A STUDY OF SURFACE ACOUSTIC WAVE AND SPIN PRECESSION USING AN ULTRAFAST LASER FOR LOCALIZED ELASTIC AND MAGNETIC PROPERTY MEASUREMENTS

DISSERTATION

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Abstract

Ultrafast laser optics is becoming a powerful tool in materials research. The interaction between femtosecond laser pulses with electrons and the subsequent relaxation process is an active research topic in recent years. In the time scale of femtoseconds to nanoseconds, several interesting physics take place. The laser pulses are short that they can be used to probe these very short time scale interactions, for example, the spin precession in GHz range. The laser can be easily focused using an objective lens, thus providing a micron-scale spatial resolution.

In this dissertation, I will start by discussing the dynamics of electron, lattice and spin after a sample absorbs focused femtosecond laser pulses and the information can be used for measurement of elastic constants and saturation magnetization. The micron-scale spatial resolution and picosecond temporal resolution of our ultrafast laser pump-probe system allows us to measure elastic, magnetic and thermal properties of materials locally. By performing such measurements on diffusion couple/multiple samples with composition gradients, we can more effectively establish composition dependent property databases than conventional ways of making single uniform alloys and measuring them one at a time.
Absorption of low power focused femtosecond laser pulses by sample surface leads to localized thermal expansion, which launches Surface Acoustic Waves (SAW) that can be used to measure elastic modulus. Such measurements must be supplemented by theoretical calculations since there are complications related to pseudo-SAWs and skimming longitudinal waves in addition to regular SAWs. It is a bit surprising that a mathematical solution to the surface response induced by a thermally expansion source on an arbitrary bulk surface (half space) of an isotropic crystal/solid is not available in the literature. By convolving the strain Green’s function with the thermal stress field created by an ultrafast Gaussian laser illumination, I solved the complete surface displacement using the reciprocity principle and programmed the semi-analytical solution into a MatLab code. The solution is validated by performing femtosecond laser pump-probe measurement in which the surface displacement is monitored by time-dependent probe beam deflection. This solution will be an important base for localized measurement of anisotropic elastic tensor. As a demonstration, I determined the elastic tensor of Si from a Si (111) wafer, with values close to the literature data.

Localized measurement of the absolute value of saturation magnetization (magnetic moment) is useful for obtaining composition dependent magnetic moment data for discovering new magnetic materials. Existing methods for localized magnetic measurement, such as scanning Hall probe, scanning SQUID, and magnetic force microscopy (MFM) either do not have the required spatial resolution (in microns) or require stringent sample size or testing condition, or do not have the ability to obtain quantitative absolute magnetic moment values. I built a time-resolved MOKE to excite
and measure spin precession in magnetic materials with a focused femtosecond laser. The precession is excited and detected within a region essentially defined by the focused laser spot (a radius of 3.6 microns with a 20X objective lens) and its frequency is used to extract the saturation magnetization (magnetic moment). It was found from my experiments on pure Fe, Ni and Co that the predominant mode of spin precession on bulk metallic samples induced by focused femtosecond laser pulses is the uniform Kittel mode. Using Kittel’s dispersion relationship which relates the Kittel mode spin frequency to the strength of the applied magnetic field and the saturation magnetization, the saturation magnetization can be evaluated. The process is quite straightforward for cubic phases with negligible crystal magneto-anisotropy. For pure Co and Co-rich alloys with the HCP crystal structure that usually has strong crystal magneto-anisotropy, the fitting to both saturation magnetization and anisotropic parameters are possible when variable applied field experiments are performed. TR-MOKE measurements were carried out in a Ni-Fe diffusion couple across the diffusion region and a composition dependent saturation magnetization data in Ni-Fe alloy are obtained and compared favorably with literature values.
To my wife Junyan and my parents
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I also want to express my thanks to Prof. P. Chris Hammel, my co-adviser. Prof. Hammel is really an amazing physicist and teacher, always has critical thinking as well as an insight into the very basics of physics. The most important thing I learnt from Prof. Hammel is the way physicists think and argue, which will benefit me for the rest of my life.

I appreciate the help from my collaborators in University of Illinois. Prof. David Cahill, who helped us in setting up the ultrafast laser system; and Prof. Richard Weaver, who guided me through the tangled thermal-elastic equations and to obtain fruitful results.

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Publications

Peng Zhao, Richard Weaver and Ji-Cheng Zhao, “Dynamic Surface Acoustic Response
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Field of Study

Major Fields: Physics

Studies in:

Experimental Condensed Matter Physics

Ultrafast laser

Acoustics and Magnetism
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Chapter 1 Overview

Ultrafast laser optics provides a powerful tool for studying relaxation dynamics at electrons, phonons and magnons [1-4]. A mode locked Ti:Sapphire laser can provide laser pulses with around 100 fs duration, this is a time scale shorter than most of the physical interactions involved in the electron/phonon relaxation processes [5]. There are three different but correlated systems that need to be taken into account; they are: electrons, phonons and spins. In metallic materials the electron bath is the first to interact with laser pulses, as it is directly coupled to the electric field of the photon. Upon absorption of the laser photons, electrons below Fermi surface are excited out-of-equilibrium instantaneously, followed by a rapid thermalization process due to electron-electron collisions. The collisions bring the electron bath back into thermal equilibrium. The excitation and subsequent relaxation can only be observed using ultrafast laser pulses, as Continuous-Wave (CW) laser has a much lower energy density [1]. The electron bath is interconnected with the phonon bath and the magnon bath through electron-phonon coupling and electron-spin coupling. As the electron bath is hot after electron thermalization while the lattice and the spins are still cold, the thermal energy transfers into the phonon and spin bath. (Figure 1.1) This process may be short (less than 100 fs)
or may take a much longer time (larger than 1 ps), depending on the electron-phonon/spin coupling parameters [1, 6]. Beaurepaire et al. first proposed a Three-Temperature-Model to quantitatively describe the process phenomenologically [7]. In this model each subsystem is given a temperature, and the heat flow between these systems is governed by the coupling constants, see Equation 1.1. It can explain experimental observations of thermal-reflectance to a great accuracy. (Equation 1.1 is copied from the publication of Beaurepaire [7])

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

(1.1)

In Equation 1.1, the left hand side is a product of specific heat (electrons \(C_e\), spins \(C_s\) and lattice \(C_l\)) and the rate of cooling, while the right hand side is the energy transfer rate due to electron-lattice, electron-spin and spin-lattice interactions (which is equal to a product between temperature difference of the systems and the coupling constants \(G_{es}\), \(G_{sl}\) and \(G_{el}\)). The \(P(t)\) term is added to the electron temperature equation as an effect of laser heating. In non-magnetic materials this model can be simplified into the Two-Temperature-Model, by excluding the spin system from the equations.
Figure 1.1. Creation of hot electrons from a Fermi distribution (a), thermalized electron bath that is still hotter than lattice (b) and the equilibrium reached between electron and lattice (c). The photons excite electrons in the Fermi sea out-of-equilibrium to energies above Fermi energy, electron-electron collision brings the whole electron system back into equilibrium (thermalization) in less than 1 ps, and energy is further transferred into the lattice. Before electrons thermalize, they transport into the depth of the sample in a ballistic way; after Fermi distribution is achieved and electron bath has a well-defined temperature, this transportation becomes diffusive. In longer time ranges (larger than 100 ps) it is purely thermal diffusion of the lattice and electrons. [1]
The time scales are very important here in understanding the whole process. Besides the pure relaxation process there are some other interesting physics taking place during the ultrafast laser radiation, e.g. ultrafast demagnetization, Inverse Faraday Effect, etc [5, 8-10]. A comparison of time scale among these processes is shown in Figure 1.2. The horizontal axis in Figure 1.2 is the time with several physical processes marked into it. (Figure 1.2 is inspired from from the work of Mathias [4]) The time range covered here is very broad, ranging from 10 fs to 10 ns. The physics involved here can be separated by considering relevant time ranges, e.g. in nanosecond time scale, when only thermal diffusion is significant. In experiment, I mostly utilize the time scale from 100 ps to 10 ns in which all the three sub-systems are in equilibrium, and thermal diffusivity is the major effect. This is also the time scale for coherent spin precession and surface acoustic waves that are the subject of my thesis.

At the very beginning of laser radiation, it is the electron bath that couples directly to the electric field of the laser pulses. At the same time, electron spins can also interact with the laser through Inverse Faraday Effect (IFE) (not shown in Figure 1.2) [5, 11] in which circularly polarized photons create an effective field in the radiated area that couples to the spin bath. This can be viewed as the inverse process of Faraday effect in which photon polarization is rotated by the sample (and that is how it gets the name). The effective field only last for around 100 fs and can sometimes be quite large (over 20T in some materials) [5], so that it is possible to flip single spin in less than half cycle of Larmor precession, making it a promising technology in magnetic information processing.
Figure 1.2. Time scale comparison of several interactions. Laser pulse in Ti:Sapphire is in the range of 10-100 fs. The time scale in this graph is in logarithm; electron thermalization is the fastest, while electron-phonon thermalization process takes around 10 ps. For longer time scales (larger than 10 ps) the thermal diffusion and coherent spin precession (not shown here) are most important physics.

Ultrafast demagnetization is another interesting physics happening in the time scale of 0.1-1 ps. Upon femtosecond laser radiation, a substantial loss in sample magnetization can be observed in the first picosecond. The origin of ultrafast demagnetization is still under debate, there are several proposed models to explain the effect, either from thermal effect, or from spin current effect and hot electron excitation [12-18]. However, how the spin angular momentum gets transferred out of the spin bath in such a short time still
needs to be answered in more details, as there is not a physical interaction strong enough to do this at such a short time scale. This question is still a frontier in ultrafast spin dynamics research.

What happens in the spin system at longer times (longer than 20 ps) is clearly understood [9]. As a result of intensive laser heating, magnetocrystalline anisotropic field is strongly suppressed, resulting in an instantaneous misalignment of magnetization and the effective field (assuming the previous magnetocrystalline anisotropic field is not perfectly aligned with external field). With the presence of an external field and the remnant magnetocrystalline field, the spins go in to a precession motion, whose frequency is determined by the gyromagnetic ratio, the effective magnetic field and the saturation magnetization. Not only can the sudden suppression of the anisotropic field, but also the IFE and even the ultrafast demagnetization (from sudden suppression of shape anisotropic field) are able to initiate the precession. Figure 1.3 is a detailed plot of the sequences.

Experimentally the electron temperature temporal profile can be measured using Time-Domain-Thermoreflectance (TDTR). In metals, especially Al, optical reflectivity is highly sensitive to temperature [19]. By measuring reflectivity in the time domain, the evolution of electron bath temperature can be accurately plotted against time with sub-picosecond resolution in an ultrafast laser pump-probe system [1]. A comparison between this TDTR measurement and the theoretically calculated temperature curve from the three-temperature model enables researchers to measure the electron-phonon coupling
constant. Wang and Cahill recently reported the measurement of electron-phonon coupling constants in Cu and Au at room temperature using TDTR, taking advantage of a thin Pt layer on top of their sample which acts as a heat transducer [6].

Figure 1.3. A) Before arrival of laser pulse, $M$ is parallel with the effective field; B) Upon arrival of the laser pulse, intensive heating suppresses the anisotropic field, instantaneously tilting the effective field; C) $M$ starts precess around effective field, and as the heat diffuse away, the effective field restores to its original state; D) Heat has diffused away, $M$ continues to precess around the effective field with Gilbert damping (spin-lattice interaction).

The relaxation process is directly related to the intrinsic physical properties of the materials, e.g. electrical conductivity, thermal expansion and magnetization, and thus the
process can be highly useful in measuring these parameters [1, 20, 21]. The high spatial and temporal resolution combined with the non-contact and non-destructive nature in this optical measurement on the relaxation dynamics is ideal for materials physical property measurements. My research work is focused on the use of the lattice and spin relaxation dynamics to measure the materials anisotropic elastic modulus from polycrystalline samples and the saturation magnetization from diffusion multiples.

Laser radiation increases the sample temperature, subsequent thermal expansion and acoustical excitations are expected to follow, which is also part of the lattice dynamics. Generally speaking, femtosecond laser excites acoustic waves by means of three different mechanisms. The first and most commonly used one is through localized thermal expansion, as a result of heating from laser pulse absorption and subsequent localized thermal expansion [22]; the second way is by using high-power laser ablation, in which the top layers on the sample surface are vaporized away from the sample, resulting a recoil force normal to the sample surface that can excite acoustic waves [23]; and the third way is through excitation of hot carriers in semiconductors that brings in an instantaneous change in strain [24]. There are also several methods to detect the surface motion. One is to use an interferometer that can code vertical surface motion into interference patterns [22], the other one is to detect beam deflection (BD) that measures the deflection of the reflected probe beam which is proportional to the surface slope [21]. Recently Higuet et al. [25] also used a beam distortion method to directly relate the surface displacement to reflectivity changes. As acoustic waves pass by, the sample surface is distorted, resulting in a reduction in total reflected probe beam intensity as the
reflected beam is broadened and get clipped by an aperture. This method has the obvious advantage that the signal is directly related to the surface displacement itself, rather than the surface slope. However, the signal to noise ratio of this method is not as good as the beam deflection measurement, partially due to the excellent common-mode rejection in the latter method. In my experiment I use the beam deflection method to measure the surface motion several microns away from the excitation spot to detect propagation of Surface Acoustic Waves (SAW). In this way I can potentially use the speed of SAW to evaluate anisotropic elastic modulus from a single grain of a polycrystalline sample to avoid the needs of growing large single crystal samples for conventional elastic tensor property measurements.

The idea to measure the anisotropic elastic modulus from polycrystalline samples stems from the prevailing needs for anisotropic elastic constant data. Previous non-contact ultrasonic method for measuring such data can only be done in a millimeter size single crystal sample [26]. It can be quite difficult to grow such a large single crystal samples for some materials. This idea is built upon our previous experiment of localized thermal expansion measurement using a femtosecond laser pump-probe setup [21]. Intensive heating from focused laser spot results in localized thermal expansion right beneath the laser spot, creating a bulge whose shape is determined by the thermal expansion coefficient. A second probe laser can detect its shape using the deflectometry thus determine the thermal expansion coefficient locally. Because the laser pulse is very short (~100 fs), this thermal expansion is almost instantaneous, and so does the resulting strain/stress. This sudden strain loading is able to launch a series of ultrasonic waves;
among them the most energy intensive mode is the Rayleigh Wave (also known as Surface Acoustic Wave, SAW) that propagates on sample surface [27]. The probe beam is placed several microns away from the excitation site to accurately measure the time evolution of the waveform. My collaborator, Prof. Richard Weaver in University of Illinois, came up with a brilliant idea of using the reciprocity principle to semi-analytically solve the temporal waveform of the acoustic field in an arbitrary cut anisotropic half-space, which I implemented into a MatLab program to make quantitative calculations to enable a direct comparison between experimental measurement and theory prediction. The pump and probe beams can be arranged to be separated less than 15 microns, which enables measurements within a single grain of a polycrystalline sample. By doing measurements along multiple orientations, I am able to plot Rayleigh Wave speed as a function of propagation direction, and further to fit the anisotropic elastic modulus using another MatLab program I wrote.

