NONLINEAR AND ULTRAFAST OPTICAL PROBING OF NANOSCALE MnAs AND GRAPHITIC FILMS

by

Jesse Jackson Dean

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Physics
University of Toronto

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Abstract

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Jesse Jackson Dean
Doctor of Philosophy
Graduate Department of Physics
University of Toronto
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This thesis reports on ultrafast linear and nonlinear optical probing of nanometer thick films. Exfoliated graphene and few-layer graphite are probed through optical second harmonic generation (SHG) with 800 nm, 150 fs pulses. Samples of varying thickness from 1 carbon layer to bulk graphite are deposited onto an oxidized silicon substrate. SHG measurements are taken as a function of azimuthal rotation angle of the films. It is found that the SHG from graphene is much weaker than that from bilayer graphene, and has a qualitatively different azimuthal pattern. As the sample thickness increases from bilayer graphene to bulk graphite, the SHG yield generally decreases. Both of these effects are explained in terms of the symmetry of graphene and graphite, and modeled using multilayer optical transfer matrices, and an identical set of nonlinear susceptibility tensor elements for the front and back surfaces. These tensors are independent of sample thickness.

MnAs films of 150 and 190 nm thickness on (001)GaAs are optically excited with 775 nm, 200 fs pump pulses. Specular SHG at 388 nm and first order optical diffraction at ∼ 400 nm are used to probe the samples on timescales up to 2 µs. It is found that the SHG probes the temperature-dependent, spatially averaged, surface strain. This strain reaches a maximum deviation in ∼ 6–100 ps after optical excitation depending on the pump fluence and initial temperature. The strain then recovers in hundreds of picoseconds, a timescale consistent with heat diffusion.

The optical diffraction probes the first Fourier component of the paramagnetic–
ferromagnetic stripes inherent to MnAs films in the 10–40°C temperature range. After optical excitation, the diffraction data show highly nonthermal behaviour in the MnAs films. If a sample is excited from the coexistence phase, the diffraction signal shows decaying oscillations with a period of $\sim 335 \pm 4$ (408 ± 4) ps for the 150 (190) nm films; this is consistent with the release of a standing acoustic wave. Decay occurs on a timescale of $\sim 2$ ns consistent with local diffusion through the films. The stripes are restored on a timescale of hundreds of nanoseconds, with a temporal behavior consistent with a diffusion process, possibly thermal in origin.
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Chapter 1

Introduction

1.1 Overview

Thin films have produced many advances in optical and electronic technology in the past 50 years. These advances often occur as a result of research on the fundamental properties of such films and how they differ from those of bulk materials. Films with nanometer thickness have recently been the subject of considerable interest by the research community. This thesis involves the study of two such systems using optical techniques. The first is graphene, a single-atom thick layer of graphite, as well as few-layer graphite. The second is manganese arsenide, a material with unusual magnetic properties which has recently been grown as a thin film.

Graphene is a single atomic sheet of carbon atoms, which, when stacked together, forms natural graphite. When one is writing with a pencil, pieces of graphene and graphite are left behind on paper because they are weakly bonded to each other. Graphene was first found to have unusual properties when it was theoretically investigated in 1947 [1] shortly after the advent of quantum mechanics. However, graphene has only recently been isolated in a controlled manner within the past decade [2]. Ironically, this isolation process is very simple, and does not involve any modern technology; it involves exfoliation which will be described later in this thesis. This discovery signaled the start of a vast wave of research into graphene, exploring many of its unique properties. Many of these properties can be measured optically, either for the purpose of determining some of the unusual properties of graphene, or to use graphene to investigate an optical process which is difficult to study using more conventional materials.

One of the techniques used in this thesis is second harmonic generation (SHG), a
nonlinear optical process. Second harmonic generation is a commonly used probe of material properties, and much of the formalism associated with interpreting SHG data is well-established. Yet it is not clear how one should proceed in modeling second harmonic generation in the extreme limit of thin films, e.g., 1, 2, or 3 layers of graphene/graphite. In this thesis, it will be shown that there is a qualitative difference in the SHG response of graphene and bilayer graphene. Linear optical effects are weak in the thin film limit (i.e., as the thickness approaches zero, transmission approaches 100%, and reflection and absorption approach zero), but SHG can actually be enhanced in the thin film limit. This thesis will describe these investigations and give a theoretical explanation for these observed effects.

The second material which is the focus of this thesis, manganese arsenide, has been a subject of research for over 100 years [3]. Superficially, its structure and properties aren’t very unusual, but some of its magnetic properties such as magnetostriction make it of interest both for the study of fundamental physics, and for possible technological applications in the spintronics community [4, 5]. For this reason, the number of reports on various properties of manganese arsenide has grown substantially, especially over the past decade. Most of the interest in MnAs is due to two related factors: its magnetic properties, and the existence of a first-order phase transition near room temperature. This phase transition is a solid-to-solid transition, and involves a change in its magnetic properties. Bulk MnAs is ferromagnetic below \( \sim 40^\circ\text{C} \), and paramagnetic above \( \sim 40^\circ\text{C} \). Additionally, there is a small change in the lattice parameters and crystal symmetry between the two phases [6]. Ferromagnetic MnAs has hexagonal symmetry, and when transforming to paramagnetic MnAs, it shrinks and changes to orthorhombic symmetry. It was recently found [7] that MnAs can be grown as a thin film on a substrate such as GaAs. Since it is attached to the substrate, it cannot expand laterally through the transition, and therefore experiences strain in the low temperature phase. This strain strongly affects the phase transition dynamics, and the interplay of stress, strain, phase, and magnetization in MnAs is the subject of ongoing research. One of the most interesting features of thin film MnAs is that in a temperature range near the phase transition temperature, both phases coexist [8], and self-organize into a stripe-like pattern over the film.

This thesis investigates the phase transition dynamics using two optical probes: specular SHG, and first order optical diffraction. The SHG probes the normal component of the strain tensor at the surface, whereas diffraction probes the stripe pattern. The main
advantage to using a pulsed laser as an experimental probe is that time-resolved studies are possible; an optical pulse can be used to excite the sample, starting from either a pure ferromagnetic phase or coexistence phase, and SHG and diffraction measure the evolution of the stripes and surface strain as the sample returns to equilibrium following excitation. It is shown in this work that it is possible to optically generate a transient striped phase or destroy the stripes depending on initial conditions, but such processes are very different from what occurs when the sample is simply heated in near-equilibrium conditions. For example, the optical creation of stripes occurs on a much longer timescale than would be expected based on thermal effects alone. Also, the optical destruction of stripes does not occur on a timescale related to lattice heating and heat diffusion, but first involves a coherent lattice oscillation. These experiments and results are described in this thesis, along with physical explanations for these effects.

Before the research performed for this thesis, there had been little research on the nonlinear optical properties of either graphene or manganese arsenide. As I show here, nonlinear optical phenomena can probe materials in unexpected ways, giving results that can provide new insight into the material, as well as improve our understanding of nonlinear optics from thin film systems in general. Additionally, there has been little reported research into the phase transition of manganese arsenide on an ultrafast timescale. Through time-resolved measurements, the work shown in this thesis investigates some of the unusual behavior exhibited by MnAs when undergoing a ‘fast’ phase transition. But first, a brief background on graphene, manganese arsenide, and second harmonic generation is given.

1.2 Graphene

Graphene is an atomically thin film of hexagonally arranged carbon atoms. Multiple graphene layers, when bonded together through van der Waals forces, form natural graphite. Graphite is usually composed of graphene layers bonded in the Bernal (AB) arrangement whereby each atomic layer is rotated by 60° (or equivalently, is shifted) relative to its neighboring layers. This arrangement is shown in Fig. 1.1. It has recently been noted however [9], that multiple layers of graphene may occur in the rhombohedral (ABC) stacking arrangement. In this arrangement, each layer is shifted relative to its neighbours such that the lattice is unchanged following a vertical shift of three layers. The ABC arrangement was found to account for only ∼ 15% of few-layer graphite, with
Chapter 1. Introduction

Figure 1.1: Structure of graphite shown in two different perspectives. The blue and red carbon atoms represent alternating layers of graphene which are clearly shifted relative to each other in the hexagonal Bernal arrangement.

the rest having the AB arrangement.

In the first quantum mechanical description of graphene in 1947 [1], Wallace showed that the electron dispersion curve is linear near the K and K’ points, or ‘Dirac points’. In other words, the electrons behave as massless fermions. It was initially thought that flat freestanding or isolated graphene could not exist [10], and in fact an isolated graphene sheet would not be discovered for over fifty years.

Graphene was first isolated and studied by Geim and Novoselov in 2004 [2], a feat that would later win them the Nobel prize in physics. Their technique involved micromechanical exfoliation, otherwise known as the ‘scotch tape method’. This essentially involves peeling layers off natural graphite with scotch tape and depositing them on a substrate. Shortly after this discovery, graphene research became extremely popular, and many interesting properties related to the linear band structure were investigated, such as the anomalous half-integer quantum Hall effect [11], and extremely high electron and hole mobilities at room temperature [12]. Graphene and similar materials have also recently been fabricated using other techniques, such as chemical vapour deposition of carbon [13], and epitaxial growth [14], which is done by high-temperature graphitization of bulk SiC.

