad \texttt{dT}(1) = (Gel*(T(2)-T(1)) + L* Pulse(t,constants,laser)) / Ce(T(1),constants,material);
29 \quad \texttt{dT}(2) = Gel*(T(1)-T(2)) / Cl(T(2),constants,material);
30 \quad \texttt{dT}(3) = R*T(3)*T(2)/Tc*(1-T(3)*cosh(T(3)*Tc/T(1)+coshE));
31 \textbf{end}

32 \texttt{options = odeset('Reltol',1e-6,'MaxStep',5e-15)};
33 \ [t,T] = \texttt{ode113}(@ode,t,initCond,options);
34
36 \texttt{M = Magnetisation(T0,H,material) / M0 * T(:,3)};
37 \ [E,B,S] = \texttt{MagneticDipole}(t,M);
38 \ [f,P] = \texttt{PowerSpectrum}(t,E);
39 \ V = \texttt{laser.BeamArea*(PenetrationDepth(laser,material)/2)};
40 \textbf{end}

B.1.6 Reservoir Coupling Models

These scripts implement the reservoir coupling models described in section 4.4.

\textbf{GFn.m}

This script calculates the coupling constants and relaxation times, as described in section 4.4.

\texttt{function} \ [GE1,Gel,Ges,Gsl,tauEl] = GFn(laser,material,T0,H) \ 
\texttt{constants = Constants();}
4 hbar = \texttt{constants.PlanckConstant/(2*pi());}
5 kB = \texttt{constants.BoltzmannConstant;}
6 e = \texttt{constants.ElectronCharge;}
7 \lambda = \texttt{material.EPInteractionFactor;}
8 wD = \texttt{material.DebyeFrequency;}
9 \alpha = \texttt{material.SpinFlipProbability;}
10 \ [TE,Teq] = \texttt{TMax(laser,material,T0,H)};
11 \tauEl = (pi()*kB*Teq)/(3*hbar*lambda*wD^2);\ 
12 \ Tdown = Teq:TE;
13 \ Cdown = \texttt{zeros(2,length(Tdown))};
14 \texttt{for} \ i=1:length(Tdown) \ 
15 \quad \texttt{Cdown}(1,i) = Ce(Tdown(i),constants,material);
16 \quad \texttt{Cdown}(2,i) = Cs(Tdown(i),H,constants,material);
17 \texttt{end}
18 \ CdownAv = \texttt{mean(Cdown,2)};
19 \ cE = CdownAv(1) + CdownAv(2);
B.1. Model Scripts

```matlab
Tup = T0:Teq;
Cup = zeros(1,length(Tup));
for i=1:length(Tup)
    Cup(1,i) = Cl(Tup(i),constants,material);
end
CupAv = mean(Cup,2);
cl = CupAv;
GEl = 1/tauEl * (cE*cl)/(cE+cl);
Gel = (1 - aey)*GEl;
Ges = aey*GEl;
Gsl = aey*GEl;
```

This script calculates the maximum electron temperature and equilibrium temperature, as defined by equations 4.65 and 4.62.

```matlab
function [TE,Teq] = TMax(laser,material,T0,H)
    constants = Constants();
    TElimit = 1500;
    dT = 1;
    C = zeros(5,TElimit*dT);
    L = LaserCoupling(constants,laser,material);
    PEDensity = L*laser.PulseFluence;
    PED = PEDensity;
    TE = T0 - dT;
    while PED >= 0
        TE = TE + dT;
        C(1,TE) = Ce(TE,constants,material);
        C(2,TE) = Cs(TE,H,constants,material);
        C(3,TE) = Cl(TE,constants,material);
        C(4,TE) = C(1,TE) + C(2,TE);
        C(5,TE) = C(4,TE) + C(3,TE);
        PED = PED - C(4,TE);
    end
    PED = PEDensity;
    Teq = T0 - dT;
    while PED >= 0
        Teq = Teq + dT;
        PED = PED - C(5,Teq);
    end
end
```
Appendix B. Model Source Code

B.1.7 Heat Capacity Models

These scripts implement the heat capacity models, as described in section 4.5.