The dynamics of spin can also be measured using the pump-probe method. There are several possible probes that are sensitive to spin ordering, including far-infrared/visible/ultraviolet light, spin polarized electrons and X-ray [5]. For the optical probes, Time-Resolved Magneto-Optical Kerr Effect (TR-MOKE) is extensively used by researchers as a direct probe of magnetization. The set-up of TR-MOKE is almost the same as conventional MOKE, other than the extra ability to have time resolution controlled by the delay time between the pump and probe pulses. The time resolution in TR-MOKE can be as short as the laser pulse duration. It is an ideal tool to study the ultrafast demagnetization and has the advantage of easy implementation [28]. However, it
is still under debate how the presence of non-magnetic artifacts induced by pump laser heating can affect the magneto-optical measurement results in the first picosecond [4]. Another optical probe to detect spin dynamics is through time-resolved Second Harmonic Generation (SHG) which is actually a non-linear effect. SHG has the advantage of high signal-to-noise ratio and exclusive sensitivity to surface and interfaces. The X-ray Magnetic Circular Dichroism (XMCD) is yet another powerful tool in studying the spin dynamics, and it has the advantage of elemental sensitivity and can reveal quantitative information on spin and orbital momentum [5]. Stamm et al. first reported in 2007 about their XMCD experiment with 100 fs time resolution [29]; Mathias et al. in 2012 reported their table-top setup of using High Harmonic Generation of extreme ultraviolet pulses for element specific spin dynamics measurement [4]. My experiment is mainly focused on the longer time (>20 ps) coherent part of the spin precession signal, so TR-MOKE is the best and simplest technique for this purpose.

I aim to perform effective measurement of saturation magnetization as a function of alloy composition using the high-throughput diffusion multiple method together with localized probe of magnetization [30]. Such data are highly desirable for industry applications and academic materials research on phase stability of magnetic alloys. The increasing demand on high performance permanent magnets from industries combined with limited supply of rare earth elements call for new magnetic materials with high saturation magnetization, high Curie temperature for stability and high coercivity without using rare earth elements [31]. The CALPHAD (CALculation of PHAse Diagrams) community is also highly interested in this database to account for the Gibbs free energy term from magnetic
ordering that affects phase stability. Conventional method of saturation magnetization measurement uses single composition alloy samples and measure one alloy at a time, thus very time consuming, especially for alloys with more than 3 elements. In contrast, the diffusion multiple method offers a highly efficient measurement [30]. It involves fabricating a single sample with concentration gradient in which wide ranges of compositions are created in one sample. The concentration gradient is formed due to inter-diffusion between/among the elemental atoms at a high temperature; and by taking localized measurement across the diffusion region; composition-dependent magnetization data can be efficiently obtained. The general idea of using diffusion multiple samples for accelerated composition-dependent material property characterization is illustrated in Figure 1.4 (which I took from Prof. Ji-Cheng Zhao’s presentation).

Localized measurement of saturation magnetization in a bulk sample with micron-scale spatial resolution is not an easy task. FMR (Ferromagnetic Resonance) is powerful and accurate but has no spatial resolution; MFM is only sensitive to field gradient outside sample and can hardly be quantitative; and scanning SQUID doesn’t have enough spatial resolution [32]. After intensive literature search, the dynamics of spin precession measured using Time-Resolved MOKE (TR-MOKE) appears to be the best choice [5, 9, 33, 34]. This method has its advantage of non-contact, high spatial resolution and high-efficiency. It also has the potential to quantitatively determine the magnetocrystalline anisotropy, (which is still in progress). I performed TR-MOKE measurement on Fe-Ni and Co-Cr diffusion couples and the result will be presented in Chapter 5. These two samples represent different regimes, one with negligible crystalline anisotropy, while the
other with high crystal anisotropy and a magnetic phase transition from anti-ferromagnetic to ferromagnetic.

Figure 1.4. The idea of diffusion multiple method and how it accelerate data collection in composition-dependent materials property measurement. The picture in the upmost part of this figure is a diffusion multiple, with several binary/ternary diffusion junctions. Several physical properties (e.g. Phase Diagrams, Diffusion Coefficients, Hardness, Modulus, Strength, Thermal Conductivity) have already been measured using available technologies, while new measurement with micron scale resolution are needed for some other property measurements [30]. Figure is from Prof. Ji-Cheng Zhao’s presentation.
Chapter 2 Theoretical background

2.1 Time-Domain-Thermoreflectance

Thermoreflectance, dR/dT, the reflectivity change as a function of temperature, has long been used for probing the heat transport properties in materials [19, 35-38]. The reflectance is a function of complex permittivity, which is directly related to temperature. The physical background of this phenomenon is believed to be the changing of band structure due to thermal expansion. Thermoreflectance measurement has long been a static measurement until recent development in ultrafast lasers that allow the measurement to be taken in the time domain [1, 7]. Thermoreflectance is a sensitive indication of the electron temperature and it has been used to experimentally investigate coupling between electron and phonon thermal baths [1, 7]. For long delay times (>10 ps) all the electron-phonon-spin baths are in thermal equilibrium, so the thermoreflectance is also a valid indication of the lattice temperature [1]. Longer time (>10 ps) TDTR signal is sensitive to thermal conductivity of the samples, as the top layer is first intensively heated.
by laser laser pulses, heat transfers into deeper part of the sample leading to a decrease of surface temperature [35]. Of most materials, Al has a higher dR/dT than other metals near room temperature and has an absorption peak at around 800 nm optical wavelength, which coincides with the laser peak power wavelength of the Ti:Sapphire laser [19]. Thus, Al serves as an ideal heat transducer. An ideal configuration for TDTR measurement of heat conduction is to put a thin Al film (around 100 nm) on top of the sample. Cahill solved the temporal heat transfer problem in layered structure that paved the way to use TDTR to measure thermal conductivity and interfacial thermal conductance [35]. The sample structure is shown in Figure 2.1. By imposing the proper boundary conditions (Gaussian laser heating on the surface and conservation of heat at the interface), he was able to solve the heat diffusion equation in a multilayer system in the time domain. The surface temperature measured by thermoreflectance is directly related to thermal conductivity and heat capacity of each layer so that a fitting to the experimentally measured data allows extraction of thermal properties [36, 38, 39].

Generally speaking, high frequency TDTR signal is more sensitive to thermal diffusivity, while low frequency measurement is sensitive to effusivity. By measuring thermoreflectance signal for both high and low frequencies, localized measurement of both thermal conductivity and heat capacity can be achieved, as shown in Figure 2.2. Details of the model and experiments can be found in the publication of Cahill’s. [35, 38].
Figure 2.1. Layered structure in TDTR measurement. Time scale of interest is mostly from 100 ps to 4 ns. Al has a higher thermoreflectance (dR/dT) than other metals and it has an absorption region around 780 nm light, so an Al film on top of sample surface serves both as a heat transducer and as a temperature indicator. The laser is assumed to be a Gaussian shape.
Figure 2.2. A TDTR signal from an experiment on Al (100 nm)/Ni substrate sample. The diagrams also show the fitting procedure using Cahill’s model: (a) $f = 9.3$ MHz; (b) $f = 118$ kHz for heat capacity. Blue lines are the initial fitting with guessed Cp of Ni. Although the curves fit well, the thermal conductivity for the high frequency and low frequency fittings are different. By fine tuning the Cp value in Ni, both experimental data sets can be fitted to obtain the same thermal conductivity parameter (the red line). The aim of the process is to find the Cp and thermal conductivity that fit both the measured curves. This figure is from a private communication with Changdong Wei.
2.2 High frequency longitudinal acoustic wave excited during TDTR measurement

With the absorption of intensive laser pulses, heat is deposited onto top 10-20 nm of Al film. This sudden change in temperature results in a sudden change in the strain field on the top layer due to thermal expansion. The strain deformation propagates into the depth in the form of a longitudinal acoustic mode, and gets reflected from the interfacial boundary. When reflected longitudinal wave hits the surface again, the surface reflectivity experiences a change due to the strain wave, which is detected by the TDTR [40]. The time of travel for the longitudinal wave to go to the interface and back to the surface is accurately calculated by dividing twice the film thickness with longitudinal sound velocity. This is an efficient way to measure the film thickness with known sound velocity, or to measure the elastic modulus with known film thickness.

High frequency longitudinal acoustic wave can also be launched through excitation of hot electrons [41]. At the time of laser pulse absorption, as shown in the upper part of Figure 2.3, out-of equilibrium hot electrons are created out of the Fermi sea of electrons. These hot electrons propagate into the depth of the sample ballistically with a speed near Fermi velocity until they thermalize with electron bath through electron-electron collision. For an Al thin film of less than 100 nm thick, the hot electrons can hit the film/substrate boundary before they thermalize, creating a sudden strain loading at the interface [1]. This strain propagates upward to the surface and is detected through TDTR. The ballistic transport of hot electrons is a very fast process, taking less than 10 fs for a 100 nm Al
film, in TDTR measurement focusing on picosecond dynamics, this time delay is neglectable. So in the TDTR signal I often observe two peaks before 100 ps that is the result of longitudinal acoustic wave, and the later one is exactly at twice the delay time of the first peak, as shown in Figure 2.3.

Figure 2.3. A TDTR in-phase signal on a Al/SiO$_2$/Si multilayer sample. The arrival of the pump pulse is marked by the signal rising to half of its maximum and is set to be time zero. The initial 50 ps reflection signal is mostly only sensitive to the Al film, with two longitudinal acoustic phonon peaks visible, one is due to hot electron thermalization at the Al/Silica interface and subsequently excited acoustic wave that propagates upward, the other is from acoustic wave generated on surface and reflected at that interface. The peak position allows accurate calculation of the Al film thickness, with known sound velocity of Al.
2.3 Thermal expansion measurement using the probe beam deflection

The same system can be used to measure thermal expansion with high spatial resolution. As the pump laser pulses are absorbed by the sample, the heating brings in a temperature increase on the illuminated area, and a bulge is formed due to thermal expansion [21]. In layered structures, because the thermal expansion coefficients of layers are not the same, there will be strains at the layer interfaces and they further contribute to the surface deformation. Zheng et al. solved this thermal expansion model analytically and gave out a solution of the surface slope as a function of elapsed time [21]. Due to the surface deformation, a probe laser near the heated region is significantly deflected and can be observed using a split-photodiode. The magnitude of this surface deflection is directly related to thermal expansion of the sample, thus enabling researchers to do a localized measurement of thermal expansion coefficient. Experimentally, the perfect overlap between pump and probe is found by maximizing the TDTR signal. Then the pump beam spot is moved by a high-accuracy rotation stage, until maximum deflection in the probe beam is achieved. This is usually at the “shoulder” of the Gaussian profile of the pump beam spot, where the slope of the Gaussian function is largest. For a 3.6 \( \mu \text{m} \) radius pump spot, this is mostly at around 2.7 \( \mu \text{m} \). The measured probe beam deflection signal as a function of delay time is then compared with the analytical solution for the determination of thermal expansion coefficient.
There is another significant factor contributing to the surface deformation, the Surface Acoustic Waves (SAW), which dominates in the time range of 1-3 ns. As a result of very rapid change in the strain field, multiple modes of acoustic waves can be excited, in which the SAW is the most powerful mode [40]. In the measured signal, unlike the probe beam deflection signal coming from thermal expansion, this SAW is propagating. When the pump and probe laser beams have some overlap (as in the case of thermal expansion measurement), the thermal expansion signal is characterized by a discontinuity at time zero; when the beams are further separated so that there is no overlap, what is detected is only the excited acoustic waves. Zheng et al. used this signal (still combined with thermal expansion contribution in his experiment) to successfully measure elastic modulus of the substrate (in his experiment the Al coating layer is only around 100 nm thick, while the SAW wavelength is determined by the diameter of pump beam spot to be 7 microns, most of the acoustic signal is coming from the substrate) [21].

This measurement inspired a novel method for measuring elastic tensor properties of anisotropic materials. The SAW wave speed is a function of propagation direction in anisotropic materials, and by measuring the speed at multiple orientations it would be possible to calculate the anisotropic elastic constants in the sample [42]. The experiment can be done with a spatial resolution of less than 25 μm, enabling such a measurement be made in a polycrystalline sample.
2.4 Surface motion due to thermal expansion source in anisotropic half space

Ultrafast laser radiation can also excite Surface Acoustic Waves that propagate on the surface [22, 27, 42-49]. In this section my solution to the surface displacement field as a result of thermal expansion from femtosecond laser heating will be introduced. Majority of this section on the theory and experiment is similar to our publication in JASA (Journal of Acoustical Society of America).

Laser ultrasonics is highly praised for its easy setup, non-contact and non-destructive nature, and potential high spatial resolution [44, 45]. Depending on the laser power, acoustic waves can be excited through thermal expansion or ablation [23]. In semiconductor materials the excitation of free electrons by ultrafast laser pulses can also launch ultrasonic waves [24]. Ablation occurs if power is sufficient to vaporize surface layers, resulting in a recoil force that excites ultrasonic waves. At lower power levels, heat absorbed from a laser pulse creates a sudden change in strain field. Surface acoustic waves (SAW) launched from it contains valuable information on elastic modulus. SAW can be excited by a highly focused line/spot laser or by overlapping two coherent laser beams, or by patterning sample surface with metallic strips [22, 27, 42, 43, 45, 46, 49]. The Somekh group used optical masks to generate narrow band SAW and employed the SAW speed to determine crystal orientations [42, 43], Hurley et al. measured elastic properties of thin film on a substrate using laser generated SAW [25, 50, 51]. Very recently, Higuet et al. excited GHz frequency ultrasonic waves in an isotropic Ti alloy.
and measured the waveform several microns away using deflectometer/beam distortion [52].

Such measurements must be supplemented by theoretical calculations for expected responses before material properties can be extracted with precision. A thermal expansion source is usually treated as a dipole in the plane of sample surface, while the ablation source is treated as an impulsive point force. The elastic wave displacement response, the Green's Dyadic, to a concentrated impulsive surface point force is a classic problem; it has been solved for layered isotropic and anisotropic homogeneous linear elastic media [53-60]. The surface response to a point impulsive force on an anisotropic half space has been solved by Every et al. using a linear combination of acoustic eigen-modes in slowness space [54, 55]. Although the solution is very efficient in terms of computation, it is hard to deal with singularities associated with SAW and bulk waves in the slowness space. With the dynamic Green’s function available, response to a surface force that is distributed in space or time is then constructible from that fundamental solution by convolution in space and/or time. Bescond and Deschamps solved the same problem using the Cagniard–de Hoop method.[53] Wu provided the Green’s function for several shapes including wedges and strips [60]. Martinez-Castro and Gallego solved the problem in a viscoelastic layer [58]. Franssens, Khojasteh et al. and Tewary derived the Green’s function in layered structures [56, 57, 59]. Excellent reviews on the physics and methods to compute the wave speed are available [45, 47, 61-64].