The optical properties of graphene have been studied intensively in recent years. One
of the first investigations involved linear reflection and absorption. It was found that each layer of graphene absorbs $\pi \alpha \approx 2.3\%$ of visible and near-infrared light where $\alpha$ is the fine-structure constant [15, 16, 17]. This property is related to the linear band structure of graphene. In order to calculate reflection and transmission from thin film systems, it is necessary to know the complex index of refraction. The index of refraction is defined as $n = \sqrt{\epsilon}$, where $\epsilon$ is the relative dielectric constant. Since $\epsilon$ is a property well-defined only in bulk materials, it is not clear if light propagation across a graphene film can be described using a complex index of refraction. However, it can; Blake et. al. [18] noted that graphene may be treated optically as bulk graphite with a thickness of 0.34 nm (the extension of the $\pi$ orbitals out of plane) and that multilayer graphene films may be treated similarly. There have been many other optical measurements in graphene. Raman spectroscopy [19, 20, 21] has been used to study graphene, particularly to identify the number of atomic layers and crystal defects. The ultrafast dynamics of photoinjected carriers have been widely studied [22, 23, 24], and have led to the application of graphene to the mode-locking of lasers [25].

Prior to the experiments described in this thesis [26, 27], nonlinear optical effects had not yet been experimentally studied in graphene or few-layer graphite. Besides the SHG reported here, there have recently been reports of other nonlinear optical phenomena including coherent control [28] and four-wave mixing [29].

### 1.3 Manganese Arsenide

Manganese arsenide was first isolated over 100 years ago [3]. It undergoes a solid-to-solid first-order phase transition at 40°C. Below 40°C, in the $\alpha$ phase, it is ferromagnetic with hexagonal symmetry ($D_{6h}$ point group, often referred to as NiAs-type). Above 40°C, in the $\beta$ phase, it is paramagnetic with orthorhombic symmetry ($D_{2h}$ point group, often referred to as MnP-type) [6]. There is a further second-order phase transition at 126°C, in which MnAs reverts to a hexagonal structure but remains paramagnetic.

MnAs crystals may be made by direct reaction of the elements [30], but they are also commonly grown as thin films epitaxially on Si or GaAs [7]. One of the most commonly studied systems is (1100)MnAs on (001)GaAs where MnAs(0001) $\parallel$ GaAs(110); this is the system studied here, and is shown schematically in Fig. 1.2. Other orientations are possible however, such as (0001)MnAs on (111)GaAs. The lattice naming convention is as follows: the a-axis, or $[\overline{1}1\overline{2}0]$, is parallel to the surface, parallel to the hexagonal plane;
the \( b \)-axis, or \([1\bar{1}00]\), is normal to the surface, parallel to the hexagonal plane; the \( c \)-axis, or \([0001]\), is parallel to the surface, normal to the hexagonal plane. These directions are also shown in Fig. 1.2.

The physical and magnetic properties of thin film MnAs depend on the thickness and growth details. In bulk MnAs, the first order phase transition at 40°C is abrupt, and has a thermal hysteresis of about 10°C [30]. For thin MnAs films grown on (001)GaAs, this transition occurs over a broad range, 10°C to 40°C. Within this range, both phases coexist, and form a stripe-like pattern, with the stripes oriented along the \( c \)-axis of the MnAs [8, 4] as shown in Fig. 1.3. This coexistence phase is a result of the significant role played by strain due to the lattice mismatch between the MnAs and GaAs substrate.

When MnAs is grown on a GaAs substrate, a regular array of misfit dislocations form because of the lattice mismatch [4]. As it is cooled from growth temperatures, the dislocations can shift around, but the total number must be conserved — in other words, the total area of the MnAs film cannot change relative to that of the GaAs. As a bulk sample is cooled below 40°C, the phase transition results in a \( \sim 1\% \) increase to the \( a \) lattice parameter (the \( c \) parameter is relatively unchanged); the lattice parameters are given by Willis et. al. [30]. This naturally causes a very large strain when the film is attached to a substrate [31]. The elastic energy density and free energy density
associated with an unstrained state contribute to the total free energy density in the films. To minimize the free energy at temperatures below 40°C a coexistence phase occurs [32] with alternating stripes of \( \alpha \)- and \( \beta \)-MnAs. Below 10°C a homogenous \( \beta \)-MnAs phase minimizes the free energy. The stripe period is a result of free energy minimization based on the periodic strain. The end result is that the stripe period, \( \Lambda \), depends only on the film thickness \( d \), as \( \Lambda \approx 4.8d \). For typical film thicknesses of \( d \sim 150 \) nm, this gives \( \Lambda \sim 720 \) nm. The filling fraction of the \( \alpha \) phase, denoted \( \xi \), decreases linearly with increasing temperature from \( \xi = 1 \) at 10°C to \( \xi = 0 \) at 40°C [8, 4]. Because of the different lattice parameters of the two phases, there is a periodic height modulation, \( \Delta d \), over the stripes. This height modulation depends on the elastic constants of MnAs (Young’s modulus and Poisson ratio), and reported values are \( \Delta d \sim 3–8 \) nm [33, 34] and depend on the film thickness.

Most previous research on MnAs films has involved the relationship between stress, strain, temperature, and magnetic properties. These are well-summarized in the review article by Däweritz [4]. There has also been some investigation of the linear optical properties [35, 36], mainly for the purpose of obtaining the frequency-dependent dielectric constant. Because of the hexagonal symmetry in the ferromagnetic phase, MnAs is uniaxial, but the difference in the ordinary and extraordinary index is only \( \sim 0.1 \). In principle, when in the paramagnetic phase, which has orthorhombic symmetry, the crystal could be optically biaxial, but because the orthorhombic distortion (difference from hexagonal symmetry) is very small, no deviation between the corresponding indices
of refraction has been reported. There is a difference in index of refraction between the paramagnetic and ferromagnetic phases of $\sim 10\%$ depending on the wavelength; this could allow one to see a small difference between the phases in the reflected light. Optical diffraction from the stripes is therefore a result of two effects: the difference in index of refraction of the two phases, and the periodic height modulation.

Prior to the work reported here, there had been little research into nonlinear optical effects or linear optical diffraction from MnAs. Similarly, ultrafast time-resolved optical phenomena have not been thoroughly investigated. Time-resolved experiments are of general interest for many materials to study various physical effects; for MnAs, time-resolved measurements are of particular interest to study the effect of ultrafast heating on the ferromagnetic–paramagnetic phase transition, and stripe creation and destruction. These types of measurements are investigated here to give insight into the nature of the phase transition on a timescale of picoseconds to nanoseconds.

### 1.4 Second Harmonic Generation

Second harmonic generation was the first nonlinear optical process generated using a laser. This was observed in quartz by Franken et. al. in 1961 [37].

It is now well-known that when a medium is exposed to weak light at frequency $\omega$, it induces a bulk polarization density of the form

$$P(\omega) = \varepsilon_0 \chi^{(1)}(-\omega; \omega)E(\omega),$$  \hspace{1cm} (1.1)

where $\chi^{(1)}(-\omega, \omega)$ is the linear susceptibility, which is mathematically described as a rank-2 tensor. But the polarization density is not just a linear function of the E-field; the right side of Eq. (1.1) is just the first term in a Taylor expansion of $P$ in $E$. There are a plethora of other terms in the Taylor expansion of $P$ corresponding to nonlinear effects such as harmonic generation, the Kerr effect, coherent control, etc. Generally, these effects can only be observed using pulsed lasers because the intensity of continuous light sources is too low to form higher order polarizations. One of the simplest nonlinear effects is second harmonic generation. This is a process whereby a material is illuminated by light at frequency $\omega$, and generates light at frequency $2\omega$. Mathematically, there is a second order contribution to the polarization density which can be written as

$$P(2\omega) = \chi^{(2)}(-2\omega; \omega, \omega)E(\omega)E(\omega),$$ \hspace{1cm} (1.2)
where \( \chi^{(2)}(-2\omega; \omega, \omega) \) is the nonlinear rank-3 tensor associated with second harmonic generation.

It is well-known that SHG of dipolar origin — along with other second order nonlinear optical effects — cannot exist in a medium possessing inversion symmetry. A material has inversion symmetry (also known as centrosymmetry) if there exists a point in the crystal lattice where the crystal is unchanged under spatial inversion. The explanation is simple: a rank-3 tensor changes sign under inversion (just as a scalar stays the same, a vector changes sign, and a rank-2 tensor stays the same). Since a centrosymmetric material stays the same under inversion, any associated property must also be unchanged. Therefore, any second order nonlinear susceptibility (a rank-3 tensor) must change signs, and yet remain unchanged; so it must be zero. Many materials possess inversion symmetry, including graphite and manganese arsenide.