Ce.m

This script implements the electronic heat capacity model from section 4.5, specifically equation 3.21.

```
function [C] = Ce(T, constants, material)
    C = material.ElecHeatCapFactor*T;
end
```

Cl.m

This script implements the lattice heat capacity model from section 4.5, specifically equation 3.19.

```
function [C] = Cl(T, constants, material)
kB = constants.BoltzmannConstant;
TD = material.DebyeTemperature;
N = material.AtomicConcentration;

    function ret = fun(x)
        ret = x.^4.*exp(x)./((exp(x)-1).^2);
    end

if T == 0
    C = 0;
else
    C = 9*N*kB*(T/TD)^3.*quadgk(@(x)fun(0), TD/T);
end
```

Cs.m

This script implements the magnetic, or spin, heat capacity model from section 4.5, specifically equation 4.79.

```
function [C] = Cs(T,H, constants, material)
mu0 = constants.MagneticConstant;
kB = constants.BoltzmannConstant;
N = material.AtomicConcentration;
Tc = material.CurieTemperature;
Msat0 = material.SatMagnetisation;
```
B.1. Model Scripts

```
B.1.8 Magnetisation.m

This script implements the magnetisation as a function of temperature, function as
described in section 4.6, by equation 4.82.

```
Appendix B. Model Source Code

B.1.9 MagneticDipole.m

This script implements the magnetic dipole radiation function as described in section 4.7, by equation 4.83.

```matlab
function [E,B,S] = MagneticDipole(t,M)
    constants = Constants();
    pi = constants.Pi;
    c = constants.SpeedOfLight;
    mu0 = constants.MagneticConstant;
    dt = t(2) - t(1);
    E = mu0/(4*pi*c)*gradient(gradient(M,dt),dt);
    B = E/c;
    S = E.*B/mu0*8*pi/3;
end
```

B.1.10 PowerSpectrum.m

This script generates a power spectrum from an electric field function, as described in section 4.7, by equation 4.87.

```matlab
function [f,P] = PowerSpectrum(t,E)
    constants = Constants();
    c = constants.SpeedOfLight;
    mu0 = constants.MagneticConstant;
    dt = t(2) - t(1);
    df = 1/dt/length(E);
    y = fft(E)*dt;
    P = zeros(ceil(length(E)/2),1);
    f = zeros(size(P));
    for i = 1:length(P)
        P(i) = 2*abs(y(length(y)-i+1)^2) / (mu0*c);
        f(i) = (i-1)*df;
    end
end
```

B.1.11 Brilloun.m

This script evaluates a Brillouin function, as defined in equation 3.10.

```matlab
function B = Brilloun(J,x)
```
B.2. Header Scripts

While MATLAB does not use header files in the traditional sense, scripts declaring variables for shared values were used. This allows the values to be maintained from a single point. It also allows laser or material models to be changed by altering a single function parameter. The interpreter does not ensure that these values are kept constant, so care must be taken to avoid altering them.

**Constants.m**

This script returns a structure containing the values of physical constants from table A.1. All values are sourced from CODATA[55].

```matlab
function [constants] = Constants ()
% Physical and Mathematical Constants
constants = struct (...
    'Pi', 3.14159, ...
    'ElectronMass', 9.10938291e-31, ...
    'BoltzmannConstant', 1.3806488e-23, ...
    'PlanckConstant', 6.62606957e-34, ...
    'AvogadroConstant', 6.02214129e23, ...
    'SpeedOfLight', 2.99792458e8, ...
    'MagneticConstant', 1.256637061435917e-6, ...
    'ElectricConstant', 8.854187871e-12, ...
    'MolarMassConstant', 1e-3, ...
    'BohrMagneton', 9.27400968e-24, ...
    'ElectronCharge', 1.602176565e-19);
end
```