The response to a sudden thermal expansion is more complicated. Such responses for an isotropic half space are available in the literature [27, 51, 65-67]. Rose formulated
an analytical solution to such a problem using the important concept of Surface Center of Expansion (SCOE), in which the thermal expansion source is treated as a stress source buried below the sample surface [22, 27, 66]. Norris formulated the acoustic response to a concentrated thermal source by considering coupled thermo-elastic equations in an unbounded medium [67]. Hurley and Spicer have shown that the plane-strain surface motion for a line thermal expansion source on a transversely isotropic half space can be expressed analytically using the Cagniard technique [51]. Achenbach calculated the surface motion due to a thermal expansion source in a transversely isotropic sample and discussed reciprocity in thermoelasticity [65, 68]. Cao made the calculation numerically [69]. However, most of the available analytical solutions are limited to certain crystal symmetries (mostly transversely isotropic) and high-symmetry orientations. Recently Higuet et al. solved surface displacement waveform in transversely isotropic case directly from solving the governing partial differential equations (PDEs) [52], and their calculation fits very well with experimental measurement on an isotropic Ti alloy. Although their direct and clean solution has the potential to be extended to the 3-dimention case, it may become very complicated mathematically due to their consideration of finite optical absorption length and non-zero heat diffusivity, both of which are not significant effects for most real cases. An explicit and simple solution to waveforms on a general anisotropic half space due to a sudden distributed thermal expansion source is highly desirable.

I derived the dynamic surface displacement response in an anisotropic half space due to a distributed thermal expansion source. I start with Rose’s expression [27] for
displacement response as a convolution of the applied thermal stress field with the gradient (with respect to source position) of the Green’s dyadic. It is argued here that a straightforward evaluation of the resulting integral expression is problematic, so it is converted, using a reciprocity argument, to a different form closely related to a more familiar and simpler Green's Dyadic calculation. I have a rough estimation on the importance of heat diffusion and optical penetration length in this situation allows us to safely ignore them during calculation, which results in a simple and clear analytical solution. Our method can be easily applied to a general anisotropic half space, while still has a simple analytical formulation.

I can make simply estimates of the effect of heat diffusivity. Looking at a dimensionless parameter $p = Dk/c$, where $D$ is thermal diffusivity, $k$ is a characteristic wavenumber of acoustic waves which can be taken as an inverse of pump beam diameter (about 7 μm) and $c$ is the wave speed. The physical meaning of $p$ is the ratio of thermal diffusion length over acoustic wave propagation length in unit time, so if $p$ is much smaller than unity I can safely ignore heat diffusion effect during the calculation of surface motion. Of the materials I measured Cu is the best thermal conductor with $D = 1.1 \times 10^{-4} \text{ m}^2/\text{sec}$. The parameter $p$ then is approximately 0.02 and I are thereby justified in neglecting heat flow.

I can also safely ignore the optical penetration depth and assume all energy is deposited on the surface. The optical penetration depth in most metals is in the range of 10-20 nm, while as a comparison, the central acoustical wavelength of our SAW is
around 7 μm. Their ratio is smaller than 0.003, meaning the limited optical penetration depth has little impact on acoustical response.

In order to accommodate the spatially distributed thermal load, I construct the response in the Fourier domain, as a function of the two-dimensional surface wavevector \( \vec{k} \) and the frequency \( \omega \). In this domain the spatial and temporal convolutions are trivial. Triple inverse Fourier transformation then gives the response in the physical \( x,y,t \) domain. The Fourier domain has, however, poles associated with surface wave arrivals, and other less severe singularities at points corresponding to surface skimming bulk waves. Here those singularities are navigated using an analytic extension to complex \( \omega \) [70]. The space and time-domain solution is then used as the basis for elastic modulus measurements by means of laser induced SAW. I performed surface displacement measurements on pure Cu and Al at multiple orientations to validate our solution. I am able to calculate surface displacements in arbitrary cut crystal surfaces and our method has the advantage of being conceptually simple and easy to implement numerically.

I first seek the elastodynamic displacement response \( G_{kz} \) of a homogeneous anisotropic half space \( z > 0 \) to a concentrated vertical impulse applied to the surface. This response will be used, in the next section, to express responses to the thermal load. The approach here is mostly conventional, see for example Every et al. [45, 54], but is described here for completeness. The material is taken to have a constant stiffness tensor \( C \), and constant material density \( \rho \). Interior to the half space, the displacement field obeys the elastic wave equation
\[ C_{ijkl} \frac{\partial^2 U_i}{\partial x_j \partial x_k} = \rho \frac{\partial^2 U_i}{\partial t^2} \]  

(2.4.1)

where \( U_i \) is material displacement in the \( i \) direction, \( x_j \) is the \( j^{th} \) Cartesian coordinate and \( t \) is time.

In \( \vec{k} - \omega \) space, (an overarrow e.g. \( \vec{k} \), indicates a vector in two dimensional space \( xy \); three-vectors are bold, e.g \( \vec{x} \)) arrived at through the following triple integral transform,

\[ \tilde{U}_i(\vec{k}, z, \omega) \equiv \int U_i(x, y, z, t) \exp(-i k_x + i k_y + i \omega t) dxdydt \]  

(2.4.2)

the wave equation is transformed into three coupled second order ordinary differential equations in the depth coordinate \( z \).

\[ [C_{i33} \partial_z^2 + i k_\mu C_{i\mu 3} \partial_z + i k_\nu C_{i\nu 3} \partial_z - C_{i\mu \nu} k_\mu k_\nu + \rho \omega^2 \delta_{ij}] \tilde{U}_i = 0 \]  

(2.4.3)

where \( z \) is the distance perpendicular to the surface into the half space. Latin indices \( i, l \) run from 1 to 3 = \( x, y, z \). Greek indices \( \mu, \nu \) run from 1 to 2 = \( x, y \).

Solutions may be found in the form \( U_i = A_i \exp(-pz) \). We arrive at

\[ [C_{i33} p_z^2 - i k_\mu C_{i\mu 3} p - i k_\nu C_{i\nu 3} p - C_{i\mu \nu} k_\mu k_\nu + \rho \omega^2 \delta_{ij}] A_i = 0 \]  

(2.4.4)

where the real part of \( p \) characterizes how the wave attenuates or grows with depth and the imaginary part corresponds to propagation in the vertical direction. Equation 2.4.4 is three coupled linear algebraic equations for the components of \( A \). It must be solved at every point in \( \vec{k} - \omega \) space. It has a non-trivial solution only if the determinant of the 3-by-3 matrix is zero, which corresponds to a sextic equation over \( p \). Of the six roots \( p \), with corresponding eigenvector \( A \), three correspond to fields that increase
exponentially with depth or that propagates upward. These are inadmissible for the present problem in which all sources are at the surface. This leaves our solution $\tilde{U}_i$ in the form of some as yet unspecified linear combination of the three permissible eigenvectors $A^{(r)}_i \exp(-p_r z)$ for $r = 1, 2, 3$,

$$\tilde{U}_i(k_x, k_y, z, \omega) = \sum_r a_r(k_x, k_y, \omega) A^{(r)}_i(k_x, k_y, \omega) \exp(-p_r z) \quad (2.4.5)$$

The coefficients $A^{(r)}_i$ are chosen to match three boundary conditions at $z = 0$.

If the source is a unit upwards vertical impulse on the surface concentrated at the origin $x = y = 0$, then the surface stress must be

$$\sigma_{i3}|_{z=0} = \delta_{i3}(x, y) \delta(t) \quad (2.4.6)$$

whose triple transform is

$$\tilde{\sigma}^{i3}(k; \omega, z)|_{z=0} = \delta_{i3} \quad (2.4.7)$$

But stress is a function of the strain

$$\sigma_{i3}|_{z=0} = C_{i3kl} \varepsilon_{kl}|_{z=0} = C_{i3kl} \frac{\partial U_i}{\partial x_k}|_{z=0} = C_{i3\mu l} \frac{\partial U_i}{\partial x_\mu}|_{z=0} + C_{i33l} \frac{\partial U_i}{\partial z}|_{z=0} = \delta_{i3} \delta(x, y) \delta(t) \quad (2.4.8)$$

Which triple transforms to

$$\tilde{\sigma}_{i3}|_{z=0} = C_{i3kl} \tilde{\varepsilon}_{kl}|_{z=0} = C_{i3\mu l}(ik_\mu) \tilde{U}_i|_{z=0} + C_{i33l} \frac{\partial \tilde{U}_i}{\partial z}|_{z=0} = \delta_{i3} \quad (2.4.9)$$
Substitution of Equation 2.4.5 into Equation 2.4.9 permits us to determine the coefficients $A^{(r)}$ as the solution to three simultaneous linear algebraic equations. The desired Green’s function thus becomes

$$\tilde{G}_{i\beta} = \sum_r a_r(k_x, k_y, \omega) A^{(r)}(k_x, k_y, \omega) \exp(-p_r z) \quad (2.4.10)$$

This is the triply transformed displacement in the $i^{th}$-direction due to a unit vertical impulse applied on the surface at the origin. On performing a triple inverse Fourier transform, one has the response at an arbitrary time and position on the surface or at depth. There are numerous clever procedures for doing the inverse triple transform. Every et al. for example, convert the integrals to integrals in slowness space, a procedure which replaces $\vec{k}$ with $\vec{s}$ where $\vec{s}$ is the slowness, and which takes advantage of the homogeneity of the integrand. The inverse temporal Fourier transform is then doable analytically, leaving only the integrals over $\vec{s}$ to do numerically, thereby decreasing the ultimate numerical burden. If however, the source is distributed in space and/or time, such that we seek not Green’s functions per se, but rather responses to distributed sources, or if the material is viscoelastic, the integrand loses its homogeneity and the technique is less attractive.

A notable feature of $\tilde{G}_{i\beta}$ is that it has singularities as a function of $\vec{k}$ and $\omega$ that can if not properly accommodated, prohibit accuracy in a numerical inverse Fourier transform. These are, however, removed by analytically extending the parameter $\omega$ to complex values. By taking $\omega$ to be $\omega + i\varepsilon$ for some judicious positive choice of $\varepsilon$ (scrutiny of the Forward transform (Equation 2.4.2) shows that this is equivalent to replacing $U(t)$ with
followed by a reinsertion of a factor $\exp(i\omega t)$ after the inverse Fourier transform, removes the singularities from the functions $\hat{\phi}_{ij}$ while retaining accuracy. The method amplifies the effects of numerical noise at late times, so it is not without some cost. There is an optimal choice for $\varepsilon$.

It will be useful also to have an expression for the dynamic stress field $\sigma_{ij}$ response to a unit vertical impulse at the origin.

\[\Sigma_{ij,3} \equiv C_{ijkl} \frac{\partial}{\partial x_l} G_{kl}\] (2.4.11)

(a comma amongst the indices does not represent, here, a derivative; rather it merely serves to help distinguish their meanings.)

Rose has derived (neglecting the secondary thermal fields generated by the mostly adiabatic expansions and compressions within elastic waves themselves) an expression for the elastodynamic response to applied thermal strain as a convolution of the associated thermal stress field with the gradient of the elastic Green’s function

\[u_n(x, t) = \int_V C_{ijkl} \varepsilon^T_{kl}(\xi, t) * \frac{\partial G_{ni}}{\partial x_i}(x; \xi; t)dV(\xi)\] (2.4.12)

The star in the middle represents convolution in time. Here $\varepsilon^T_{kl}(\xi, t)$ is the strain corresponding to the thermal expansion. When due to pulsed laser heating, Rose argues that it may be written as

\[\varepsilon^T_{ij}(x_r, x_y, \xi_z; t) = \alpha_{ij} T(\xi_x, \xi_y) \delta(\xi_z - d) \Theta(t)\] (2.4.13)

Here, $\alpha$ is the tensor thermal expansion coefficient, $T$ is the temperature field that creates thermal expansion (taken to be a Gaussian function corresponding to the laser
beam profile), d is a small quantity indicating the depth of the source under the surface (the limit of d approaching zero is taken later). Equation 2.4.13 describes the thermal strain as being concentrated a small distance d beneath the surface and as being a step function of time corresponding to a sudden deposition of heat and no significant heat diffusion on the time scales of interest.

The first two factors in the integrand of Equation 2.4.13 may be termed the thermal stress $\sigma_{ij}$ at position $\xi$. Equation 2.4.13 represents the dynamic response as propagation from this thermal stress source by means of a propagator which may be termed a strain Green’s function. The needed strain Green’s function is the gradient, with respect to source position $\xi$, of the response at $x$ in the $n$ direction, to buried forces at $\xi$ acting in each of the three directions $i$. As such, it is more complex than the simpler Green’s function derived above corresponding to a surface force in the vertical direction.

Rose obtained the surface response at $x$ due to a buried thermal expansion source of infinitesimal diameter using the Cagniard-de Hoop method. The result is composed of two parts, one is direct wave propagation from the buried source, and the other is due to reflections of the wave from the surface. The solution procedure requires an analytical solution of the displacement field from a buried mechanical loading. This is very complicated in an anisotropic material. Perhaps for this reason the response to a thermal expansion source has not previously been presented. Here I develop an alternate integral expression based on reciprocity and find that it is mathematically and conceptually simpler.
The key insight is to recognize that G in Equation 2.4.12 is symmetric \( G_{ij} = G_{ji} \) and reciprocal \( G(x, \xi) = G(x, \xi) \), and that C is symmetric \( C_{ijkl} = C_{klij} \). Thus Equation 2.4.12 can be re-written as (and I confine my attention to \( n = 3 \), thus to vertical displacement responses)

\[
\begin{align*}
    u_3(x, t) &= \int_V \varepsilon_{kl}^T(\xi, t) \ast C_{kl,ij} \frac{\partial G_{ij}}{\partial x_j}(\xi; x; t) dV(\xi) = \int_V \varepsilon_{kl}^T(\xi, t) \ast \Sigma_{kl,3}(\xi; x; t) dV(\xi) \\
    &\text{(2.4.14)}
\end{align*}
\]

This form is readily interpreted. Our desired dynamic displacement response (in the vertical direction at position x on the surface) to a buried thermal strain source is written in terms of the stress response \( \Sigma \) at \( \xi \) to a unit vertical impulse at x contracted and convolved with the thermal strain field \( \varepsilon^T(\xi) \). In as much as \( \Sigma \) is a trivial extension of the already determined Green’s function, it is easy to evaluate.