Nevertheless, there are many ways to obtain SHG from materials with inversion symmetry, either by breaking the inversion symmetry of the material, or using a subtly different nonlinear process than that shown in Eq. (1.2). SHG in a medium with inversion symmetry was discovered experimentally by Terhune \textit{et. al.} in calcite [38]. In such media, there are several sources of SHG. The inversion symmetry is broken at the surface layer of the material, as is the case at any interfaces between centrosymmetric media. There is therefore a two-dimensional second harmonic polarization sheet at interfaces given in the same form as Eq. (1.2). There is also a bulk quadrupolar source, whereby an electric quadrupole density (rather than an electric dipole density) is generated in the medium at the second harmonic frequency, as well as a magnetic dipole source, whereby a magnetic dipole density is generated at \( 2\omega \). These are usually written in terms of an effective \( 2\omega \) polarization: 

\[
P_i^{(2\omega)} = \Gamma_{ijkl}E_j^{(\omega)}\nabla_kE_l^{(\omega)}
\]

where \( \Gamma_{ijkl} \), being a rank-4 tensor, is generally nonzero even in centrosymmetric media. Surface dipolar, and bulk quadrupolar/magnetic dipolar SHG are allowed for any crystal system, and are the main sources of second harmonic light in centrosymmetric media when there are no external influences acting on the medium. There have been many reports of SHG from interfaces and thin film systems, both experimental [39, 40, 41, 42], and theoretical [43, 44]. Since a significant portion of the SHG occurs at surfaces for centrosymmetric media, SHG is very sensitive to interface properties and symmetry.

There are several methods to produce SHG from centrosymmetric media through slightly different nonlinear phenomena involving different tensors. Some examples include applying a DC electric field [38] to break the inversion symmetry, applying a magnetic
field [45], or putting an electric current through the material [46].

Crystal symmetry may be changed by applying stress. If the stress is inhomogeneous (i.e., it varies with position) then the inversion symmetry is broken and electric dipole SHG is allowed [47]. If the stress is homogenous, the crystal structure will be changed through the resultant strain [48, 49]. This would still affect SHG through modified electronic orbitals in the bulk and surface. This situation applies to thin films of manganese arsenide; when the phase transition occurs (or just through thermal expansion depending on the temperatures involved) a homogenous strain forms, which can affect the second harmonic generation.

1.5 Research Objective

Until the work presented in this thesis, there had not been any experimental reports of nonlinear optical processes in extremely thin films, on the order of 1–5 atoms thick with a well-defined single-domain crystal. It is important to have a single-domain crystal over an area of several microns (the diameter of a typical focused laser spot) in order to be sensitive to the crystal symmetry. The absence of such research is because, until recently, such materials have not been available. Graphene and few-layer graphite are unique in that it is relatively easy to have a film of a known thickness down to one atom, and have a single crystal domain over a range of $\sim 20 \mu m$.

The motivation to measure SHG from graphene and few-layer graphite is two-fold: to study graphene using SHG; and to study SHG using graphene. The latter motivation, to study the fundamentals of SHG using graphene, is related to the fact that graphene offers a unique opportunity to use extremely thin, yet single-domain, crystals. Just as it was unclear (yet later measured) if an index of refraction could apply to a one-atom thick material, it is unclear if a nonlinear susceptibility for surface SHG can apply. Normally for centrosymmetric thin films, both the front and back surfaces produce SHG, and the net SHG yield is their sum. It is not intuitive that this should apply when the film is one, or even a few, atoms thick since the front and back surfaces are essentially the same. On the other hand, as samples change from few layers to bulk, eventually both surfaces must have independent SHG yields. It is therefore useful to measure SHG from graphene and few-layer graphite to determine how best to build a physical model for SHG from thin films. The former motivation, to study graphene with second harmonic generation, is essentially to probe the rotational symmetry of graphene and few-layer graphite, a
measurement which is not possible with linear optics. As with linear optics, there is expected to be a thickness-dependent SHG from graphene/graphite. This may enable thickness measurements using SHG or other nonlinear effects.

Both phases of manganese arsenide possess inversion symmetry; thus a weak SHG signal is expected. As films, they are relatively unstrained for \( T > 40^\circ C \), but become very strained when cooled through the phase transition. SHG is generally sensitive to strain, suggesting that such a technique may be used to monitor the strain as a function of temperature and on an ultrafast timescale. Since the index of refraction of MnAs only shows a \( \sim 10\% \) change between the phases, the change in reflection would likewise be small as the sample changes from the paramagnetic to the ferromagnetic phase. The advantage to SHG is that the strain-free signal (at \( > 40^\circ C \)) is weak, so any strain-induced signal is comparatively strong.

Specular SHG is sensitive to the average strain (or any other averaged property), but is not sensitive to a spatially varying property from the stripes. In principle, a higher order diffracted SHG signal would be sensitive to the stripes, but because of the weakness of SHG from centrosymmetric media, this is impractical. Instead, first order diffraction is used. This is essentially a probe of the stripes in terms of both the varying index of refraction, and height modulation. In an MnAs film in equilibrium conditions, the diffracted signal would clearly be zero below \( \sim 10^\circ C \) and above \( \sim 40^\circ C \) where the stripes disappear, and would be maximized near \( 25^\circ C \).

SHG and linear diffraction are therefore used together to provide a ‘view’ of the surface of MnAs films. The advantage to using short laser pulses to study these films is that they can provide time-resolved measurements under non-equilibrium conditions. One laser pulse can excite/heat the film on a few-picosecond timescale, and then a delayed probe pulse can be used to measure the SHG, or linear diffraction. Alternatively, a continuous wave laser beam can be used to measure the diffraction for timescales limited only by the detector response time. These experiments and results are described here with the aim of studying the excitation and cooling dynamics of MnAs films in terms of the stripes and strain.

1.6 Thesis Outline

In chapter 2, I will start by providing a theoretical framework for the SHG and diffraction experiments. Section 2.2 gives a detailed mathematical description of SHG from
thin film systems, and graphene and few-layer graphite in particular. Section 2.3 shows how the strain in MnAs films produces SHG. Section 2.4 describes a model for heat diffusion in MnAs films, and section 2.5 shows how much light might be diffracted from the stripes under various conditions. Chapter 3 begins with a description of the fabrication of graphene and MnAs, and gives some measured physical characteristics using well-established methods in section 3.2. The rest of chapter 3 describes the experimental setups used to perform the SHG and diffraction measurements. The results for the graphene SHG experiment are given in chapter 4, first through simple symmetry arguments in section 4.2, and then using a full tensor element analysis in section 4.3. Chapter 5 shows the results for the MnAs experiments; the SHG results are given in section 5.2, and the diffraction results over short and long timescales are given in section 5.3. Chapter 5 finishes with a description of the ultrafast phase transition dynamics in MnAs films in section 5.4. A summary of the results and concluding remarks appear in chapter 6.
Chapter 2

Theory

2.1 Overview

In this chapter, a theoretical formalism is presented with the aim of describing optical second harmonic generation and diffraction from thin film systems in terms of various phenomenological constants. In section 2.2.1, I start by describing the formalism used for linear thin film propagation, and apply it to the graphene/graphite system. In section 2.2.2, I investigate the polarizations that are generated at the interfaces in the graphitic system at the second harmonic frequency, paying particular attention to the thin film limit. In section 2.2.3, I calculate the SHG radiated from each of these polarization sheets. This is completed in section 2.2.4 where I calculate the net radiation produced through SHG. In section 2.3, I give a theoretical basis for strain-induced SHG, which will be used to describe the temperature-dependent SHG in MnAs films. To describe the effect of heating MnAs films through ultrafast laser excitation, I present a model for laser heating and heat transport specific to these films in section 2.4. Finally, in section 2.5, I give an analytical description of the diffraction efficiency of the stripes on MnAs.

In the literature, it has been shown that many properties of graphene evolve to those of bulk graphite by about 10 layers depending on the property being measured [50, 19], leading to some confusion in terminology (e.g., graphene vs. multilayer graphene vs. graphite etc.). To eliminate confusion, the term ‘graphene’ will hereafter only be used as per the original definition: a one-atom thick hexagonal film of carbon. The term ‘C-film’ will be used to mean a film of one or more atomic layers of graphene, from single-layer to bulk graphite (multilayer C-film means two or more atomic layers). Bulk graphite means a sufficiently thick C-film that very little light can travel through, and is therefore
experimentally indistinguishable from an infinitely thick C-film when being studied in a reflection geometry.

2.2 Nonlinear Optics in Thin Film Systems

To model the fundamental and second harmonic fields in a thin film system, the formalism used here is the same as that used by Sipe et. al. [43]. The coordinate system is chosen such that the z-axis is the surface normal, and the beam propagates in the x-z plane (the E-field of s-polarized light is in the y-direction). It is worth noting that this coordinate system is natural for C-films, where the c-axis is normal to the surface, but this is different from the coordinate system used for MnAs films, which is shown in Fig. 1.2.

This work is specifically meant to model SHG in C-films, but will also be used to provide information for the MnAs system. For reasons discussed in section 3.2.1, the C-films are deposited on a substrate which consists of 300 nm of SiO$_2$ on bulk (001)Si. For the C-films, there are 4 physical media: 1=air, 2=C-film (thickness of $d_2 = 0.34 \text{ nm} \times \text{number of layers}$), 3=SiO$_2$ (thickness of $d_3=300 \text{ nm}$), 4=(001)Si. In an interface between two media, when calculating the second harmonic polarization, the fundamental E-field may be evaluated either immediately above or below the interface, and the radiated SHG light may be treated as being generated from a 2-dimensional polarization sheet either immediately above or below the interface. Both conventions describe the same effect, but use different (essentially renormalized) nonlinear tensor elements. The convention used here is that between any two media (e.g., the C-film and SiO$_2$), there is an infinitesimally thin vacuum layer; the fundamental E-field is evaluated and the second harmonic polarization sheet exist in this layer. Note that an infinitesimally thin layer has no effect on linear optical propagation. The SHG sources used in this convention are shown in Fig. 2.1.