B.2.1 Laser Parameters

These scripts each return a structure with the relevant parameters for a particular laser. The parameters are those contained in table 4.2.
Appendix B. Model Source Code

ExpLaser.m

This script returns a structure containing the laser parameters for the unfocused laser used experimentally, for the reference Indium Arsenide sample.

```matlab
function [laser] = ExpLaser()

laser = struct (...
'MeanWavelength', 790e-9,...
'PulseRepetitionFrequency', 75e6,...
'LaserPower', 400e-3,...
'PulseLength', 10e-15,...
'BeamDiameter', 2e-3,...
'AOI', 45*pi()/180,...
'PolarisationAngle', 0);

laser = DerivedLaser(laser);
end
```

ExpLaserFocused.m

This script returns a structure containing the laser parameters for the focused laser used experimentally, for ultrafast demagnetisation.

```matlab
function [laser] = ExpLaserFocused()

laser = ExpLaser;
laser.BeamDiameter = 50e-6;

laser = DerivedLaser(laser);
end
```

BeaurepaireLaser96.m

This script returns a structure containing the laser parameters for the laser used by Beaurepaire et al. in their 1996 paper. This laser model is used for the examples of models in section 4.3.

```matlab
function [laser] = BeaurepaireLaser96()

laser = struct (...
'MeanWavelength', 620e-9,...
'PulseRepetitionFrequency', 5e3,...
'LaserPower', 250e-6,...
'PulseLength', 60e-15,...
'BeamDiameter', 30e-6,...
'AOI', 45*pi()/180,...
end
```
B.2. Header Scripts

**BeaurepaireLaser04.m**

This script returns a structure containing the laser parameters for the laser used by Beaurepaire *et al.* in their 2004 paper. This laser model is used for the example models in section 4.7.

```matlab
function [laser] = BeaurepaireLaser04()
    laser = struct('MeanWavelength', 800e-9, 'PulseRepetitionFrequency', 1e3, 'LaserPower', 200e-3, 'PulseLength', 100e-15, 'BeamDiameter', 5e-3, 'AOI', 45*pi()/180, 'PolarisationAngle', 0);
    laser = DerivedLaser(laser);
end
```

**DerivedLaser.m**

This script calculates derived properties for each laser and appends them to the structure. The expression for beam area $A$ is given by equation 4.1, the expression for pulse energy $W_p$ at equation 4.2, the expression for photon energy $\epsilon$ at equation 4.3 and the expression for fluence $W_p/A$ follows trivially.

```matlab
function [laser] = DerivedLaser(laser)
    constants = Constants();
    laser.BeamArea = constants.Pi * (laser.BeamDiameter/2)^2;
end
```
B.2.2 Material Parameters

These scripts each return a structure containing the parameters for a simulated material. The values are those from table A.2.

Cobalt.m

This script returns a structure containing the material parameters for Cobalt.

```matlab
function [cobalt] = Cobalt()
%Material parameters for Cobalt

cobalt = struct(...
'AtomicConcentration', 8.89e28, ...
'CurieTemperature', 1388, ...
'DebyeTemperature', 445, ...
'Density', 8.9e3, ...
'MagneticMoment', 1.72, ...
'SpinFlipProbability', 0.011*5, ...
'SpinFlipProbabilityOpt', 0.049*5, ...
'ElecHeatCapFactor', 0.7631e3, ...
'JQuantumNumber', 9/2, ...
'Resistivity', 5.80e-8, ...
'ResistivityOpt', 17.3e-8, ...
'REfractionIndex', 3.53 + 4.88i, ...
'SpeedOfSound', 4720, ...
'EPInteractionFactor', 0.325, ...
'FermiEnergy', 1.9114e-18, ...
'PlasmaFrequency', 9.5934e14);

cobalt = DerivedMaterial(cobalt);
end
```