In the Fourier domain, our response is (after replacing d with 0 and evaluating for x on the surface)

\[
\tilde{u}_3(k, z = 0; \omega) = (-\widetilde{T}(k) / i\omega) \alpha_{kl} \tilde{\Sigma}_{kl,3}(k; z = 0; \omega) \quad \text{(2.4.15)}
\]

Finally I perform a numerical inverse triple Fourier transform.

\[
\begin{align*}
    u_3(x, y, z = 0, t) &= \frac{\exp(i\varepsilon t)}{(2\pi)^3} \int \tilde{u}_3(k_x, k_y, z = 0, \omega + i\varepsilon) \exp((ik_x x + ik_y y - i\omega t)dk_xdk_yd\omega) \\
    &\text{(2.4.16)}
\end{align*}
\]

In practice I find that the chief numerical burden is in evaluating \( \Sigma \), not in the inverse numerical Fourier transform.
2.5 The dynamics of electron spins in ferromagnetic materials

In ferromagnetic materials electron spins are strongly correlated with each other due to the exchange effect and dipolar fields. Microscopically, a single spin in ferromagnetic materials may experience magnetic field from several sources, they are: (1) external applied field; (2) magneto-crystalline anisotropy field; (3) exchange field; and (4) demagnetization field [71]. The vector sum of these fields is often defined as “effective field” that determines the dynamics of spin/magnetization through Landau-Lifshitz-Gilbert (LLG) equation [9].

\[
\frac{d\vec{M}}{dt} = -\gamma (\vec{M} \times \vec{H}_{eff}) + \lambda \vec{M} \times (\vec{M} \times \vec{H}_{eff})
\]  

(2.5.1)

In which \(\gamma\) is the gyromagnetic ratio, and \(\lambda\) is the Gilbert damping constant, \(\vec{H}_{eff}\) is the effective field defined as

\[
\vec{H}_{eff} = \vec{H}_{ext} + \vec{H}_{a} + \vec{H}_{exch} + \vec{H}_{d}
\]  

(2.5.2)

The \(\vec{H}_{ext}\) is the external field, \(\vec{H}_{a}\) is the anisotropic field (originate from spin-orbit coupling and the crystal field) while \(\vec{H}_{exch}\) is the exchange field and \(\vec{H}_{d}\) is the demagnetization field (due to shape anisotropy). These fields are determined by energy terms related to these interactions and are discussed in details below. The dynamics of spin predicted by the LLG equation is quite simple; and the magnetization is precessing around the direction of the effective field, as shown in Figure 2.4 [72].
2.5.1 Energy terms in ferromagnetic materials

As mentioned above, there are several energy terms associated with a spin in ferromagnetic materials. The actual effective field is determined by choosing the right magnetization vector that minimizes the total free energy. The discussion below on free energy terms in magnetic materials is mostly following the textbook [73].

**Zeeman Energy**

Free energy associated with an external field is written as (Zeeman energy)
The minimum of Zeeman energy is achieved by aligning magnetization with the applied field.

**Anisotropy Energy**

The second important energy term is the magneto-crystalline anisotropy energy. Spin is coupled to orbital momentum through spin-orbit interaction; and crystal anisotropy can interact with spin via orbital momentum in the presence of crystal field. Phenomenologically, the free energy can be expressed in the equation below for hexagonal crystals (e.g. Co) [74]

\[
F_a = \int (K_1 \sin^2 \theta + K_2 \sin^4 \theta) dV
\]  

(2.5.4)

In which \( \theta \) is the angle between magnetization and the c-axis of the crystal.

And for cubic crystals

\[
F_a = \int [K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2] dV
\]  

(2.5.5)

In which \( \alpha \) are the direction cosines of the magnetization vector.

The crystal anisotropic field determines the direction of magnetization at zero external fields, thus the easy magnetization axis in the crystal. For example, in Co, \( K_1, K_2 > 0 \), so to minimize the anisotropy energy, the c-axis in the HCP structure is the easy axis. The same rule can also be applied to the cubic crystals, in which for Fe \( K_1 > 0 \), meaning the \([001], [100] \) and \([010] \) are easy axes, while in Ni crystals \( K_1 < 0 \), the easy axis is \([111] \).
An effective field can be derived from the energy terms to represent the anisotropy energy at the equilibrium direction.

\[
\frac{\partial f_a}{\partial \theta} = \mu_0 H_a M_s \sin \theta \quad (2.5.6)
\]

\[
H_a = \frac{1}{\mu_0 M_s \sin \theta} \left( \frac{\partial f_a}{\partial \theta} \right)_{\text{equilibrium}} \quad (2.5.7)
\]

In which \( f_a \) is the free energy density and \( M_s \) is the saturation magnetization.

**Exchange Energy**

The exchange interaction is the origin of ferromagnetism. Spins tend to be aligned (ferromagnetism) or anti-aligned (ferrimagnetism/antiferromagnetism) due to exchange interaction. A convenient model to deal with this energy is the Heisenberg model, in which the Hamiltonian is written as

\[
H_{ex} = - \sum_{i,j} J_{ij} S_i S_j \quad (2.5.8)
\]

\( J_{ij} \) is the exchange integral which is a strong function of spin-spin distance, typically decrease to zero rapidly as when the distance becomes larger. So it is reasonable and quite safe to only include the nearest neighbor spins in this Hamiltonian. When \( J_{ij} \) is positive, spins prefer to get aligned; while when it is negative, spins tend to get anti-aligned.

The magnitude of exchange integral can be estimated from Curie temperature \( T_C \) based on the classic Weiss molecular field theory.
\[ J = \frac{3kT T_C}{2zS(S + 1)} \]  

(2.5.9)

Where \( z \) is the number of nearest neighbor atoms, \( S \) is the spin number. The total exchange energy can be quite large; in some cases it can play an important role in determining the phase of a magnetic alloy. For example, it is believed that Fe has a BCC structure at room temperature due to the high magnetic moments of BCC phase. It contributes about -0.3 eV/atom of energy into the Gibbs free Energy. When temperature goes over the Curie temperature, the magnetic ordering disappears, which results in a phase transition in Fe from BCC to FCC [75].

Microscopically the exchange energy can also be written as a function of local magnetization

\[ E_{exch} = A \int_V (\nabla \hat{m})^2 dV \]  

(2.5.10)

In which \( A = 2JS^2/\alpha \) is the spin exchange stiffness constant (\( \alpha \) is the lattice constant) while \( \hat{m} \) is the unit vector of magnetization. The effective field from exchange interaction is

\[ \tilde{H}_{exch} = 2A \nabla^2 \hat{m} \]  

(2.5.11)

This is totally isotropic, in contrary to the magneto-crystalline anisotropy field.

**Demagnetization Energy**
The demagnetization energy is also known as shape anisotropy energy, which is closely related to the shape and magnetization direction. Its nature is based on magnetic dipolar interactions. Gauss’s law requires that the divergence of $\mathbf{B}$ is zero, as

$$\nabla \cdot \mathbf{B} = \nabla \cdot \mu_0(\mathbf{H} + \mathbf{M}) = 0$$  \hspace{1cm} (2.5.12)

So that a stray field is present

$$\nabla \cdot \mathbf{H}_d = -\nabla \cdot \mathbf{M}$$  \hspace{1cm} (2.5.13)

The related energy term would be

$$F_d = -\frac{1}{2}(\int \mathbf{M} \cdot \mathbf{H}_d) dV$$  \hspace{1cm} (2.5.14)

A simple way to characterize the demagnetization field is by using the demagnetization tensor, which is determined by the sample geometry.

$$\mathbf{H}_d = -\mathbf{N} \cdot \mathbf{M}$$  \hspace{1cm} (2.5.15)

In ellipsoidal samples with uniform magnetization, $\mathbf{N}$ reduces to scalars along the three major axes. And

$$N_x + N_y + N_z = 1$$  \hspace{1cm} (2.5.16)

In some high symmetric cases, the demagnetization factor can be simply inferred as below (the three numbers are along x,y,z directions; in thin film z is normal to the film plane; while in rod samples z is along the longitudinal direction, all are in SI units):

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>1/3</td>
<td>1/3</td>
<td>1/3</td>
</tr>
<tr>
<td>Thin film</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Rod</td>
<td>1/2</td>
<td>1/2</td>
<td>$\frac{1}{2}$</td>
</tr>
</tbody>
</table>
2.5.2 Frequency of spin precession derived from the LLG equation

With the knowledge of all the energy terms; it is possible to solve the Landau-Lifshitz equation and obtain the spin precession frequency in ferromagnetic materials. There are several possible modes of spin waves that exist in ferromagnetic samples, most importantly, the Kittel mode, in which all spins precess with the same phase [76]; and the Perpendicular Standing Spin Wave (PSSW), [34] as well as the Deamon-Eschbach magneto-static waves [77]. The Kittel mode is also called the uniform mode; and in this mode all the magnetizations are uniform and precess with the same phase (wavenumber $k = 0$), resulting in a macroscopic magnetic charge distribution on sample surfaces. The resulting dipolar field (demagnetization field) together with the external field and the anisotropy field determines the frequency of the Kittel’s mode. Its energy is the lowest of all the possible magnetostatic modes, making it a preferred relaxation channel for spin systems [9, 33, 34]. When spins precess with non-zero k, macroscopic magnetic charge does not exist anymore, instead magnetic charges build up inside the sample because the magnetization is not uniform. At the same time, exchange interaction kicks in as a result of misalignment of neighboring spins. Both volume and surface waves can exist in this case and will be discussed in more details later [9]. In magnetic thin films, the PSSW can also be excited; and it is mainly a result of the exchange interaction in which forward
going and reflected spin waves form standing waves across the depth of the film. The wavelength is quantized, which is a signature of standing waves [34].

The dispersion relationship of Kittel’s mode, the most important mode observed in my experiment, is discussed below. The equations are partially following the discussions in the thesis of Kaufmann [78].

**Kittel’s Mode**

It is easier to solve the Landau-Lifshitz equation in spherical coordinate. [79]

Starting from magnetization vector as

\[
dM = M_s dr e_r + M_s d\theta e_\theta + M_s \sin \theta d\phi e_\phi
\]

(2.5.17)

In which \( M_s \) is the saturation magnetization.

As mentioned before, the effective field can be derived directly from the free energy as

\[
H_{eff} = -\frac{1}{\mu_0 M_s} \frac{\partial F}{\partial m}
\]

(2.5.18)

\[
= -\frac{1}{\mu_0} \left( \frac{\partial F}{\partial r} e_r + \frac{1}{M_s} \frac{\partial F}{\partial \theta} e_\theta + \frac{1}{M_s \sin \theta} \frac{\partial F}{\partial \phi} e_\phi \right)
\]

During the precession motion, the magnitude of magnetization is kept constant, so the time derivative of magnetization is only dependent on the angle.

\[
\frac{dM}{dt} = M_s \frac{d\theta}{dt} e_\theta + M_s \sin \theta \frac{d\phi}{dt} e_\phi
\]

(2.5.19)

\[
M \times H_{eff} = \frac{1}{\mu_0 \sin \theta} \frac{\partial F}{\partial \phi} e_\theta - \frac{1}{\mu_0} \frac{\partial F}{\partial \theta} e_\phi
\]

(2.5.20)
By taking these equations into the LLG equation, I arrive at

\[
\frac{d\theta}{dt} = -\frac{\gamma}{M_s \sin \theta} \frac{\partial F}{\partial \phi}
\]

\[
\frac{d\phi}{dt} = \frac{\gamma}{M_s \sin \theta} \frac{\partial F}{\partial \theta}
\]

(2.5.21)

(2.5.22)

Now the free energy can be expanded around the equilibrium using the Taylor series as

\[
F = F_0 + \frac{1}{2} \left( F_{\theta \theta} \theta^2 + 2 F_{\theta \phi} \theta \phi + F_{\phi \phi} \phi^2 \right)
\]

(2.5.23)

With harmonic oscillation of \( \theta \) and \( \phi \) around the equilibrium direction, Equation 2.4.21 and 2.4.22 can be written in the frequency domain as

\[
\left( \frac{\gamma F_{\theta \theta}}{M_s \sin \theta} - i\omega \right) \theta + \frac{\gamma F_{\phi \phi}}{M_s \sin \theta} \phi = 0
\]

(2.5.24)

\[
\frac{\gamma F_{\theta \theta}}{M_s \sin \theta} \theta + \left( \frac{\gamma F_{\phi \phi}}{M_s \sin \theta} + i\omega \right) \phi = 0
\]

(2.5.25)

The non-trivial solution to this equation sets requires that the determinant of parameter matrix to be zero, resulting in a solution for \( \omega \)

\[
\omega = \frac{\gamma}{M_s \sin \theta} \sqrt{\left( \frac{\partial^2 F}{\partial \theta^2} \right)^2 - \left( \frac{\partial^2 F}{\partial \theta \partial \phi} \right)^2}
\]

(2.5.26)

By inserting all the free energy terms into Equation 2.5.26, the precession frequency for the Kittel’s mode becomes available. This solution is quite general and can be applied to materials with high magnetocrystalline anisotropy field, as to be discussed in Chapter 5.
Real Case Analysis

In uniaxial anisotropy field, the free energy can be evaluated and applied to Equation 2.5.26 to get the frequency. Assuming the c-axis lies along [1 0 0] orientation in the spherical coordinate ([0 0 1] direction in Cartesian coordinate), the free energy is written as (\(K_x\), \(K_y\), and \(K_z\) are the magnetocrystalline anisotropic constants with respect to each major axes, and assuming magnetization \(M\) is in the direction of \((1, \theta, \phi)\):

\[
F = -K_x \sin^2 \theta \cos^2 \phi - K_y \sin^2 \theta \sin^2 \phi - K_z \cos^2 \theta \\
- \mu_0 M_s (H_x \sin \theta \cos \phi + H_y \sin \theta \sin \phi + H_z \cos \theta) \\
+ 1/2\mu_0 M_s^2 \cos^2 \theta
\] (2.5.27)

As mentioned in the previous Chapter, I need to take derivatives of free energy as a function of \(\theta, \phi\) to obtain the effective field; this is done at the equilibrium direction. In my experiment, samples are mostly thin plates, and the demagnetization field dictates that the easy axis is in-plane. The direction of external field is also in-plane along the diffusion line during the measurement, so if there is no significant out-of-plane anisotropy filed, the magnetization is mostly in-plane. Assuming the external field is along the \(x\) direction, then

\[
\frac{\partial^2 F}{\partial \theta^2} |_{\phi=0} = (-2K_x + 2K_z - \mu_0 M_s^2) \cos 2\theta + \mu_0 M_s (H_x \sin \theta + H_z \cos \theta) \] (2.5.28)

\[
\frac{\partial^2 F}{\partial \phi^2} |_{\phi=0} = (2K_x - 2K_y) \sin^2 \theta + \mu_0 M_s H_x \sin \theta \] (2.5.29)
\[ \frac{\partial^2 F}{\partial \theta \partial \phi_{\phi=0,H_x=0}} = 0 \]  \tag{2.5.30}

Inserting all these derivatives into Equation 2.5.26, I obtain

\[ \omega = \frac{\gamma}{\sin \theta} \sqrt{\left( -\frac{2K_x}{M_s} + \frac{2K_y}{M_s} - \mu_0 M_s \right) \cos 2\theta + \mu_0 H_x \sin \theta + \mu_0 H_z \cos \theta} \]

\[ \sqrt{\left( \frac{2K_x}{M_s} - \frac{2K_y}{M_s} \right) \sin^2 \theta + \mu_0 H_x \sin \theta} \]  \tag{2.5.31}

In real samples the crystal structure and lattice orientations can be determined using EBSD (Electron Back-Scattering Diffraction), such that with known external field and saturation magnetization, the anisotropy field can be calculated using the above equation from the spin precession frequency. I will discuss this process in more details in Chapter 5.
Chapter 3 Femtosecond laser pump-probe system

I rely on the femtosecond laser pump-probe system for all my experiments. In this Chapter, I explain the detailed equipment setup and make relevant noise analysis.