Depending on the crystal symmetry involved, it can be difficult to separate the surface and bulk contributions. Graphite is in the D$_{6h}^4$ space group; it has a 3-fold axis of symmetry, as well as a 6-fold screw axis (a vertical shift of one layer spacing, followed by a 60° rotation leaves it unchanged). Therefore, the surface has 3-fold rotational symmetry (C$_{3v}$), while the bulk effectively has 6-fold rotational symmetry. A rank-3 tensor (nonlinear susceptibility associated with dipole-induced SHG) can be sensitive to a 3-fold rotational symmetry, whereas a rank-4 tensor (nonlinear susceptibility associated with quadrupole-induced SHG) is not sensitive to a 6-fold rotational symmetry. Therefore,
any bulk quadrupole contribution to the SHG from the bulk of a C-film is isotropic with respect to an axial rotation. Furthermore, it is known that under either p- or s- polarized illumination, there is no isotropic s-polarized bulk quadrupole SHG [43]. Finally, any bulk contribution scales with the sample thickness, and therefore approaches zero in the thin film limit. In my analysis, the bulk contribution is assumed to be significantly smaller than the surface and interface contributions, and is ignored. A failure in this approximation would manifest itself as a discrepancy between the theory and experimental results for thicker samples.

For the following calculations, it is important to note that many of the variables (transfer matrices, etc.) depend on the thickness, or number of layers, of the C-film. This thickness dependence is not explicitly written, and is only included in numerical calculations at the end.

2.2.1 Thin Film Propagation

The E-field in any medium, labelled \( u \), in full form, is the sum of those generated by the upward (+) and downward (-) propagating fields of s- and p- polarization,

\[
\mathbf{E}_{u \pm}(\mathbf{r}) = \left( \mathbf{s} \mathbf{E}_{u \pm}^s + \hat{\mathbf{p}}_{u \pm} \mathbf{E}_{u \pm}^p \right) e^{\pm ik_u z} e^{ik_x x}.
\]  

(2.1)

The spatial phase dependence of the E-field \((\mathbf{k}_u, \mathbf{r})\) has been split into its \( z \) component \((k_u z)\) and \( x \) component \((k_x x)\); if all interfaces are parallel to the \( x-y \) plane, and the media
are isotropic, $k_x$ does not depend on the medium:

$$ k_x = \frac{2\pi}{\lambda} \sin(\theta), $$

$$ k_{uz} = \frac{2\pi}{\lambda} \sqrt{n_u^2 - \sin^2(\theta)}, \quad (2.2) $$

where $\theta$ is the angle of incidence, $\lambda$ is the fundamental wavelength, and the sign of $k_{uz}$ is defined such that $\text{Im}(k_{uz}) > 0$.

Graphite is highly anisotropic, so the formulae above need to be adjusted for p-polarized light. For C-films stacked in the usual sense (the c-axis is normal to the surface) the optical axis is normal to the surface; this means the above formulae are valid for s-polarized light which only sees the ordinary index, but the k-vector for p-polarized light, which sees both the ordinary and extraordinary indices ($n_o$ and $n_e$), must be adjusted:

$$ k_x = \frac{2\pi}{\lambda} \sin(\theta), $$

$$ k_{uz}^o = \frac{2\pi}{\lambda} \sqrt{n_{uo}^2 - \sin^2(\theta)}, $$

$$ k_{uz}^e = \frac{2\pi}{\lambda} \sqrt{n_{ue}^2 - \frac{n_{uo}^2}{n_{ue}^2} \sin^2(\theta)}. \quad (2.3) $$

The direction of the p-polarized field $\hat{p}_\pm E_\pm$ explicitly depends on whether it is upward (+) or downward (-) propagating, whereas the direction of the s-polarized field $\hat{s}E_s^*$ does not. In terms of the axes defined above, these directions are

$$ \hat{p}_\pm = \frac{k_x \hat{z} \mp k_{uz} \hat{x}}{|k_u|}, $$

$$ \hat{s} = \hat{y}. \quad (2.4) $$

The E-field may be described using the vector

$$ e_u(z) = \begin{bmatrix} e_{u+}(z) \\ e_{u-}(z) \end{bmatrix} = \begin{bmatrix} E_{u+} e^{ik_{uz}z} \\ E_{u-} e^{-ik_{uz}z} \end{bmatrix}. \quad (2.5) $$

The E-fields at various depths may then be related using the product of transfer matrices, $\mathbf{m}_{uv}$ at an interface between medium $u$ and $v$, and $\mathbf{m}_u(d_u)$ for propagation through medium $u$ of thickness $d_u$. The transfer matrices are given by

$$ \mathbf{m}_u(d_u) = \begin{bmatrix} e^{ik_{uz}d_u} & 0 \\ 0 & e^{-ik_{uz}d_u} \end{bmatrix}, $$

$$ \mathbf{m}_{uv} = \frac{1}{r_{uv}} \begin{bmatrix} 1 & r_{uv} \\ r_{uv} & 1 \end{bmatrix}. \quad (2.6) $$
Here, $r_{uv}$ and $t_{uv}$ are the Fresnel reflection and transmission coefficients for the $u$ to $v$ interface. Note that $t_{uv}$, $r_{uv}$, and $k_{uz}$ (in the case of a uniaxial medium such as graphite) depend on the polarization, and in the case of p-polarization, both the ordinary and extraordinary indices of refraction. These transfer matrices and electric field vectors $e_u(z)$ are meant to apply for s- and p- polarized light separately. The transfer matrix through a composite system is the product of the transfer matrices of each element. At opposite ends of a composite system (i.e., from medium 1 at $z = 0$ to medium 4 at $z = -d$), the E-fields are related by $e_1(0) = \mathbf{m}_{14} e_4(-d)$ where $\mathbf{m}_{14} = \mathbf{m}_{12} \mathbf{m}_{23} \mathbf{m}_{34}(d_2) \mathbf{m}_{34}(d_3) \mathbf{m}_{34}$. The script $\mathbf{m}$ indicates that it is a product of transfer matrices rather than just one representing a single interface. Therefore, the composite transfer matrix for the system may be written in terms of the total effective transmission and reflection coefficients,

$$
\mathbf{m}_{14} = \frac{1}{t_{14}} \left[ \begin{array}{cc} t_{14} t_{11} r_{14} t_{11} & r_{14} \\ -r_{41} & 1 \end{array} \right],
$$

(2.7)

where the script $r$ and $t$ indicates that they are effective fresnel coefficients rather than standard coefficients corresponding to a simple interface.

At position $z$ the total E-field in each direction is

$$
E_x = (-e^p_+ (z) + e^p_-(z)) \cos(\theta), \\
E_y = e^s_+ (z) + e^s_-(z), \\
E_z = (e^p_+ (z) + e^p_-(z)) \sin(\theta).
$$

(2.8)

Above the top surface, the E-field is the incident field $E_{1-} = E_0$ propagating downwards and its reflection:

$$
e_1(0) = \left[ \begin{array}{c} r_{14} \\ 1 \end{array} \right] E_{1-},
$$

(2.9)

where the reflection coefficient may be found from Eq. (2.7) to be $r_{14} = \frac{m_{12}^1}{m_{14}}$, and the superscripts for $m$ refer to the row and column number. The E-field components can then be directly calculated using Eq. (2.8). This gives

$$
E_x(z = 0+) = (-r^p_{14} + 1) \cos(\theta) E^p_0, \\
E_y(z = 0+) = (r^s_{14} + 1) E^s_0, \\
E_z(z = 0+) = (r^p_{14} + 1) \sin(\theta) E^p_0,
$$

(2.10)

where $z = 0+$ implies that it’s immediately above the top surface, and $r^{s,p}_{14}$ are the effective reflection coefficients calculated from the product of transfer matrices described above. Their analytic form is fairly long, so will not be explicitly shown here.
The E-field in the top vacuum interface, $e_{v1} = e_1(-d_2)$, (where the position $z = -d_2$ is taken to be inside the vacuum interface between the C-film and the SiO$_2$) can be calculated in a similar manner:

$$e_{v1} = \bar{m}_{12} \bar{m}_2(-d_2) \bar{m}_{21} e_1(0). \quad (2.11)$$

The E-field above the top surface, $e_1(0)$, has been determined from Eq. (2.9). This gives

$$e_{v1} + e_{v1} - E_1 = \bar{m}_{v1} \left[ \frac{r_{14}}{1} \right] E_{1-}, \quad (2.12)$$

where $\bar{m}_{v1} = \bar{m}_{12} \bar{m}_2(-d_2) \bar{m}_{21}$ and $r_{14}$ is the effective reflection coefficient from the whole system as calculated above. The actual E-fields can then be given in terms of the incident s- and p- polarized light:

$$E_x(z = -d_2) = (-\tilde{e}_{v1+}^p + \tilde{e}_{v1-}^p) \cos(\theta) E_0^p,$$

$$E_y(z = -d_2) = (\tilde{e}_{v1+}^s + \tilde{e}_{v1-}^s) E_0^s,$$

$$E_z(z = -d_2) = (\tilde{e}_{v1+}^p + \tilde{e}_{v1-}^p) \sin(\theta) E_0^p, \quad (2.13)$$

where $\tilde{e}_{v1+}$ is the electric field in the same form as $e_{v1+}$ but normalized to the incident field (i.e., $\tilde{e}_{v1+} = \frac{e_{v1+}}{E_0^p}$). This gives the electric fields in the same form as Eq. (2.10): a unitless factor multiplied by the incident (s- and p-) fields.