Gadolinium.m

This script returns a structure containing the material parameters for Gadolinium.

```matlab
function [gadolinium] = Gadolinium()
%Material parameters for Gadolinium

gadolinium = struct(...
'AtomicConcentration', 3.02e28, ...
'CurieTemperature', 292.5, ...
'DebyeTemperature', 200, ...
'Density', 7.89e3, ...
'MagneticMoment', 7.63, ...
'SpinFlipProbability', 0.06*5, ...
'SpinFlipProbabilityOpt', 0.06*5, ...
'ElecHeatCapFactor', 0.3360e3, ...
'JQuantumNumber', 7/2, ...
'FermiEnergy', 1.9114e-18, ...
'PlasmaFrequency', 9.5934e14);
end
```
B.2. Header Scripts

This script returns a structure containing the material parameters for Iron.

```matlab
function [iron] = Iron()
% Material parameters for Iron

iron = struct(...
'AtomicConcentration', 8.5e28, ...
'CurieTemperature', 1043, ...
'DebyeTemperature', 420, ...
'Density', 7.87e3, ...
'MagneticMoment', 2.22, ...
'SpinFlipProbability', 0.024*5, ...
'SpinFlipProbabilityOpt', 0.037*5, ...
'ElecHeatCapFactor', 0.7077e3, ...
'JQuantumNumber', 2, ...
'Resistivity', 9.80e-8, ...
'ResistivityOpt', 8.10e-8, ...
'RefractiveIndex', 2.94 + 3.39i, ...
'SpeedOfSound', 4910, ...
'EPInteractionFactor', 0.34, ...
'FermiEnergy', 1.7784e-18, ...
'PlasmaFrequency', 9.8932e14);

iron = DerivedMaterial(iron);

end
```

Nickel.m

This script returns a structure containing the material parameters for Nickel.

```matlab
function [nickel] = Nickel()
% Material parameters for Nickel

nickel = struct(...
'AtomicConcentration', 9.04e28, ...
'CurieTemperature', 627.2, ...
'Density', 7.87e3, ...
'MagneticMoment', 2.22, ...
'SpinFlipProbability', 0.024*5, ...
'SpinFlipProbabilityOpt', 0.037*5, ...
'ElecHeatCapFactor', 0.7077e3, ...
'JQuantumNumber', 2, ...
'Resistivity', 9.80e-8, ...
'ResistivityOpt', 8.10e-8, ...
'RefractiveIndex', 2.94 + 3.39i, ...
'SpeedOfSound', 4910, ...
'EPInteractionFactor', 0.34, ...
'FermiEnergy', 1.7784e-18, ...
'PlasmaFrequency', 9.8932e14);

nickel = DerivedMaterial(nickel);

end
```
Appendix B. Model Source Code

```matlab
function [material] = DerivedMaterial(material)
    constants = Constants();
    muB = constants.BohrMagneton;
    muat = material.MagneticMoment;
    N = material.AtomicConcentration;
    vs = material.SpeedOfSound;
    material.SatMagnetisation = muat*muB*N;
    material.DebyeFrequency = vs*(3/(4*pi())*N)^(1/3);
end
```

DerivedMaterial.m

This script calculates derived properties from the material parameters and appends them to the structure. The expression for saturation magnetisation at 0 K ($M_0$) is given at equation 3.13. The expression for the Debye frequency ($\omega_D$) is given at equation 3.28.

1. function [material] = DerivedMaterial(material)
2.     constants = Constants();
3.     muB = constants.BohrMagneton;
4.     muat = material.MagneticMoment;
5.     N = material.AtomicConcentration;
6.     vs = material.SpeedOfSound;
7.     material.SatMagnetisation = muat*muB*N;
8.     material.DebyeFrequency = vs*(3/(4*pi())*N)^(1/3);
9. end