3.1 Femtosecond laser pump-probe system setup for the TDTR

Figure 3.1 is a schematic of our femtosecond laser system used for the TDTR measurement [80].
Figure 3.1. Pump-probe system for the TDTR measurement. A mode locked Ti:Sapphire laser emits laser pulses with 100 fs duration. A combination of two half wave plate and polarizing beam splitter enable us to separate the pump and probe beams with tunable power. The pump beam path is controlled by a delay stage for tuning the arrival time of the pump pulses. The delay stage has 6 micron accuracy, which transforms into 40 fs time resolution. The beams are focused through the same objective lens, giving us a spatial resolution of around 3.6 microns (laser spot size). A double modulation technique is used for gaining higher Signal-to-Noise Ratio (SNR), which is explained in the next section. This figure is copied from Changdong Wei through private communications.

We have the Spectra-Physics Tsunami Ti:Sapphire mode locked laser as the laser source, it has a repetition rate of 80 MHz and the pulse width is around 100 fs. The laser passes
through a pair of half wave plates for the pump-probe beam total power tuning and power distribution tuning. In between the half wave plates is the optical isolator that prevents reflection from lens/sample surfaces back into the Tsunami laser cavity. The output from Ti:Sapphire Tsunami laser is a little bit elliptical at the best cavity alignment (corresponding to highest output power), the beam divergence in the x-y direction is also not the same, so we designed a “telescope system” for divergence and shape tuning. This “telescope” combined with a 2 m lens placed right after it serves as a collimator, and the key principle for the location of the 2 m lens is to make sure that the beam waist is at the sample surface with the mechanical delay stage is at its central location. This arrangement is to make sure that the diameter of the pump beam does not change significantly due to a longer beam path, as the sample surface is always within the Rayleigh Length of the beam. The Rayleigh length is calculated as:

$$z_R = \frac{\pi \omega_0^2}{\lambda}$$  \hspace{1cm} (3.1.1)

In which $\omega_0$ is the beam waist and $\lambda$ is the wavelength. Our wavelength is around 800 nm and the beam waist is around 1 mm, the calculated Rayleigh Length is 4 m. By putting the beam waist at the sample surface when mechanical delay stage is in the central position, I can make sure that the sample surface is always inside the Rayleigh Length no matter where the mechanical delay stage is, so the focused beam spot diameter keeps almost the same in the whole range of delay time that I am interested (mostly from -10 ps to 4 ns, corresponding to 1.5 m in the movement of mechanical delay stage and 3 m change in the pump beam path length). The beam is then split with a Polarizing Beam
Splitter (PBS) into pump and probe beams. The pump beam goes to a retroreflector mounted on the mechanical delay stage, so that by moving the delay stage I can accurately control the time of arrival between pump and probe pulses. The accuracy in the delay stage position control is 6 microns, corresponding to a time resolution of 40 fs in the time domain.

For better Signal-To-Noise Ratio (SNR) I use Electro-Optical Modulator (EOM) running at 9.3 MHz in TDTR thermal conductivity measurement for a high-frequency pump modulation and a chopper placed on the probe beam for a low-frequency probe modulation [21, 35, 37-39, 81]. The modulated signal is finally fed into a RF lock-in amplifier synchronized to the EOM for the first stage demodulation and then the analog output signal from the lock-in amplifier is read by a PC based DAQ card, which I use a LabView based software to do a second stage demodulation for the chopper. The chopper is running at approximately 200 Hz, a frequency low enough for the implementation of this low-cost demodulation.

Both the pump and probe beams are focused through the same objective lens onto the sample surface. The reflected probe beam is then directed to the photodiode detector for reflectivity measurement. This is also the system Changdong Wei (our group member) used to do heat capacity measurement, by changing the modulation frequency from 9.3 MHz to around 100 KHz [80].

The laser power we use is different for each application. For TDTR thermal property measurement, the pump and probe powers are equal and is usually around 15 mW. The
upper limit of the power is determined as follows: pump power should not be too high in order to lower pump scattering into the photodiode, and probe power should not saturate the photodiode detector. In this basis the powers should be as large as possible to decrease laser shot noise. For the probe beam deflection measurement, the pump power I use is typically 50 mW; and for the spin precession measurements, I use the maximum power I can get from our laser for the pump, typically 170 mW. The probe power is kept the same as around 10 mW. Both of these experiments require high pump power for heating and the detectors are home-built photodiode bridge circuit (the pump scattering is cancelled by the bridge circuit so pump scattering is not a big concern here).

3.2 Femtosecond pump-probe system for surface motion measurement

It did not take much effort to change the above TDTR settings for surface motion measurement. I use the deflection of the probe beam to measure the surface slope change as a result of the intensive laser heating. The reflected probe beam from sample surface is fed into a split-photodiode, which has two separate active photodiode areas that can measure the position of laser beam (as shown in Figure 3.2, the same principle is also used in AFM for cantilever motion detection), and all other components in the TDTR system is kept the same. In measurement, I first use the maximum of the thermoreflectance signal to perfectly align pump and probe beams (the focused pump and probe beam are in perfect overlap if the thermoreflectance signal is maximized).
The pump beam is then accurately tilted at the Polarizing Beam Splitter (PBS) right before the objective lens, so that when focused using the objective lens, this tilting results in a lateral movement of the focused beam spot. Thus I have an accurate control of pump-probe distance with an accuracy of 0.1 microns determined by experiments.

### 3.3 Time-Resolved MOKE setup

I used the same laser pump-probe system to do time-resolved MOKE measurement. One problem I need to solve in this setup is that I am interested in the polarization of the reflected probe beam, so when reflecting back from sample surface, it has to avoid passing through the Polarizing Beam Splitter (PBS). A separate optical path is designed to divert the probe beam away from the PBS and fed the probe beam directly into the MOKE polarization analyzing system. That system is composed of a half wave plate, a Glan laser polarizer, and a homemade photodiode bridge circuit for measuring differential signal from s and p polarized light. The whole system is shown in Figure 3.3.

In the MOKE side, the measurement is most sensitive to the out-of-plane part of magnetization, as shown in Figure 3.4 for MOKE geometry and Figure 3.5 for my measurement.
Figure 3.2. (a) Schmetics of the optical path in the probe-beam-deflection measurement system. This system is essentially to the one used to do TDTR by Changdong Wei shown in the previous section, with an exception of the detection region. This measurement requires that pump and probe beams are separated by several microns and the use of home-made split-photodiode for detecting the location of the laser spot. (b) Sketch of the split-photodiode, the red dot represents the reflected probe laser beam. In this case it is shifted to the left, so the left half of the photodiode measures a higher optical signal than the left. The differential signal between the two halves is proportional to the laser beam position.
Figure 3.3. Schematic of the Time-Resolved MOKE system. The laser pump-probe path and signal modulation parts are the same as the TDTR measurement setup. For polarization measurement, the reflected probe beam is diverted to a home-made polarization analysis detector, composed of a half wave plate, a Glan-Laser polarizer and a photodiode bridge circuit. An electromagnet is used for an external field.
As mentioned before, I first use the thermoreflectance signal to perfectly align the pump and probe beams. The radius of both beams is measured using a knife-edge method, and the result is 3.6 microns. For the pump beam, average power before the half mirror is 150 mW in my experiment, consider that the half mirror chops off half of the power, the energy density on sample surface is approximately 2.3 mJ/cm^2, which is more than enough to initiate the precession of spins.
Figure 3.5. Three geometries in Magneto-Optical Kerr Effect. MOKE is only sensitive to the partial component of magnetization along the beam incident direction. Generally speaking, there are three possible MOKE geometries: Polar, Longitudinal and Transverse. Polar MOKE signal is usually 10 times larger than the longitudinal and transverse geometry ones.
Figure 3.6. a) Polarization state of the reflected probe beam, the light gets a small elliptical component. During measurement I use a half wave plate to tune the bridge photodiode into balance, meaning the polarization is almost 45 degrees with respect to the main axis of the polarizer. The first order effect of this ellipsometry is canceled. For simplicity I only detect the linear polarization part; b) MOKE geometry in my experiment. Although the DC magnetization vector is mostly in-plane, I am interested in the AC part of the magnetization. So my measurement is actually in a polar MOKE geometry.

MOKE has three possible geometries, the polar, longitudinal and transverse [82]. In polar MOKE geometry the magnetization is normal to the sample surface, while in the longitudinal and transverse geometry the magnetization is parallel to the surface. Usually polar MOKE has a signal many times stronger than longitudinal and transverse modes. The reflected light not only changes its polarization but also has changes in ellipsometry,
as shown in Figure 3.6 (a). However, the ellipsometry is mostly very small and it requires more equipment for accurate measurement. In my setup, I only measure the change in polarization, which is enough for the detection of spin dynamics. Figure 3.6 (b) shows the precession of spins in the measurement geometry. In my experiments, external field is applied parallel to the sample surface and the direction of the incident laser light is almost perpendicular to the sample surface (being focused through a 20X objective lens with 10 mm focal length). When precession starts, the magnetization vector has an oscillating out-of-plane component that is picked up by the laser in the Polar geometry.

The MOKE signal is in the sub-millidegree range, thus for accurate detection of an MOKE signal, I built a “photodiode bridge circuit” for polarization detection. The circuit is based on a previous design of Jay Jung in Prof. Chris Hammel’s group and Jim Burns in our electronic shop, and it proved to be highly successful, (Figure 3.7). I also learnt a lot from Crooker’s thesis for the circuit design [83]. The principle of this bridge circuit is to measure the differential signal from the two photodiodes and fed it to op-amp for initial amplification. In this case, the probe beam is polarized horizontally before the objective lens, then after reflecting from sample surface, and picking up the MOKE signal, it goes through a half-wave plate, which turns its polarization into 45 degrees between horizontal and vertical. The half-wave plate also has the effect of compensating polarization changes due to mirror reflections and focusing through the objective lens. As I am measuring the frequency of spin precessing, which is only sensitive to the AC part of the MOKE signal, I can compensate this DC part signal without disturbing the frequency measurement. After the half wave plate, the light is fed into a Glan-Laser
polarizer, which splits the probe laser into s and p polarization parts. The s and p beams are then fed into the photodiode bridge circuit for differential signal extraction. This circuit also has the advantage of high common mode rejection.

Because the laser polarization is at 45 degrees, the s and p parts have almost equal power in the DC part. This can be used as an indicator for the half wave plate rotation to make sure the bridge is balanced. During measurement, I rotate the half wave plate according to DC part of the differential signal observed in oscilloscope to make sure that the DC part is almost zero.

The ellipsometry of the reflected beam is also an indicator of spin precession; however, it requires extra equipment (a quarter wave plate) and very fine tuning for a good measurement. Here in the bridge circuit, as shown in Figure 3.7, the differential signal due to ellipsometry is almost canceled out to the first order, and the measured signal is very insensitive to ellipsometry. The polarization itself can provide enough information on the precession frequency, so here I only focused on polarization measurement.

The output of the photodiode bridge circuit can be related to the laser polarization angle as shown in Figure 3.8.
Figure 3.7. Schematic diagram of the photodiode bridge circuit. In real applications the load resistor R3 is changed to 10K ohms for high-frequency application and also to suppress self-oscillation of the circuit, at a price of 10 times lower amplification.
Figure 3.8. Schematic of the polarization angle as a function of circuit output signal, purple arrow is the original state (at 45 degrees) when the bridge circuit is balanced, black arrow is the changed polarization due to the Kerr effect.

When the two arms of the bridge circuit is balanced (polarization at 45 degrees), for a small change of polarization of the probe beam, the E-component at the x-arm is

\[ E_1 = A \cos(45 + \theta) \]  \hspace{1cm} (3.3.1)

And in the y-arm

\[ E_2 = A \sin(45 + \theta) \]  \hspace{1cm} (3.3.2)
the differential signal is

\[
\frac{I_1 - I_2}{I_1 + I_2} = \frac{E_1^2 - E_2^2}{E_1^2 + E_2^2} = \cos(90 + 2\theta) = \sin(2\theta) \approx 2\theta
\]  

(3.3.3)

and it is clear that the differential signal is proportional to precession angle.

In the bridge circuit, the op-amps are carefully chosen as OPA627 produced by Texas Instrument, for its wide bandwidth and low noise characteristics. For optimal noise suppression and better spatial resolution, I chose to operate the circuit at modulation frequency of 500 KHz (higher frequency results in lower 1/f noise) so that I replaced the load resistor in the original design into a 10K ohms resistor, here the trans-impedance gain is around 10^4 V/A. A key issue in this circuit design is to minimize the wire length and offer some kind of shielding at the connection between two photodiodes and the differential signal op-amp, shown in the circuit diagram as the area in a rectangular box.

**3.4 Frequency domain analysis and noise**

I use double modulations to achieve very high SNR during the measurement. As shown in the schematics of our set-up, I use Electro-Optical Modulator (EOM) for pump beam power modulation at a very high frequency. The EOM acts like a fast switch that operates at 50% duty cycle in our experiment. An rf-lockin amplifier is synchronized to the EOM frequency for probe signal demodulation. This eliminates noise from pump power drifting. On the probe beam path, a mechanical chopper is installed for a low frequency
modulation (200 Hz), a DAQ card based software demodulation process eliminates noise from probe power fluctuations and in-balance in the photodiode circuit, as well as the pump scattering into the detector. This low frequency modulation is highly essential as most of the background noise is induced from pump scattering and coherent pickups.

It is essential to understand the frequency behavior of the signals and the principle of lock-in amplifiers. The discussion below is inspired by Kato’s previous work and SRS844 manual [84].

A lock-in amplifier is behaving as a combination of mixer and low-pass-filter. In the frequency domain, assuming that I have a signal with frequency $f_0$ and some background signal

$$B + A \sin(2\pi f_0 + \phi)$$

(3.4.1)

A mixer is multiplying the input signal with a reference signal at $f_0$, so that

$$\begin{align*}
(B + A \sin(2\pi f_0 t + \phi)) \ast \sin(2\pi f_0 t + \phi_r) &= B \sin(2\pi f_0 t + \phi_r) + \frac{1}{2} A \cos(\phi_r - \phi) - \frac{1}{2} \cos(4\pi f_0 t + \phi_r + \phi) \\
&= B \sin(2\pi f_0 t + \phi_r) + \frac{1}{2} A \cos(\phi_r - \phi) - \frac{1}{2} \cos(4\pi f_0 t + \phi_r + \phi)
\end{align*}$$

(3.4.2)

It can be seen that the remaining output has 3 frequency components, one is DC part (the only desired signal is present in this part), and frequency at $f_0$ and $2f_0$. Consequently I want to get rid of the $f_0$ and $2f_0$ frequency parts using a low pass filter.
In our SRS844 lock-in amplifier, the low-pass filter is Butterworth filter, I am able to choose the filter orders of 1, 2, 3 and 4, the corresponding filter slopes are 6, 12, 18, 24 dB/octave. The filter cut-off frequency is determined by the time constant I choose.

The Butterworth filter has a frequency spectrum of

\[ [1 + (f/f_c)^{2n}]^{1/2} \]  

(3.4.3)

In which the cut-off frequency is related to the time constant as

\[ t_c = 1/(2\pi f_c) \]  

(3.4.4)

One criterion for time constant selection is to make sure that the cut-off frequency is much smaller than the modulation frequency so that the \( f_0 \) and \( 2f_0 \) parts are efficiently rejected. For TDTR and beam deflection measurements, I usually chose a time constant of 300 micro-seconds with 6 dB/Oct slope, so the cut-off frequency is 530 Hz. The attenuation at the usual measurement frequency at 9 MHz is more than enough to fulfill this requirement.