Finally, the electric fields in the lower vacuum interface, $e_{v2} = e_1(-d)$, (where the position $z = -d$ is taken to be inside the vacuum interface between the SiO$_2$ and Si) can be calculated in the same way. The upward and downward propagating fields are

$$\begin{bmatrix} e_{v2+} \\ e_{v2-} \end{bmatrix} = \bar{m}_{v2} \left[ \frac{r_{14}}{1} \right] E_{1-}, \quad (2.14)$$

where $\bar{m}_{v2} = \bar{m}_{13} \bar{m}_3(-d_3) \bar{m}_{32} \bar{m}_2(-d_2) \bar{m}_{21}$. Therefore the actual E-fields are

$$E_x(z = -d) = (-\tilde{e}_{v2+}^p + \tilde{e}_{v2-}^p) \cos(\theta) E_0^p,$$

$$E_y(z = -d) = (\tilde{e}_{v2+}^s + \tilde{e}_{v2-}^s) E_0^s,$$

$$E_z(z = -d) = (\tilde{e}_{v2+}^p + \tilde{e}_{v2-}^p) \sin(\theta) E_0^p. \quad (2.15)$$

### 2.2.2 Nonlinear Tensor Elements

At this point, the electric field $E(z)$ has been found; specifically, I have calculated a unitless ratio between the incident E-fields ($E_0^s$ and $E_0^p$) and the directional components of
the E-field above the C-film (Eq. (2.10)), between the C-film and the SiO₂ (Eq. (2.13)), and between the SiO₂ and Si (Eq. (2.15)). The next step is to calculate the second harmonic polarization density generated from the E-fields. In bulk, this is \( \mathbf{P}(2\omega) = \chi^{(2)}(\omega) \mathbf{E}(\omega) \). For interfacial SHG, this is given as \( \mathbf{P}(2\omega) = \Delta^{(2)}(\omega) \mathbf{E}(\omega) \delta(z_+), \) where the delta function implies an SHG polarization plane immediately above the surface (or between each layer in other cases).

In bulk media possessing inversion symmetry, there is no electric dipole SHG. It is tempting to apply such an argument for graphene since it possesses a point (the center of a hexagonal ring) around which the crystal structure appears centrosymmetric. Similarly, a bilayer C-film would appear to have a point of inversion symmetry (midway between the layers, between two carbon atoms). However, an inversion symmetry argument should not be applied to films, and as will be shown below, would give the wrong results. It is also possible to consider sufficiently thin films as generating a single 2-dimensional polarization sheet. In this case, the corresponding nonlinear tensor would depend on the film thickness, and it is unclear how thick a film would have to be to necessitate treating both surfaces independently. In the following analysis, the top and bottom surfaces of the C-film will be treated as generating independent 2-dimensional second harmonic polarization sheets.

Electric dipole interfacial SHG is governed by a rank-3 tensor having the same symmetry as the crystal surface. The surface symmetry is defined only by the sets of rotations about the \( z \)-axis, and mirror planes perpendicular to the \( x-y \) plane that leave the crystal unchanged. The bulk of graphite has a 6-fold screw axis of symmetry, but a screw axis symmetry cannot apply to the surface. Therefore, the surface of multilayer C-films has one 3-fold axis of symmetry, and 3 mirror planes, thus it has \( C_{3v} \) symmetry. Graphene has one 6-fold axis of symmetry, and 6 mirror planes, giving it \( C_{6v} \) symmetry.

The rank-3 tensor having \( C_{3v} \) symmetry has, in general, 5 independent nonzero components [51]: \( xzx = yzy, xxz = yyz, zxx = zyy, zzz, yyy = -yxx = -xyy = xyy \) (with coordinates chosen such that a mirror plane is perpendicular to \( \hat{y} \)). For SHG, the positions of the second and third indices are reversible, so the first two of these tensor elements are identical (\( xzx = xxz \)). In this case, the SHG tensor may be written in the
common $3 \times 6$ matrix notation:

$$
\mathbf{P} = \begin{bmatrix}
P_x \\
P_y \\
P_z
\end{bmatrix} = \begin{bmatrix}
\partial_{11} & -\partial_{11} & 0 & 0 & \partial_{15} & 0 \\
0 & 0 & 0 & \partial_{15} & 0 & -\partial_{11} \\
\partial_{31} & \partial_{31} & \partial_{33} & 0 & 0 & 0
\end{bmatrix} \begin{bmatrix}
E_x^2 \\
E_y^2 \\
E_z^2 \\
2E_yE_z \\
2E_xE_z \\
2E_xE_y
\end{bmatrix}, \quad (2.16)
$$

where the polarization has a frequency of $2\omega$ for electric fields at frequency $\omega$. The corresponding equation for $C_{6v}$ symmetry is the same, with $\partial_{11} = 0$.

The experiments described in the following chapters involve measuring the SHG as a function of the azimuthal angle of rotation, $\phi$. Therefore, the linear optics are the same, but the tensor must be rotated about the $z$-axis. It is also important to note that the SHG tensor elements are different between the top and bottom surfaces of the C-film. This is both because the C-film/air interface is physically different from the C-film/SiO$_2$ interface, and because it is vertically flipped (C-film above, rather than below the interface). For the top surface,

$$
\begin{bmatrix}
P_x \\
P_y \\
P_z
\end{bmatrix} = \begin{bmatrix}
\cos(3\phi)\partial_{11}^t & -\cos(3\phi)\partial_{11}^t & 0 & 0 & \partial_{15}^t & -\sin(3\phi)\partial_{11}^t \\
-\sin(3\phi)\partial_{11}^t & \sin(3\phi)\partial_{11}^t & 0 & \partial_{15}^t & 0 & -\cos(3\phi)\partial_{11}^t \\
\partial_{31}^t & \partial_{31}^t & \partial_{33}^t & 0 & 0 & 0
\end{bmatrix} \begin{bmatrix}
E_x^2 \\
E_y^2 \\
E_z^2 \\
2E_yE_z \\
2E_xE_z \\
2E_xE_y
\end{bmatrix}, \quad (2.17)
$$

where the $t$ superscript indicates the top surface (air/C-film interface). The $(3\phi)$ dependence makes it clear that SHG from multilayer C-films will be anisotropic with 3-fold rotational symmetry. Since graphene has $C_{6v}$ symmetry where $\partial_{11} = 0$, it is immediately clear that the anisotropy vanishes.

For the bottom surface of the C-film (C-film/SiO$_2$ interface), the same symmetries apply, since the SiO$_2$ is amorphous. Equation (2.17) applies to the bottom surface with $t$ replaced with $b$, indicating possibly different susceptibility elements. It is known, however, that the film is only weakly (van der Waals) bonded to the SiO$_2$, so a reasonable simplification is to assume that the tensor is physically the same as that for the top
surface. Because the $z$-axis is flipped, the substitutions become

$$\partial_{11} = \partial'_{11} = \partial''_{11},$$

$$\partial_{31} = \partial'_{31} = -\partial''_{31},$$

$$\partial_{33} = \partial'_{33} = -\partial''_{33},$$

$$\partial_{15} = \partial'_{15} = -\partial''_{15}. \quad (2.18)$$

Thus, all the tensor elements except $\partial_{11}$ change sign between the top and bottom surfaces. This would be exact for suspended C-films, and is expected to be approximately true for C-films weakly bonded to a substrate.

It is worth examining the infinitesimally thin case, where the C-film does not affect linear optical propagation at all. This applies (approximately) to one-layer (graphene) and two-layer C-films. The E-fields at the top and bottom surfaces are equal, and the effective polarization sheet is the sum of those from the top and bottom surfaces. This is mathematically the same as a single surface SHG source generated by a nonlinear tensor which is the sum of those for the top and bottom surfaces.

For graphene, all nonzero tensor elements change sign between the top and bottom surfaces, so the infinitesimally thin limit gives exactly zero for all tensor elements. Physically, the SHG generated from the top surface is exactly out of phase with that generated from the bottom surface; this is essentially the same reason that reflection from any infinitesimally thin film is zero. Note that if one considers a single polarization sheet corresponding to $C_{6v}$ symmetry, an isotropic SHG signal would result. Furthermore, an inversion symmetry argument would give zero SHG from graphene.

For a multilayer C-film, the only nonzero tensor element that does not change sign between the top and bottom surfaces is $\partial_{11}$, which always has a $\cos(3\phi)$ or $\sin(3\phi)$ factor. This gives a purely anisotropic tensor — all terms independent of $\phi$ are zero, while all terms which depend on $\phi$ are doubled, thus generating an E-field of the form $E \propto \cos(3\phi)$ or $\sin(3\phi)$ depending on which polarizations are involved. An inversion symmetry argument would necessarily apply to both graphene and bilayer graphene, therefore any SHG from bilayer graphene disproves an inversion symmetry argument for thin films. The infinitesimally thin limit implies a zero-absorption and zero-depth film, and is not reached even in the case of graphene, which absorbs $\sim 2\%$. However, these arguments imply that graphene may only generate a very weak isotropic SHG signal. Furthermore, it is expected that few-layer C-films only generate a strong 3-fold symmet-
ric SHG signal with a weak isotropic component (which may be difficult to separate from the Si background).

In the following theoretical analysis, the samples will be assumed to have two or more layers, and thus have $C_{3v}$ symmetry. SHG from graphene will not be used in analyzing the nonlinear tensor elements.

The SHG from the substrate is treated phenomenologically, so it is not necessary to examine the tensors involved. It will only be assumed that the radiated SHG is 4-fold rotationally symmetric.

### 2.2.3 Radiated SHG

At this point, the fundamental E-fields at the relevant depths have been calculated in terms of the incident field, and the SHG polarizations have been calculated in terms of the fundamental E-fields. Next, it is necessary to calculate the E-fields generated by the $2\omega$ polarization sheets and, using the transfer matrix formalism, determine the SHG radiated through the top of the sample.

Since fields at frequency $\omega$ and $2\omega$ are considered in the following sections, lowercase quantities ($m$ and $k$) refer to $\omega$ fields, and uppercase variables (including the polarization $P$) refer to $2\omega$ fields. E-fields ($E$ and $e$) follow the same notation as defined in Eqs. (2.1) and (2.5) since the implied frequency is clear. Polarization directions ($\hat{s}$ and $\hat{p}_\pm$) are independent of frequency.

A polarization sheet in a vacuum generates an upward (+) and downward (-) propagating wave with fields [52]

$$E_{\pm} = E_{s\pm} \hat{s} + E_{p\pm} \hat{p}_\pm,$$

$$E_{s\pm} = \frac{iK^2}{2Kz\varepsilon_0} \hat{s} \cdot P,$$

$$E_{p\pm} = \frac{iK^2}{2Kz\varepsilon_0} \hat{p}_\pm \cdot P,$$

(2.19)

where $K = 2\omega/c$ is the wavenumber in air and $K_z = K\cos(\theta)$.

The SHG generated from the C-film/air interface and radiated from the top surface is the sum of the upward propagating wave and the reflected part of the downward propagating wave. This may be calculated using the transfer matrix formalism, with a discontinuity in the E-field corresponding to the polarization sheet. If the polarization sheet is defined to be sandwiched between $z = 0^+$ and $z = 0^-$, which is immediately
above the top surface, then
\[ e_1(0^-) = \mathbf{M}_{14} e_1(-d), \]
\[ e_1(0^+) = \mathbf{v} + e_1(0^-), \] (2.20)

where \( e_1(-d) \) is the E-field at the top of the Si, \( e_1(0^+) \) is the E-field above the system, \( \mathbf{M}_{14} \) is the composite matrix from Eq. (2.7) and \( \mathbf{v} \) is the discontinuity produced from the polarization sheet from Eq. (2.19):

\[
\mathbf{v}_s = \frac{i K^2}{2K_z \varepsilon_0} \begin{bmatrix}
\hat{s} \cdot \mathbf{P} \\
-\hat{s} \cdot \mathbf{P}
\end{bmatrix},
\]
\[
\mathbf{v}_p = \frac{i K^2}{2K_z \varepsilon_0} \begin{bmatrix}
\hat{p}_+ \cdot \mathbf{P} \\
-\hat{p}_- \cdot \mathbf{P}
\end{bmatrix}. \quad (2.21)

Through algebraic substitution, with the fact that \( e_1(0^+) \) has no downward propagating component, it is possible to solve for its upward propagating component \( E_{2\omega}^{s,t} \) to obtain

\[
E_{2\omega}^{s,t} = \frac{i K^2}{2K_z \varepsilon_0} P_y \left( 1 + \frac{\mathbf{M}_{14}^{1,2}}{\mathbf{M}_{14}^{2,2}} \right),
\]
\[
E_{2\omega}^{p,t} = \frac{i K^2}{2K_z \varepsilon_0} \begin{bmatrix}
\left( \frac{\mathbf{M}_{14}^{1,2}}{\mathbf{M}_{14}^{2,2}} + 1 \right) K_x P_z \\
\left( \frac{\mathbf{M}_{14}^{1,2}}{\mathbf{M}_{14}^{2,2}} - 1 \right) K_z P_x
\end{bmatrix}. \quad (2.22)

The \( 2\omega \) polarizations can then be used to find the radiated E-field generated from the top surface. For simplicity, only incident and emitted s- and p- polarized light is considered. The s- and p- polarized E-fields generated from a \( g \)-polarized (\( g \) is s or p) fundamental field are a sum of products of nonlinear tensor elements \( \partial_x \) where \( x = (11), (15), (31), (33), \) and linear terms \( a, b \) and \( c \):

\[
\frac{E_{gs,t}^{2\omega}}{E_g^2} = F \epsilon_{t,11}^{gs} \partial_{11}^t \sin(3\phi),
\]
\[
\frac{E_{gp,t}^{2\omega}}{E_g^2} = F [h_{l,11}^{gp} \partial_{11}^l \cos(3\phi) + \sum_x \alpha_{t,x}^{gp} \partial_{x}^l],
\]

where \( F = \frac{i K^2}{2K_z \varepsilon_0} \). (2.23)

The coefficients are listed in table 2.1.
$$c_{t,11}^{sa} = \left( 1 + \frac{3M_{12}^2}{2M_{14p}^2} \right) (r_{14s} + 1)^2$$

$$c_{t,11}^{pa} = - \left( 1 + \frac{3M_{12}^2}{2M_{14p}^2} \right) (-r_{14p} + 1)^2 \cos^2 (\theta)$$

$$b_{t,11}^{sp} = - \left( \frac{3M_{12}^2}{2M_{14p}^2} - 1 \right) \cos (\theta) (r_{14s} + 1)^2$$

$$l_{t,11}^{pp} = \left( \frac{3M_{12}^2}{2M_{14p}^2} - 1 \right) (-r_{14p} + 1)^2 \cos^3 (\theta)$$

$$a_{t,31}^{sp} = \left( \frac{3M_{12}^2}{2M_{14p}^2} + 1 \right) (-r_{14p} + 1)^2 \sin (\theta) \cos^2 (\theta)$$

$$a_{t,31}^{pp} = \left( \frac{3M_{12}^2}{2M_{14p}^2} + 1 \right) (-r_{14p} + 1)^2 \sin (\theta) \cos^2 (\theta)$$

$$a_{t,33}^{pp} = \left( \frac{3M_{12}^2}{2M_{14p}^2} + 1 \right) (r_{14p} + 1)^2 \sin^3 (\theta)$$

$$a_{t,15}^{pp} = 2 \left( \frac{3M_{12}^2}{2M_{14p}^2} - 1 \right) (-r_{14p} + 1) \cos^2 (\theta) \sin (\theta) (r_{14p} + 1)$$

---

Table 2.1: Radiated E-field coefficients from the top surface

The SHG contribution from the top vacuum interface may be calculated similarly. If the SHG polarization is on the plane $z = -d_2$ which is inside the infinitesimally thin vacuum interface, then the E-fields across the structure are

$$e_1(0) = \mathbf{M}_{12} \mathbf{M}_2 (d_2) \mathbf{M}_{21} e_1 (-d_2^+)$$

$$= \mathbf{M}_{11} e_1 (-d_2^+) ,$$

$$e_1(-d_2^+) = \mathbf{v} + e_1 (-d_2^+) ,$$

$$e_1(-d_2^-) = \mathbf{M}_{13} \mathbf{M}_3 (d_3) \mathbf{M}_{34} e_1 (-d) ,$$

where $\mathbf{M}_{11} = \mathbf{M}_{12} \mathbf{M}_2 (d_2) \mathbf{M}_{21}$.

(2.24)

The emitted SHG field above the system may then be found through algebraic substitution as described before. The results are the same as Eq. (2.23), but with the $t$ replaced by $b$, and coefficients given in table 2.2. The variables $\tilde{e}_{1\pm}$ refer to the upward (+) or downward (-) propagating E-field at the top vacuum interface normalized to the incident E-fields.