There is another issue needs to be taken care of. Both the EOM and mechanical chopper are running like on/off switches, so instead of a single modulation frequency \( f_0 \), the signal do have higher harmonic parts at \( 3f_0, 5f_0, 7f_0 \ldots \), as well as the reference signal. All of these higher-harmonics can mix with the reference signal and significantly contribute to the DC part after the mixer, which can pass through the low-pass. A solution to this problem is to add a home-built resonance circuit after the photodiode. The resonance circuit is very easy to make, by just adding an inductor in series into the circuit (a parallel
capacitor may be needed for required resonance frequency). This component significantly amplifies signal within the range of its passing bandwidth (it is actually a band pass filter, with a quality factor of around 10) and suppress higher frequency harmonics. After I feed this signal to a pre-amp I add another low-pass filter with cut-off frequency at 30 MHz to further cut the higher harmonics off. This filter combination efficiently filters out unwanted higher harmonics and at the same time amplifies the signal.

The output of the rf-lockin amplifier is further sent into a NI DAQ card and a computer based software lock-in for demodulation. The software based lock-in has a frequency that is synchronized to the chopper frequency. I do it this way in order to minimize the cost of the system, as a software lock-in is much cheaper than a physical lock-in amplifier and it can still do a good job at 200 Hz. The selection rule of the chopper frequency is to make sure that the first lock-in time constant is small enough for the low-pass filter not to filter out chopper frequency; also the sampling frequency required by Nyquist theorem does not exceed the maximum sampling frequency of the computer based DAQ card.

However, the frequency domain spectrum is more complicated than previously mentioned. Due to the pulse nature of our laser, there is another frequency term that comes into play. The laser repetition rate is 80 MHz, so in the frequency domain, the laser itself has a frequency spectrum composed of infinite number of delta-functions at frequencies of multiples of 80 MHz. When the pump beam is modulated at some frequency $f_0$ (e.g., 9 MHz), I am actually adding very sharp side lobes to both sides of the original comb-like spectrum at odd multiples of $f_0$. For TDTR measurement, in the time
domain, the measured signal is a product of temperature change and the probe beam intensity, which changes into a convolution between frequency response of the temperature change and the frequency spectrum of the comb-like probe beam in the frequency domain. Delay time $t$ contributes to the measured signal in the forms of a phase shift. This was discussed in detail in Cahill’s paper [35].

The modulation frequency also determines the thermal diffusion length. For a point heat source on the surface of a half space, as calculated in by Cahill [35], the temperature at a distance $r$ from the heat source is

$$g(r) = \frac{\exp(-qr)}{\sqrt{\pi} \Lambda r}$$  \hspace{1cm} (3.4.5)

In which

$$q^2 = \frac{i\omega}{D}$$  \hspace{1cm} (3.4.6)

$D$ is the heat diffusivity of the material, $\omega$ is the frequency and $\Lambda$ is the thermal conductivity.

It can be seen that the temperature field has its characterization of spherical waves. The imaginary part of $q$ is the wavevector of the heat wave and the real part of $q$ determines its attenuation. Cu has a diffusivity of $1.1 \times 10^4 \ m^2/s$, and in Al the number is $8.5 \times 10^4 \ m^2/s$, both of them are relatively at the higher end of thermal diffusivity values. The calculated heat penetration depth is
\[ \delta = \sqrt{\frac{D}{\omega}} \] (3.4.7)

So for a high frequency modulation at 9.3 MHz (usually used for TDTR thermal conductivity measurement and in probe-beam deflection measurement), the heat diffusivity is 1.3 \( \mu \)m and 1.1 \( \mu \)m for Cu and Al respectively. Compared to the beam radius of 7.5 \( \mu \)m (when using the 10X objective lens), it is clear that the heat wave is almost going into the depth perpendicularly, as shown in the Figure 3.9. The spatial resolution in this measurement is determined by the beam spot size in this situation.

However, when it comes to the heat capacity measurement (which must be carried out at low modulation frequency at around 100 KHz) the thermal diffusion length is increased by about 10 times. For Al this increases to about 10 \( \mu \)m, comparable to the beam spot size. So the actual spatial resolution at this low frequency measurement is about the sum of the beam diameter and the thermal diffusion length.
Figure 3.9. Heat wave penetration depth and spatial resolution; (a) at 9.3 MHz modulation frequency, heat conduction is more likely 1-D; (b) low frequency modulation (around 100 KHz), there is more lateral heat transfer (heat penetration depth is about 10 microns). The effective volume is like a “spherical cap” in the high frequency case. Both has an Al top layer and assuming the laser beam radius is 7.5 μm.

For the MOKE photodiode circuit running at 500 KHz, the major source of noise is the photon shot noise. On a balanced bridge circuit, each arm should have same laser power.
Consider that the circuit is in fact a transimpedence amplifier, and assuming each arm has a power of \(1/2I_0\), the induced photon shot noise would be

\[
\sigma = \sqrt{I_0 hf} \quad \text{Watt/Hz}
\]  

(3.4.8)

And the noise in differential signal is

\[
\frac{I_A - I_B}{I_A + I_B} = \sqrt{\frac{2hf}{I_0}} = 2\theta_{min}
\]  

(3.4.9)

This is the noise limited sensitivity of the MOKE detector. As I use 800 nm laser photons for the measurement, the photon energy is close to 1.55 eV, and with a probe power close to 0.5 mW in front of the bridge circuit, the minimum detectable Kerr rotation angle would be around \(2 \times 10^{-6}\) degrees.

3.5 Beam spot size measurement

It is critical to make accurate beam spot size measurement. There are two methods available, one is the knife edge method, and the other is by moving the pump beam relative to the probe beam while detecting the pump-probe overlap [85].

I tried both methods and they gave consistent results. For the knife edge method, I have a very sharp knife edge placed on the focal spot of the objective lens, and the reflected pump beam intensity is measured using a photodiode. The knife edge is mounted vertically on a computer controlled mechanical stage so that the movement of the knife
edge is controlled with sub-micron-scale accuracy. The beam diameter is determined by
the movement of the knife edge between 10% light reflection and 90% light reflection.
This measurement is carried out in both horizontal and vertical directions and the beam
spot size is RMS of the two results.

Compared to the knife edge method, the beams overlapping method is easier to
implement and takes less time to carry out. In the perfectly overlapped condition (pump
and probe overlap with each other), the TDTR signal is at maximum. As both pump and
probe beams are Gaussian, the overlap area between the two beams as a function of beam
separation is also Gaussian with the same FWHM (Full Width Half Maximum). I am able
to easily move the pump beam on the focal plane by moving a high-accuracy rotation
stage which mounts the polarizing beam splitter right before the objective lens. As the
pump beam is rotated, at the focal plane the tilt is translated into a lateral movement as

$$\delta x = F \delta \theta$$  \hspace{1cm} (3.5.1)

In which F is the focal length of the objective lens and $\delta \theta$ is the tilting angle. This lateral
movement is in linear relationship with tilting angle and thus can be accurately measured.

An example of beam spot measurement is shown in Figure 3.10.

As the same with the knife edge method, the accepted beam radius is taken as RMS of the
vertical and horizontal measurement values.
Figure 3.10. Beam spot measurement by measuring pump-probe beam overlapping in the TDTR system, using a 10X objective lens, and then fitting result with a Gaussian curve. The overlapping area of the pump and probe beams is also a Gaussian, as a function of beam separation. Assuming pump and probe have same beam spot size, I can obtain the beam radius using the Gaussian fitting parameter, as discussed in the text. The measured beam radius is 7.5 μm [80], this figure is from a private communication with Changdong Wei.
Chapter 4 Surface Acoustic Wave Measured Using Femtosecond Laser Pump-Probe system

4.1 Calculated surface displacement field in Cu (001) surface

Based on the semi-analytical solution described in Chapter 2, the surface displacement due to laser induced expansion source can be calculated. A MatLab code is programmed to implement the solution and the code is listed in Appendix. The code is capable of calculating the surface motion as a function of elastic modulus, density and laser beam profile at any arbitrary cut crystal surface. Using this code, I have evaluated the surface responses due to laser induced thermal expansion source for two cases, they are the (001) surface of aluminum and copper. The elastic modulus of aluminum is taken from literature as $c_{11} = 108.2$ GPa, $c_{12} = 61.3$ GPa, $c_{44} = 28.5$ GPa, while copper has a $c_{11} = 169.0$ GPa, $c_{12} = 122.0$ GPa, $c_{44} = 75.3$ GPa [54, 86]. The calculation results are compared with my experimental ultrafast probe beam deflection measurements. The calculation results for Cu (001) and Al (001) are shown in Figure 4.1. Both the pump and probe laser
spots are assumed to be a perfect Gaussian shape, and the $1/e^2$ beam radius is 3.6 microns—the same value as our experimental beam spot measurement as discussed in Chapter 3. The frequency spectrum of SAW is determined by dividing the SAW speed in a particular material with the pump beam diameter. I then take derivative of the calculated surface displacement along the horizontal direction to be consistent with our probe beam deflection method. The result is further taken an average using a Gaussian window with 3.6 micron radius to account for the finite size of the probe beam. This acts as a low-pass spatial filter with the same central frequency as the excited SAW. The snapshot shown in Figure 4.1 is for a time of 4.7 ns after the pump beam deposit its energy. Both the SAW arrivals and skimming bulk wave arrivals are clearly visible. In the Cu (001) surface the pseudo-SAW (PSAW) modes are clearly visible as expected, while in the Al (001) surface PSAW modes are not present. Al has a much lower anisotropy than Cu such that the SAW arrival in the Al (001) surface is almost circular. To verify our calculations, I performed ultrafast laser pump-probe measurements using the set-up discussed in the previous Chapter. The pulse width is approximately 100 fs, which is much shorter than the propagation time of acoustic waves such that the pulse’s time profile can be considered as a delta-function. The pump power is 30 mW while the probe beam is 10 mW and the fluence is 0.92 mJ/cm$^2$ and 0.30 mJ/cm$^2$ respectively. Both were focused using a 20X long working distance objective lens. The transverse distance between pump and probe beam was controlled by the high accuracy rotation stage. After reflection from the sample surface, the position of the probe beam was detected by a split photodiode. The pump beam was modulated by an electro-optical modulator (EOM) operating at $~9$
MHz, and the probe beam was modulated using a mechanical chopper with a 200 Hz frequency. This double-modulation technique is very helpful in increasing the signal to noise ratio (SNR) to make the signal more visible. I used the deflection of the probe beam as a means to detect the surface motion, thus I was actually measuring the slope of the surface displacement at the detection point. This is accommodated by taking a derivative along the direction of probe beam deflection (in this case, the horizontal direction) in the real space after the inverse Fourier transform. The result is further averaged using a 2-D Gaussian function to account for the Gaussian shape of the probe beam, which has the same radius as the pump beam. This can also be completed by multiplying ik to the solution in k-ω space and time it with another Gaussian function to account for the probe beam. I choose to do it in real space for its simplicity in programming and ease of debugging. Figure 4.2 compares the calculation and experimental results, showing good agreement between them.
Figure 4.1. Dynamic surface displacements (going out of plane) for Cu (001) surface (a) and Al (001) surface (b). Both calculated images are taken at 4.7 ns after the pump beam arrives. The skimming longitudinal waves are marked as L, and the Rayleigh wave is marked as R. The existence of PSAW in the Cu (001) surface can be clearly seen in (a).
In Figure 4.2 the open circles are the experimentally measured deflection data with a pump-probe separation of 10 μm and a beam spot radius of 3.6 μm. Experiments were performed on single crystal Cu and Al samples. The delay time is the time it takes for the SAW to travel to the detection spot, and is in the range of nano-seconds. The experimental data and calculated ones are normalized to make a meaningful comparison (peak-to-peak amplitude is set to 1). In the experiment, the separation between pump and probe beams was larger than their combined radius; so that the thermal expansion single/effect can hardly be seen, as characterized by the smooth transition when the data go across zero delay time. The good agreement between the calculated curve and the experimental values serves as a validation of the calculation method for the thermal expansion source. For the Cu (001) surface, Figure 4.2 (a) is plotted along 7 degrees from the [100] orientation, in which the theory predicts the existence of Rayleigh Wave mode only which is consistent with the experimental results. Figure 4.2 (b) is along the direction 43 degrees from [100], the major peak is actually a PSAW mode. Our theory predicts that PSAW propagates faster than Rayleigh wave in this case, which is observable in Figure 4.2, either from time-of-flight or from the central wavelength (although the effect is subtle). The calculation shows that the PSAW has larger amplitude than the Rayleigh Wave, which was also observed in the experiment (not shown in the figure due to normalization).
Figure 4.2. Comparison between experimental and calculated surface deflection vs. delay time: (a) on the Cu (001) surface 7° from the [100] orientation with 8 μm beam separation; (b) on the same Cu surface and beam separation, 43° from the [100] orientation; (c) on Al (001) surface, along [100] orientation with a beam separation of 8 μm; and (d) on the same Al surface 43° from [100] orientation with 9 μm separation.

Figure 4.2 (c) and (d) show the calculated surface response for the Al (001) surface in comparison with experimental results. Figure 4.2(c) plots a comparison taken along the
[100] orientation. The Al (001) is almost isotropic in elastic properties; thus there is little change in the actual waveform for measurements made along different orientations in comparison with the results of Cu. A comparison is made near the [110] orientation (Figure 3(d), 43 degrees from [100]) with 9 μm beam separation, again showing good agreement between theory and experiment. The good agreement between the calculated and experimentally measured values on both Cu and Al along multiple orientations serves as a validation of both the theory and the experimental measurement.

4.2 Anisotropic elastic constants calculation using the SAW speed

One goal of my research is to efficiently measure anisotropic elastic constants $C_{ij}$ through measurement of SAW speed along several orientations on a polished surface. Although other methods can achieve higher accuracy (e.g. Acoustic Scanning Microscopy), the laser ultrasonic method has its advantage of easy alignment and high spatial resolution [22, 43, 45, 87, 88]. Such measurement can be performed in my setup by either rotating the sample itself or by moving the pump beam around relative to the probe beam, and computing the wave speed by the propagation distance divided by time-of-fly of the SAW wave.
The SAW wave speed can be calculated efficiently using the algorithm I programmed and discussed in Chapter 2. The same MatLab code can also be used for SAW speed calculations. Another piece of code is developed for the backward fitting of angular/orientation-dependent SAW speed to obtain the elastic constants. As the acoustic “modes” are actually where acoustic resonance happens, there are “poles” associated with these modes where resonance takes place. I introduced a small imaginary part into the frequency term to mediate the poles to make them visible. By choosing an appropriate imaginary part, the resonance peaks become sharp enough for accurate sound speed reading while still being visible.