The final contribution is from the Si, which is treated phenomenologically here. From symmetry considerations, it is known that the total E-field produced from (001)Si (surface dipolar and bulk quadrupolar contributions) is 4-fold rotationally symmetric, and the s-polarized SHG E-field has no isotropic contribution [40]. For linearly $g$-polarized ($g$ is s or p) fundamental light it is assumed that the $h$-polarized ($h$ is s or p) SHG E-field $E_{gh}^{2\omega}$
\begin{align*}
\epsilon_{b,11}^{ss} &= \left( m_{1,1}^{1,1} - \frac{m_{1,1}^{2,1} m_{1,1}^{2,1} - m_{1,1}^{2,2} + m_{1,1}^{2,2}}{m_{1,1}^{2,2} m_{1,1}^{2,2} - m_{1,1}^{2,2} + m_{1,1}^{2,2}} \right) \left( \tilde{\epsilon}_{v,1+}^{s} + \tilde{\epsilon}_{v,1-}^{s} \right)^2, \\
\epsilon_{b,11}^{sp} &= - \left( m_{1,1}^{1,1} - \frac{m_{1,1}^{2,1} m_{1,1}^{2,1} - m_{1,1}^{2,2} + m_{1,1}^{2,2}}{m_{1,1}^{2,2} m_{1,1}^{2,2} - m_{1,1}^{2,2} + m_{1,1}^{2,2}} \right) \left( \tilde{\epsilon}_{v,1-}^{p} - \tilde{\epsilon}_{v,1+}^{p} \right)^2 \cos^2 (\theta), \\
\epsilon_{b,11}^{sp} &= - \left( m_{1,1}^{1,1} + \frac{m_{1,1}^{2,1} m_{1,1}^{2,1} - m_{1,1}^{2,2} + m_{1,1}^{2,2}}{m_{1,1}^{2,2} m_{1,1}^{2,2} - m_{1,1}^{2,2} + m_{1,1}^{2,2}} \right) \cos (\theta) \left( \tilde{\epsilon}_{v,1+}^{s} + \tilde{\epsilon}_{v,1-}^{s} \right)^2, \\
\epsilon_{b,11}^{pp} &= - \left( m_{1,1}^{1,1} + \frac{m_{1,1}^{2,1} m_{1,1}^{2,1} - m_{1,1}^{2,2} + m_{1,1}^{2,2}}{m_{1,1}^{2,2} m_{1,1}^{2,2} - m_{1,1}^{2,2} + m_{1,1}^{2,2}} \right) \left( \tilde{\epsilon}_{v,1-}^{p} - \tilde{\epsilon}_{v,1+}^{p} \right)^2 \cos^2 (\theta) \sin (\theta), \\
\epsilon_{b,33}^{pp} &= \left( m_{1,1}^{1,1} - \frac{m_{1,1}^{2,1} m_{1,1}^{2,1} - m_{1,1}^{2,2} + m_{1,1}^{2,2}}{m_{1,1}^{2,2} m_{1,1}^{2,2} - m_{1,1}^{2,2} + m_{1,1}^{2,2}} \right) \left( \tilde{\epsilon}_{v,1+}^{p} + \tilde{\epsilon}_{v,1-}^{p} \right)^2 \sin^2 (\theta), \\
\epsilon_{b,15}^{pp} &= \left( m_{1,1}^{1,1} + \frac{m_{1,1}^{2,2} m_{1,1}^{2,2}}{m_{1,1}^{2,2} m_{1,1}^{2,2}} \right) \left( \tilde{\epsilon}_{v,1-}^{p} - \tilde{\epsilon}_{v,1+}^{p} \right)^2 \cos^2 (\theta) \left( \tilde{\epsilon}_{v,1+}^{p} + \tilde{\epsilon}_{v,1-}^{p} \right) \sin (\theta). \\
\end{align*}

Table 2.2: Radiated E-field coefficients from the C-film/SiO₂ interface.

from the silicon depends on the downward propagating \(g\)-polarized E-field in the SiO₂/Si interface, \(e_{v,2-}^g = e_{v,2-}^g(-d)\):

\begin{align}
E_{gs}^{2\omega} &= \frac{iK^2}{2K\varepsilon_0} \alpha_{gs} \sin (4\phi) \left( e_{v,2-}^g \right)^2, \\
E_{gp}^{2\omega} &= \frac{iK^2}{2K\varepsilon_0} \left( \beta_{gp} + \alpha_{gp} \cos (4\phi) \right) \left( e_{v,2-}^g \right)^2. 
\end{align} \tag{2.25}

The \(\alpha\) and \(\beta\) are phenomenological constants accounting for both the surface and bulk contributions and are complex valued. The angle \(\phi\) is taken relative to the [100] direction in the Si. The SHG light is treated as originating from the top of the Si, and must propagate through the system. From Eq. (2.7), and solving for the transmitted E-field to the top surface, \(\Sigma_{41}\), the radiated SHG from the Si may be written as

\begin{align}
\frac{E_{gs}^{2\omega}}{(E_g^2)^2} &= \frac{iK^2}{2K\varepsilon_0} \frac{s_{gs} \alpha_{gs} \sin (4\phi)}{s_{gs} \alpha_{gs} \sin (4\phi)}, \\
\frac{E_{gp}^{2\omega}}{(E_g^2)^2} &= \frac{iK^2}{2K\varepsilon_0} \left( \beta_{gp} + \alpha_{gp} \cos (4\phi) \right) \frac{s_{gp}}{s_{gs} \alpha_{gs} \sin (4\phi)},
\end{align} \tag{2.26}

where \(s_{gh} = (m_{1,1}^{1,1} - \frac{m_{1,1}^{2,1} m_{1,1}^{2,2}}{m_{1,1}^{2,2} m_{1,1}^{2,2}}) (e_{v,2-}^g)^2\). The unitless parameter \(s_{gh}\) incorporates all the linear optical properties for the fundamental and SHG fields in the multilayer structure.
\[ f_{pp}^0 = |\beta_{pp} s_{pp} + a_{31}^{pp} \partial_{31} + a_{33}^{pp} \partial_{33} + a_{15}^{pp} \partial_{15}|^2 + \frac{|\alpha_{pp} s_{pp}|^2}{2} + \frac{|\beta_{pp} t_{11}|^2}{2} \]
\[ f_{pp}^3 = 2\text{Re} \left[ (\beta_{pp} s_{pp} + a_{31}^{pp} \partial_{31} + a_{33}^{pp} \partial_{33} + a_{15}^{pp} \partial_{15}) (b_{11}^{pp} \partial_{11})^* \right] \]
\[ f_{pp}^6 = \frac{|b_{11}^{pp} \partial_{11}|^2}{2} \]
\[ f_{sp}^0 = |\beta_{sp} s_{sp} + a_{31}^{sp} \partial_{31}|^2 + \frac{|\alpha_{sp} s_{sp}|^2}{2} + \frac{|b_{11}^{sp} \partial_{11}|^2}{2} \]
\[ f_{sp}^3 = 2\text{Re} \left[ (\beta_{sp} s_{sp} + a_{31}^{sp} \partial_{31}) (b_{11}^{sp} \partial_{11})^* \right] \]
\[ f_{sp}^6 = \frac{|b_{11}^{sp} \partial_{11}|^2}{2} \]
\[ f_{ps}^0 = |s_{ps} a_{ps}|^2 + \frac{|c_{11}^{ps} \partial_{11}|^2}{2} \]
\[ f_{ps}^6 = -\frac{|c_{11}^{ps} \partial_{11}|^2}{2} \]
\[ f_{ss}^0 = |s_{ss} a_{ss}|^2 + \frac{|c_{11}^{ss} \partial_{11}|^2}{2} \]
\[ f_{ss}^6 = -\frac{|c_{11}^{ss} \partial_{11}|^2}{2} \]

Table 2.3: Fourier elements of the total SHG intensity

### 2.2.4 Total SHG intensity

All of the SHG E-fields have now been evaluated at the top surface of the system, and written in terms of the linear optical properties, propagation distances, and nonlinear susceptibilities. These fields must be added coherently to find the SHG intensity. The C-film SHG coefficients from the top and bottom surfaces add together \((c_{ss}^{tt}, c_{ss}^{bb} = c_{ss}^{11}, \text{etc.})\), along with the SHG from the substrate. The C-film is generally placed on the substrate at a random angle \(\delta\) relative to the [100] direction of the substrate. The resultant SHG intensity \(I_{2\omega g}^h(\phi)\) may be analyzed in terms of Fourier components,

\[
\frac{I_{2\omega g}^h(\phi)}{(I_g^{2\omega})^2} = |F|^2 \sum_m f_{gh}^m \cos m(\phi - \delta_m),
\]

where the incident and outgoing polarizations are \(g\) and \(h\) respectively, and the Fourier elements \(f_{gh}^m\) are constants dependent on the number of layers. When the isotropic, 3-fold, and 4-fold contributions add (modulus squared), they generate other Fourier elements \((0, 1, 3, 4, 6, 7, 8)\) with a phase shift dependent on the sample orientation \(\text{i.e. } \delta_3 = \delta_6 = \delta \text{ and } \delta_0 = \delta_4 = 0\). Because the 4-fold contribution from the Si is significantly weaker than its isotropic contribution and the C-film’s 3-fold contribution (as shown in section 4.3), the strongest remaining elements are 0, 3, and 6 [40, 26]. These Fourier elements are shown in table 2.3.
This gives the SHG intensity Fourier components in terms of the C-film nonlinear tensor elements ($\partial_x$), calculable linear parameters ($a$, $b$, $c$, and $s$) which depend on the number of layers, and the effective nonlinear parameters of Si ($\alpha$ and $\beta$). The linear parameters may be numerically calculated as described above. Although this involves complex matrix calculations, the final results are unitless numbers that depend on the number of layers. Some of these are shown in Fig. 2.2 for the parameters used in the experiment described here (fundamental wavelength of 800 nm, 60° angle of incidence, and sample structure described above).

Several patterns may be noted from the parameters $a$, $b$, and $c$ which effectively give weight to the nonlinear tensor elements ($\partial_x$) for the C-film and substrate. Those for $\partial_{11}$ are all greatest for 2 layers, and decay with thickness. This is the element which gives the 3-fold symmetry as shown in Eq. (2.17). All others (for $\partial_{31}$, $\partial_{33}$, $\partial_{15}$) are weakest for 2 layers, and increase with C-film thickness. These elements give an isotropic contribution which adds to that from the substrate, which will have a contribution which decreases with C-film thickness. These trends are not absolute however; there exist oscillations in these weighting factors with layer-number on top of the general increasing/decreasing trends which are due to thin film interference effects. All the $s$ parameters corresponding to SHG from the substrate decrease with increasing C-film thickness as expected. These observations agree with those inferred in the thin film limit: the strongest 3-fold SHG will result from bilayer C-films, and the anisotropy will decrease with thicker C-films. The variation of the magnitude of the isotropic response with C-film thickness is not obvious because the contribution from the C-film will increase, and the contribution from the substrate will decrease for thicker films.