Theories suggest that there is dispersion associated with SAW modes in multi-layer structures [45]. Waves at different frequencies have different speeds, so that the shape of the wave changes during propagation. However, for a single substrate the dispersion is absent. Dispersion can also be safely ignored for samples with a very thin capping layer, e.g. less than 100 nm, as the dispersion is a function of \(hk\), in which \(h\) is the capping layer thickness and \(k\) is the wavevector of the SAW wave. The central frequency of the SAW wave induced by laser thermal expansion sources is determined by the wave speed divided by the laser beam diameter. For Si and a 3.6 micron beam spot this is about 800 MHz, a very rough estimate of \(hk\) number is around 0.1, which is well below the limit for a serious consideration of dispersion. Si has a relatively high wave speed; for other materials, the \(hk\) number is even smaller, satisfying the condition for safely neglecting dispersion.
By neglecting dispersion in the measurement, the shape of the recorded SAW waveform should not change during propagation. So a simple method for SAW speed measurement is by using the wave propagation distance and then divides it with the time of fly, which can be demonstrated by our calculations shown in Figure 4.3.

Figure 4.3. Calculated SAW propagation waveform on Si (001) surface, along the [100] orientation. The beam spot size is 3.6 microns, and pump-probe beam distance is from 6.2 to 12.2 microns with an 1 micron spacing for each data curve.
A regular way for wave speed extraction is by using Fourier transforms of the surface displacement curve at three different locations and obtain the phase shift at certain frequencies.

After measuring the surface motion at 3 consecutive locations with a separation of $\Lambda x$, and surface motion in the time domain is $s(x,t)$

$$S(x, f) = F[s(x, t)] = A(x - x_0) \exp[i\theta(x - x_0, f)]$$  \hspace{1cm} (4.2.1)

for Fourier transform.

It is easy to obtain the principle argument function of the Fourier transformed signal, and if three data points are available I have

$$k = \frac{\theta(x_0 + \Delta x, f) - \theta(x_0 - \Delta x, f)}{2\Delta x}$$  \hspace{1cm} (4.2.2)

And using the definition of

$$v = \frac{\omega}{k}$$  \hspace{1cm} (4.2.3)

The phase velocity can be evaluated.

There are, however, several obstacles in measuring the velocity this way; one is the limited delay time window available on our laser setup. The mechanical delay stage can delay a maximum of 4 ns (a 0.6 m delay stage accounts for 1.2 m change in laser beam path length, corresponding to 4 ns). This Fourier transform method requires a full oscillation pattern be recorded, but in most cases 4 ns delay time is not sufficient to
capture a full pattern. Thermal expansion signal needs to be excluded in the measurement, and thus the beam separation has to be equal or larger than twice the beam radius, e.g. 7 microns when a 20X objective lens is used. This leaves little room for the 4 ns time window to cover an entire wave package.

An easier way for wave speed determination is by looking at some specific point on the waveform, e.g. the highest peak position, and tracking its position/delay time as a function of beam separation, as shown in Figure 4.4. Since there is little or no dispersion, the waveform shape should not change in the propagation process. A plot of the delay time of the measured peak vs. beam separation should be a straight line, whose slope is the wave slowness.

I have performed such a measurement on a single crystal Si sample, and measured the probe beam deflection signal for multiple orientations. The Si sample is a (111) cut surface, with 6-fold symmetry. The wave speed reported in literature and that from my calculation ranges from 4550 m/s to 4750 m/s, depending on the measurement orientation on the (111) surface.
Figure 4.4. Linear fitting of the delay time at the peak location and zero point location as a function of beam separations, based on the calculation shown in Figure 4.1. The peak position and zero point show a clear linear relationship as a function of beam separations, as expected. The slope of this linear fitting is used to calculate wave speed.
Figure 4.5. Calculated image of surface displacement on Si (111) at 2 ns as a result of laser induced thermal expansion source with 3.6 micron radius (the lateral units are in meters) using the semi-analytical solution. Multiple acoustic modes can be seen with the outmost ring being the longitudinal mode (almost isotropic) while the inner peaks with 6-fold symmetry are the SAW modes. The calculation shows that majority of the acoustic energy are distributed to the SAW mode.
Figure 4.6. Measured beam deflection signal as a function of delay time on Si (111) surface, along the (1 -1 0) direction, at various beam separations indicated in the inset of the graph (in microns). At larger separations, the signal jump at time zero diminishes, indicating that there is no overlap of the beams and the influence from thermal expansion is also diminished.
Figure 4.7. Backward fitting of the elastic constants from angular/orientation dependent SAW speed on the Si(111) surface. The speed vs angle plot is a periodic function with a period of 60 degrees due to the 6-fold symmetry.

It is almost impossible to calculate the elastic constants directly from the wave speed measurement. I used a least-squire fit method to extract the elastic constants. As a cubic crystal, Si has three independent elastic constants, $c_{11}$, $c_{12}$ and $c_{44}$. The crystal orientation is identified by a marker on the Si wafer. Due to the 6-fold symmetry on the (111) surface,
the wave speed has a period of 60 degrees, as shown in Figure 4.7. A consecutive wave speed measurement in a 30 degrees range is enough to obtain the whole speed information as well as the elastic constants.

In the experiments, I fixed the probe beam and gradually moved the pump beam away from it, and recorded the probe beam deflection signal as a function of delay time for each pump-probe beam separation. For each orientation, 5 measurements were taken and for the linear fitting to get the SAW speed. This process is repeated for each new orientation, as the sample is rotated to the next wave propagation direction.

Figure 4.7 shows one of the fitting results. In the fitting process, I first randomly chose a set of elastic constants, then compute the speed curve vs. propagation angle. The error between computed curve and measurement data is minimized each time when the values of the elastic constants are adjusted, using greedy algorithm.

And finally the result is $c_{11} = 155.7$ GPa, $c_{12} = 65.6$ GPa, $c_{44} = 80.9$ GPa, in comparison with literature values of $c_{11} = 165.7$ GPa, $c_{12} = 63.9$ GPa, and $c_{44} = 79.6$ GPa. The error is around 6.5% for $c_{11}$, 2.7% for $c_{12}$ and 1.1% for $c_{44}$.

Future work on this project is to introduce artificial gratings on the sample surface and excite narrow band SAW. With known wavelength and accurate evaluation of frequency (from Fourier transform) the wave speed as well as the elastic constants can be determined with much higher accuracy.
Chapter 5 Time-Resolved MOKE measurement of coherent spin precession and its application in localized saturation magnetization measurement

5.1 The reason for the use the dynamics of spin precession to measure saturation magnetization

Saturation magnetization is a very important property in magnetic materials. It is also a strong function of alloy composition, lattice parameter and crystal structure [73]. When electrons fill the orbits, Hund’s rule dictates that the unpaired electrons would have parallel spins, which makes them magnetic. Within crystals, when the distance between these magnetic atoms is appropriate, exchange interaction lowers the total energy when the spins of the atoms are parallel/antiparallel, forming the ferromagnetic/antiferromagnetic (or ferrimagnetic) materials. The number of unpaired electrons together with the lattice parameters (thus the magnitude of exchange integral)
determines the saturation magnetization. In metal alloys, the 3d electrons are mostly shared among individual atoms as conducting electrons and alloy composition controls the electron density as well as the lattice parameters. The famous Slater-Pauling (Figure 5.1) curve provides lots of information on the effect of alloying over magnetization. Among all the alloying systems Fe-Co has the highest magnetron number per atom (and very low crystal anisotropy), and thus is a very good soft magnetic material.

Figure 5.1. (a) Slater-Pauling curve for alloys between 3d elements showing significant effect of alloy composition on the magnetic moments; (b) spin-only magnetic moment/atom of Co-Fe alloy [89].
We are interested in experimentally determine more composition-dependent magnetic moment data, not only for binary alloys but also for ternary or higher order alloy systems [30]. The data will be very useful for discovering better magnetic materials, especially for rare-earth free permanent magnets with high crystal anisotropy. Such data are also highly valuable for the Material Genome Initiative, in which the magnetic interactions affects the phase stability through the Gibbs free energy [90].

However, as mentioned previously, all the currently available techniques have some drawbacks one way or the other that prevent them from being used for facile, accurate measurement of local (micron-scale) saturation magnetization. Most importantly, magnetic interaction is a long range effect and the collective excitations in spins are mostly not localized. It requires special techniques to individually manipulate spins (like the FMRFM) [91, 92]. Ultrafast laser pump-probe system has the required ability to locally excite and probe the dynamics of spin system that may be utilized for magnetization measurement.

5.2 Coherent spin precession in thin film samples

Spin coherent precession excited by ultrafast laser pulses in thin film samples has been experimentally observed for a long time [7]. The origin of this precession was discussed in Chapter 2. In addition to the thermal variation of magnetocrystalline anisotropy [93-95],
the temperature dependency of saturation magnetization can also initiate this precession motion, through abrupt change in shape anisotropy [96]. Using the TR-MOKE experimental setup that I developed, I was able to measure such coherent precession in magnetic thin film samples to verify that the experimental system functions properly. Figure 5.2 is a set of TR-MOKE data taken on a 10 nm Ni film on Si substrate at 0.24 T of external field applied in-plane. The sample was thermally evaporated onto a Si substrate, and the film thickness is controlled using a crystal thickness monitor during thermal evaporation.

Due to the precession motion of the magnetization vector, the time-resolved MOKE signal is very sensitive to the out-of-plane component of the magnetization, and displays a sinusoidal function of time with the same frequency as the precession. Due to the relaxation nature of this precession and the coupling between spin and crystal lattice, the energy and angular momentum of the spins keeps relaxing into the lattice, thus the sinusoidal function of the TR-MOKE signal is expected to have an exponential decay envelope [9] such that a function of

$$A \exp(-x/B) \sin(\omega t + \phi) + z$$

serves a very good fitting model for this signal allowing the extraction of the precession frequency. By neglecting the (a very reasonable assumption for FCC Ni) the Kittel’s equation shows

$$\omega = \gamma \sqrt{B_{ext}(B_{ext} + M_s)}$$

(5.2.2)
In which $\omega$ is the precession frequency and $\gamma$ is the gyromagnetic ratio, at room temperature the saturation magnetization of Ni is approximately 0.6 T. By inserting all the values into this dispersion relationship, the computed $\omega$ is the same as the experimental value of about 13 GHz. A further experiment on Ni film samples with
varying applied field was carried out to validate that the Kittel’s dispersion relationship works well when the crystalline anisotropy can be neglected.

5.3 Coherent spin precession in bulk materials (plates)

It is quite interesting to see how the precession behaves when film thickness becomes much larger than the optical penetration depth. An interesting set of experiments were performed by Lenk and his collaborators to measure the coherent precession in a wedged Ni film sample with thickness ranging from 80 nm to 180 nm [34]. Several possible modes of spin waves could be excited in these samples, including the uniform Kittel’s mode, the Perpendicular Standing Spin Waves (PSSW), Damon-Eshbach Surface Spin Waves, and Volume Modes (mostly observed in ceramic samples when optical penetration depth is in mm scale) [11]. The exact mode excited in a particular sample is highly dependent on the sample shape, geometry and laser penetration depth [97-99]. In generally, eigen-modes with profiles most similar to the laser energy deposition profile are the preferred relaxation channel. For thin film metallic samples, when the film thickness is smaller or comparable to the laser penetration depth (about 30 nm for Ni at 800 nm laser wavelength), the film is almost uniformly heated by the laser pulses such that the uniform Kittel mode is most favored mode of excitation. When the film thickness goes much larger than the optical penetration depth (e.g. over 100 nm), significant asymmetric laser heating preferably excites the surface spin waves as observed by Lenk et al. on Ni films [34]. Interestingly, for thicker films (e.g. 180 nm) when external field is
larger than 90 mT, majority of excited spin wave energy is redistributed to the Kittel mode, and the surface wave mode is almost invisible in their frequency spectrum, which is quite surprising and unexpected. They explained this phenomenon by introducing a non-linear effect and mode-crossing of two harmonic oscillations with adjacent frequencies and the fact that the Kittel mode has a lower frequency (thus lower excitation energy). This phenomenon may have another explanation. The excitation of surface spin wave mode and PSSW mode is mostly due to highly asymmetric laser heating on the surface. However, in order to effectively couple to the corresponding spin wave modes, the lateral pump laser beam diameter needs to match the spin wave wavelength. In their experiment they used a 60 micron diameter pump beam. At low fields (lower than 90 mT) the DE surface mode has a wavelength of around 3 microns (by fitting to the dispersion relationship with a propagation direction perpendicular to the magnetic field). With increasing applied filed, the wavelength of DE spin wave is expected to decrease. When a threshold wavelength is reached, coupling to DE surface mode is no longer preferred; and lower energy \( k = 0 \) Kittel mode becomes a favored mode for relaxation.

In my experiments, all diffusion multiple samples are in bulk forms, with millimeter scale thickness. When the laser pulses arrive at the sample surface, only the top 50 nm thick material undergoes the intensive and ultrafast temperature increase, accompanied by ultrafast demagnetization and coherence precession, while the rest of the sample is not affected. During the precession, the boundary between the excited spins and non-excited spins is defined by the laser beam acting as virtual walls where magnetic charge builds up as a result of the precession of the dynamic part of magnetization vector. The dynamic
field is present as a result and its behavior is very similar to spins in a circular thin film sample. In this case the Kittel mode is a favored relaxation channel, in which almost all the spins precess with the same phase and frequency. The demagnetization factors for precession frequency calculation in the Kittel’s formula can simply be taken as those for circular thin film samples magnetized along the surface.

This argument is supported by our experimental observations of precession frequency as a function of external field, shown in Figure 5.3 and Figure 5.4, assuming the saturation magnetization of Fe being 2.1 T and Ni being 0.6 T, and a gyromagnetic ratio of 2.8 MHz/Gauss.

It is clear that the measured and computed results agree very well, to ensure saturation, the applied external fields are all above 0.3 T and samples are magnetized along the longitudinal direction (longest direction with a very high aspect ratio, so it is the easy magnetization direction in terms of shape anisotropy).

In those experiments both the pump and probe beams are focused using a 20X objective lens, and the beam radius is measured to be around 3.6 microns. I moved the pump beam around the probe beam to see if there is any propagating spin wave excited, the result is negative. Careful analysis of the time-domain data also excludes the existence of any PSSW or surface modes. The conclusion here is that uniform Kittel mode is the favored relaxation channel in bulk metallic samples and it is safe to correlate the precession frequency with external field and saturation magnetization using the Kittel’s dispersion equation.
Figure 5.3. Measured TR-MOKE signal and fitted sinusoidal function of an Fe plate sample. The fitted frequency is 29 GHz, at an external field of 0.42 Tesla. The sample is pure Fe with a thickness around 0.5 mm, length of 20 mm and width of 10 mm. An exponential decay sinusoidal function fits the measured precession data well.
Figure 5.4. Field dependency on the precession frequency measured experimentally in comparison with the calculated frequency using the Kittel equation for an Fe plate (with an aspect ratio larger than 15).
Figure 5.5. Field dependency on precession frequency measured experimentally in comparison with the calculated frequency using the Kittel equation for a Ni plate with an aspect ratio larger than 15. Both this figure and Figure 5.4 on Fe plate show clear evidence that the precession frequency can be predicted by the Kittel equation as a function of the applied field, thus the magnetization can be calculated from the Kittel equation.
5.4 Saturation magnetization measurement in diffusion couples with negligible crystal anisotropy

The next step is to measure the precession frequency on diffusion couple samples. The first sample is a Ni-Fe diffusion couple sample with nearly 1 mm diffusion length. The method of making this diffusion couple was discussed in Chapter 1. Figure 5.7 is an SEM image of the interested area (diffusion region) and corresponding Energy Dispersive Spectroscopy (EDS) measurement of local composition across the diffusion couple. The sample was made by pressing pure Ni and Fe bars together and annealed at 1000 °C for 1000 hours. Significant diffusion took place and resulted in a continuously changing composition. Fe and Ni are completely solvable in each other in the FCC phase at high temperatures. The sample was water quenched to room temperature to maintain the high temperature FCC phase. However, Fe-rich compositions underwent a martensitic transformation during quenching to form the stable BCC phase at room temperatures. EBSD phase identification was performed on a similar Ni-Fe couple that underwent the same process, and it shows that the Fe rich side (0 to ~ 35 at.% Ni) is BCC and Ni-rich side is FCC, shown in Figure 5.6.

Figure 5.7 shows an SEM backscatter electron image together with the EDS scan across the diffusion zone, along the location of the white line shown in (a)
Figure 5.6. (a) EBSD phase identification on a similar FeNi diffusion couple sample that underwent the same quenching process. (result obtained from Oxford Instruments and thanks to our collaborators at the Wayne State University); (b) Optical image of the measured Ni-Fe sample with the two phases revealed by the difference in optical reflectivity in the FCC (left, Ni side) and BCC (right, Fe side).
Figure 5.7. SEM image of the diffusion region in the Ni-Fe diffusion couple (top) and corresponding EDS measurement result (bottom). The diffusion region in this sample is over 600 microns. Several indents were put on the diffusion couple to mark the location of the sample where EDS measurement was performed in order to correlate the EDS measured local composition with laser measured saturation magnetization.
Time-resolved MOKE measurement was performed on the Ni-Fe diffusion couple with an external field applied perpendicular to the concentration gradient. A scan at 10 microns step size across the diffusion region was carried out and the saturation magnetization data was calculated based on the measured precession frequency and Kittel’s equation. The TR-MOKE signal obtained from this sample is quite interesting, as shown in Figure 5.8. Strong precession signals were observed on both pure metal sides; while going from the Ni side to the Fe side, unusual behavior was observed. A sharp change in the precession frequencies (and thus the saturation magnetization) was observed at ~ 35% Ni where the FCC to BCC transition was observed. Another unexpected phenomenon is the disappearance of precession at around 42 at.% of Ni. The exact reason of this disappearance is not known yet, a plausible reason is the Invar effect, which occurs in the range of 36 to 45 at.% Ni, characterized by much reduced (and nearly zero for some alloys) thermal expansion at room temperature and a huge magnetostriction effect [100-102]. The rest of the measured saturation magnetization data generally agrees with literature values at room temperature, as show in Figure 5.9. The literature data is taken from the works of Swartzendruber [103].
Figure 5.8. Saturation magnetization measured by the laser probed spin dynamics (top) and SEM image/EDS composition mapping (middle and bottom). The horizontal axis scale is the same for all three graphs and aligned, so that a comparison between measured magnetization and composition can be made.
Figure 5.9. A comparison between the measured saturation magnetization from the Ni-Fe diffusion couple (red dots) with literature values (blue line, extrapolated/assessed from several sets of experimentally measured data) at room temperature. The measured magnetization decreases with Ni content as expected in the BCC phase, and after the BCC-FCC phase transition the measured magnetization generally agrees with literature values except the region between 42% and 50% Ni in which an unexplained suppression in the precession motion is observed.
5.5 The effect of crystal anisotropy on the precession frequency--the cobalt example

In the previous section, I showed measurements of saturation magnetization in Fe-Ni diffusion couple which contains both BCC and FCC solid solutions. Cubic phases are known to have low magneto-crystalline anisotropy. In fact, at a particular composition (Fe-80 at% Ni) the famous Permalloy exhibits nearly zero anisotropy. The Fe-Ni solid solutions with other compositions do have some anisotropy, but still very low in magnitude. A simple calculation suggests that the maximum possible anisotropy energy in pure Fe is only about 10% of the Zeeman energy (assuming 0.5 T external field), when the magnetization vector is along the [111] crystal orientation. When magnetization points in any other orientation, the anisotropy energy is even smaller, which allows me to safely ignore its contribution to the observed spin precession frequency and use the Kittel’s equation without an anisotropy correction.

Cobalt and cobalt-rich alloys with a HCP crystal structure is a totally different case with a much larger anisotropy than cubic crystals. The same energy terms calculation suggests that the anisotropy energy can be almost in the same magnitude as the Zeeman energy. (Assuming 0.5 T of external field) is applied to pure Co, when magnetization vector lies in the basal plane. The anisotropy has to be considered when analyzing precession data in Co and its HCP alloys [73].

Careful analysis of the precession frequency as a function of applied field can be used to evaluate the magnetocrystalline anisotropy constants of the material when the crystal
orientation is known. The crystal structure and orientation can be measured using EBSD. EBSD detects back scattered electron diffractions, whose pattern is used to evaluate crystal structure and orientation. Electrons injected into samples by the SEM electron gun are bounced back by the lattice in the sample. When the backscattered electrons exit through the sample volume they previous penetrated, they are diffracted by the crystal lattice. During EBSD measurement, sample is usually tilted at a high angle (70 degrees) and the back scattered electron diffraction patterns are collected by a phosphorus screen. The diffraction pattern consists of bright and dark bands (similar to Kikuchi bands) and a series of mathematical transforms and fittings are used to obtain crystal structure and lattice orientation which is routinely done in the field of materials science. The spatial resolution is in microns for EBSD detection as the interaction volume is determined by the electron penetration depth.

An EBSD measurement was carried out on a Co-Cr diffusion couple, using an EDAX EBSD detector mounted on a Quanta SEM in our Campus Electron-Optics Facility (CEOF). The data was analyzed using OIM Analysis software developed by the same company. On the pure Co side of the Co-Cr diffusion couple, the EBSD data show an HCP crystal structure with the c-axis is lying parallel to the sample surface, as shown in Figure 5.10. A MatLab program was developed to calculate the precession frequency with crystal anisotropic field included based on the theories provided in Chapter 2. It first determines the direction of magnetization vector by minimizing the total energy, and then uses the solution to Landau-Lifshitz equation listed in Chapter 2 for precession frequency calculation.
Figure 5.10. EBSD measurement on an area of a Co-Cr diffusion multiple. The far left is pure Co and the crystal is hexagonal with crystal orientation shown in the bottom part of the figure. Co is uniaxial in magneto crystalline anisotropy with the c-axis as the easy axis. External field is applied in the upward direction in this graph. The crystal orientation of the Co is later used to calculate the crystal anisotropy constant of Co.

With known crystal orientation and the saturation magnetization, the anisotropy constants can easily be obtained using a least square fitting process quite similar to the one used for elastic constants determination. The only difference is that here I only have one fitting parameter, making the process much easier and faster. When both the saturation magnetization and crystal anisotropy parameters are unknown for a particular measurement, both values can be fitted at the same time.
Figure 5.11. Fitting onto the precession frequency as a function of external field for pure Co. The angle between the applied field and the c-axis of the crystal is 65 degrees as shown in Figure 5.10. The fitting results show ~ 10% accuracy in comparison with the literature data. Calculation shows that a $0.5 \times 10^6$ erg/cc change in crystal anisotropy results in ~ 3 GHz change in precession frequency in this situation.

The result for pure Co is shown in Figure 5.11. The precession frequency is highly sensitive to the crystal anisotropy field in this scenario, the best fitting is found at around
4.4x10^6 erg/cc, with a saturation magnetization of 1.6 T. The literature number is at 4.0e6 erg/cc, the current measurement error is ~10%. Although not as accurate as the torque method for anisotropy determination, this method has its advantage of high spatial resolution (in microns) and measurement speed (less than 10 minutes for a single point/composition measurement).

Measurement data on other parts of the Co-Cr sample is being processed and I hope to be able to extract saturation magnetization and crystal anisotropy simultaneously using this method.
Chapter 6 Conclusion and future work

In this dissertation, I described our theoretical work on the solution to the surface motion in an anisotropic half space due to instantaneously created thermal strains created by femtosecond laser illumination. Probe beam deflection measurements were performed using a femtosecond laser in a pump-probe configuration to study the surface response induced by the pump beam. The results on Al (001) surface and Cu (001) surface, obtained from such experimental measurements agree with my calculations. The agreement validates the semi-analytical solution of the surface response. This model can also be used in other arbitrarily cut surface of anisotropic materials. Using this model I can also calculate the SAW speed along any propagation directions in anisotropic materials, and from the orientation dependent SAW propagation speed it is possible to extract the anisotropic elastic constants with a back-fitting process. An orientation dependent measurement of SAW speed was performed on Si (111) surface and a least square fitting process was applied for the extraction of anisotropic elastic constants in Si. The data agrees with literature values with an error less than 7%. Such a measurement
can be performed within 20 microns in space, thus it is possible to fit both the pump and probe beams into a single grain in a polycrystalline sample, which will allow single-crystal elastic constants to be measured from large-grained polycrystalline samples. This method, thus, eliminates the need for growing large single crystal samples as required by conventional ultrasonic methods of measuring anisotropic elastic constants.

The other study I performed during my dissertation research is on magnetic spin precession initiated by femtosecond laser pulses and being detected using Time-Resolved MOKE. The time duration of this precession ranges from 20 ps to 1 ns, and the frequency of the precession is dictated by both the external field and the saturation magnetization. Highly focused pump laser pulses heat up the area under illumination and instantaneously alter the direction of the effective magnetic field in that area. The magnetization vector starts its precession as a result of misalignment between instantaneous effective field and the starting/equilibrium effective field; and the precession can last well into nanosecond time scale. I built a TR-MOKE apparatus to detect the frequency of this precession and thus measure the saturation magnetization of materials with a sub-picosecond time resolution and a spatial resolution determined by the focused laser beam spot size. A benchmark study was carried out in Fe and Ni plate samples; and shows good agreement between the measured precession frequency with that calculated using Kittel’s dispersion equation. A further experiment is carried out on a Ni-Fe diffusion couple sample for composition dependent saturation magnetization measurement. The result is presented in Chapter 5, again showing agreement between measured data and the literature values. The idea of measuring magnetocrystalline anisotropy constant in samples with high
magnetic anisotropy is also described. The crystal orientation of a pure Co sample was first measured using EBSD and then precession frequency was measured with TR-MOKE at multiple external fields. The frequency data are compared with calculations and the magnetocrystalline anisotropy constant can be obtained by a fitting process. The result agrees with the literature value with a 10% error. Higher accuracy and more reliability are possible when more data points are collected.

All of the measurements presented at this dissertation were performed at room temperature. One of our future goals in equipment development is to add temperature control units into the system and make measurements at both low and high temperatures. Another improvement we are looking for is to further increase spatial resolution by using an objective lens with a higher numerical aperture, so that the laser can be focused to a smaller spot.
Bibliography


85. X. Zheng, C.Wei. Private Communications


96. Koopmans, B., Private Communications.


Appendix

Code for surface motion calculation in anisotropic material as a result of thermal strains induced by ultrafast laser pulses.

```matlab
function G=anisotropic(kx,ky,omega,C,density)
%this file is used to calculation anisotropic response from point impulsive
%function, C(i j k l) is the elastic tensor, G is a 3by3 matrix of greens
%function
%for silicon
a=zeros(3);b=zeros(3);c=zeros(3); d=zeros(3,3,3); Temp=zeros(3);
%%calculate the sextic equation
for m=1:3
    for n=1:3
        a(m,n)=-C(m,1,n,1)*kx*kx-(C(m,1,n,2)+C(m,2,n,1))*kx*ky-
        C(m,2,n,2)*ky*ky;
        b(m,n)=1i*(C(m,1,n,3)+C(m,3,n,1))*kx-
        1i*(C(m,2,n,3)+C(m,3,n,3))*ky; %the minus sign is from the p
        c(m,n)=C(m,3,n,3);
        d(:,m,n)=[c(m,n) b(m,n) a(m,n)+density.*(m==n)*omega.^2];
    end
end
Det=conv(d(:,3,3),conv(d(:,1,1),d(:,2,2)))+conv(d(:,3,1),conv(d(:,1,2),
    d(:,2,3)))+conv(d(:,2,1),conv(d(:,1,3),d(:,3,2)))-
    conv(d(:,3,1),conv(d(:,1,3),d(:,2,2)))-
    conv(d(:,3,3),conv(d(:,1,2),d(:,2,1)))-
    conv(d(:,1,1),conv(d(:,2,3),d(:,3,2)));
P=roots(Det);

%now pick up the right 3 p
j=1;PP=zeros(3,1);
for i=1:6
    if(real(P(i))>0)
        PP(j)=P(i);
        j=j+1;
    end
end
```
generally the P do not degenerate, if any unusual things happen check this

Temp1=zeros(3);U=zeros(3); %Temp is used for calculating the eigenvector

for j=1:3
    % evaluate the matrix
    for m=1:3
        for n=1:3
            Temp(m,n)=polyval(d(:,m,n),PP(j));
        end
    end
    [UU,D,V] = svd(Temp,0);
    U(:,j)= V(:,end);
end
if(abs(det(U))<1e-6)
    if((abs(PP(1)-PP(2)))<1e-5*abs(PP(1)))
        flag=3;
        else if ((abs(PP(2)-PP(3)))<1e-5*abs(PP(2)))
            flag=1;
            else flag=2;
        end
    end
    if(flag~=3)
        if(Temp(2,3)~=0)
            U(3,3)=-(Temp(2,1)+Temp(2,2))./Temp(2,3);
            tt=sqrt(2+abs(U(3,3)).^2);
            U(1,3)=1./tt; U(2,3)=U(1,3);
            U(3,3)=U(3,3)./tt;
        else
            if(Temp(2,1)~=0)
                tt=sqrt(1+abs(Temp(2,1)./Temp(2,2)).^2);
                U(1,2)=Temp(2,1)./Temp(2,2)./tt;
                U(2,2)=U(1,2);
                else
                    U(:,3)=[0;0;1];
                end
            end
        end
    else
        for m=1:3
            for n=1:3
                Temp(m,n)=polyval(d(:,m,n),PP(2));
            end
        end
        if(Temp(2,3)~=0)
            U(3,2)=-(Temp(2,1)+Temp(2,2))./Temp(2,3);
            tt=sqrt(2+abs(U(3,2)).^2);
            U(1,2)=1./tt; U(2,2)=U(1,2);
            U(3,2)=U(3,2)./tt;
        else
            if(Temp(2,1)~=0)
                tt=sqrt(1+abs(Temp(2,1)./Temp(2,2)).^2);
                U(1,2)=-Temp(2,1)./Temp(2,2)./tt;
                else
                    U(:,2)=[0;0;1];
                end
            end
        end
    end
end

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\begin{verbatim}
U(2,2)=1/\Omega; U(3,2)=0;
else U(:,2)=[0;1;0];
end
decend
end
decend

for m=1:3
   for n=1:3
      Temp1(m,n)=sum(sum(C(:,:,m,3).*(U(:,n)*[i*kx i*ky -PP(n)]));
   end
end

A=i*Temp1/eye(3)./omega;
G=U*A;
end
\end{verbatim}