As mentioned in section 2.2.2, graphene must be treated separately from multilayer C-films. In that case, $\partial_{11}=0$, or equivalently all the associated linear parameters ($c_{11}^{ps}$, $b_{11}^{pp}$, etc.) are zero. Other parameters ($a_{33}^{pp}$, $a_{15}^{pp}$) are very small for graphene, as shown in Fig. 2.2. The main contribution is from the substrate ($i.e.$, $s_{pp}$ and $s_{sp}$ are the only linear parameters that do not approach zero). Therefore, the SHG intensity from either graphene or the bare substrate will have a $\phi$ dependence with only 0th and 4th Fourier elements (from Eq. (2.27)).

Once the linear parameters are incorporated, the Fourier elements $f_{gh}^m$ only depend on the C-film and substrate nonlinear tensor elements $\partial_x$, $\alpha$, and $\beta$. This suggests the use of simple fitting to find the tensor elements, and except for trivial ambiguities ($i.e.$, phase factors and normalization), they can be uniquely determined.
The 4-fold anisotropy of the substrate is very weak compared to that from the C-film [26], thus for qualitative discussion, $\alpha$ may be ignored, and the phase of the substrate SHG with the p-in, p-out combination may be taken to be real. Of particular note is that the (ps) and (ss) polarization combinations involve only the $\partial_{11}$ tensor element. Therefore this can be determined to within a phase factor. For sufficiently thin samples, both (pp) and (sp) combinations involve only the $\partial_{11}$ and $\beta_{pp}$ elements; therefore the phase of $\partial_{11}$ may be determined. With thicker samples, using the (sp) combination, only $\partial_{11}$ and $\partial_{31}$ contribute; therefore the magnitude and phase of $\partial_{31}$ may be found from the 0th and 3rd Fourier elements (and for thin samples, the magnitude and phase of $\beta_{ps}$ may then be found if desired). Finally, the (pp) polarization combination involves both of these and $\partial_{33}$ and $\partial_{15}$, which leaves some ambiguity in solving for both of the latter.

The theory described above applies only for s/p incident, and s/p observed polarization, but a similar analysis can also be used for diagonally polarized incident light with observed s-polarization (ds). This case is more complex because, as suggested by Eq. (2.17), the generated E-field has a complex term proportional to $\sin(3\phi)$, and a complex
term proportional to $\cos(3\phi)$. The corresponding 3-fold symmetry will therefore have a magnitude and phase shift involving both terms. These may be calculated in the same way as the other polarization combinations, but is not explicitly shown here. Since the $P_y$ polarization is observed, and it is generated by diagonally polarized E-fields which have $x$, $y$, and $z$ components, Eq. (2.17) shows that only the $\partial_{11}$ and $\partial_{15}$ tensor elements are involved (for thicker samples, where the substrate is blocked). Thus, from the 0th and 3rd Fourier elements (and confirmed through the phase of the 3rd element) the magnitude and phase of $\partial_{15}$ may be found. Finally, $\partial_{33}$ may be found through the (pp) combination.

2.3 Strain-Induced Second Harmonic Generation

The optical properties of a material, such as its SHG efficiency, are determined by the electronic orbitals. These, in turn, are determined by many factors such as the crystal lattice structure. The lattice of a material can be altered by strain, either through the application of stress, or through thermal expansion. Strain can therefore be probed using SHG [47, 48, 49]. Bulk MnAs experiences a sudden lattice change during the phase transition, as well as a continuous change due to thermal expansion/contraction. In thin film form, the situation is more complicated, but clearly the lattice changes with temperature, and these changes can be observed through SHG.

When MnAs passes through the phase transition temperature, the $a$ and $b$ lattice parameters (see Fig. 1.2 in section 1.3) change by $\sim 1\%$ while the $c$ lattice parameter remains nearly fixed. When grown as a thin film however, the MnAs film remains attached to the substrate, and cannot change in lateral size relative to the substrate. Therefore, the average $a$ and $c$ lattice parameters remain fixed (subject to the relatively small thermal expansion of the substrate). This situation gives rise to a very high stress and strain, and this strain can be observed through SHG. Although the $a$ and $c$ lattice parameters are held fixed in a spatially averaged sense, there can be a modulation of the lattice parameters (shown in Fig. 1.3); these stripes do not affect the spatially averaged lattice parameters. For SHG in a specular reflection geometry, only the spatially averaged strain (or zeroth Fourier component) is relevant; the periodic modulation from the stripes may cause SHG at other angles (analogous to diffraction), but this is not studied here. This section gives a theoretical discussion of strain-induced SHG from MnAs films.

The notation for the discussion of stress and strain used here is the same as that used
by Kaganer et. al. [32]. The total strain, $\epsilon$, is the sum of the elastic strain $\epsilon$ and the internal strain $\eta$. If the MnAs were not attached to the substrate, the lattice parameters would change relative to some reference state due to thermal expansion and the sudden change during the phase transition. The difference in the lattice parameters between the reference state and unstressed state at a certain temperature is the internal strain. The elastic strain is the quantity which is proportional to stress. The total strain is then the net change in the lattice relative to some reference state. As usual, the stress tensor $\sigma$ represents the force per unit area acting on each surface. It is to be understood that although the strain (internal and elastic) might be periodically modulated, in all the discussion relating to SHG, $\epsilon$, $\epsilon$, $\eta$, and $\sigma$ refer to their spatially averaged values along the $x$-direction.

The coordinate system used here is shown in Fig. 1.2, and is the same as that used by Kaganer et. al. [32]. The $a$ lattice direction is along $\hat{x}$, $b$ is along $\hat{y}$, and $c$ is along $\hat{z}$. In tensor notation, the $x$, $y$, and $z$ components are denoted as ‘1’, ‘2’, and ‘3’. Note that in this coordinate system, the surface normal is $\hat{y}$, which is different from the coordinate system used for the graphene SHG experiment.

Because of the hexagonal symmetry of the MnAs films and the fact that there is no shear stress, all off-diagonal elements of $\epsilon$, $\epsilon$, and $\eta$ are zero. Since the MnAs film is fixed in the $x$-$z$ plane, the $xx$ and $zz$ components of the total strain are zero. Therefore, the only nonzero component of strain is in the $y$-direction ($\epsilon_{22}$). Since the sample is free to expand in the $y$-direction, the $\sigma_{22}$ component of the stress is zero. Finally, since the orthorhombic distortion is minimal, the internal strain in the $x$- and $y$- directions are equal. To summarize,

$$
\epsilon_{ii} = \epsilon_{ii} + \eta_{ii}, \\
\epsilon_{11} = \epsilon_{33} = 0, \\
\sigma_{22} = 0, \\
\eta_{11} = \eta_{22}.
$$

(2.28)

Hooke’s law in full tensor form is $\sigma_{ij} = c_{ijkl}\epsilon_{kl}$, where $c_{ijkl}$ is the elastic modulus tensor. Because of the hexagonal symmetry, the $x$- and $y$- directions are equivalent in
terms of the elastic constants \((c_{1133} = c_{2233}, \text{ etc.})\). In contracted notation,

\[
\begin{align*}
\sigma_{11} &= c_{11}e_{11} + c_{12}e_{22} + c_{13}e_{33}, \\
\sigma_{22} &= c_{12}e_{11} + c_{11}e_{22} + c_{13}e_{33}, \\
\sigma_{33} &= c_{13}e_{11} + c_{13}e_{22} + c_{33}e_{33}.
\end{align*}
\] (2.29)

The elastic constants are given in reference [53]:

\[
\begin{align*}
c_{11} &= 40 \text{ GPa}, \\
c_{12} &= 8 \text{ GPa}, \\
c_{13} &= 10 \text{ GPa}, \\
c_{33} &= 110 \text{ GPa}.
\end{align*}
\] (2.30)

For MnAs films, the only nonzero component of total strain is \(\epsilon_{22}\), so this is the quantity which is relevant to strain-induced SHG. From Eqs. (2.28) and (2.29), it is straightforward to find the following simple relationship:

\[
\epsilon_{22} = \frac{1}{(c_{12} - c_{11})} \sigma_{11},
\] (2.31)

\(i.e.,\) the total strain in the \(y\)-direction is directly proportional to the stress in the \(x\)-direction (the proportionality constant is negative because a compressive stress in the \(x\)-direction acts to expand the film in the \(y\)-direction). This is true regardless of any stress in the \(z\)-direction (caused by thermal expansion) which causes a strain in the \(y\)-direction through the appropriate Poisson ratio. Equation (2.31) is useful because the \(xx\) component of the stress \((\sigma_{11})\) is given as a function of temperature in reference [31], figure 2. The magnitude of the strain is nearly zero at 40°C and increases as the sample cools through the phase transition region toward 10°C, and continues increasing at a reduced rate as the sample is further cooled due to negative thermal expansion. Furthermore, above 40°C, the magnitude of the strain increases slowly because of thermal expansion.

These trends should also show up in strain-induced SHG, but it is not convenient to read off values from the graphs in reference [31] because they are limited to \(-10 \text{ to } 70^\circ\text{C}\), and the weak increase above 40°C is barely visible given signal/noise considerations. It is therefore worthwhile to find \(\epsilon_{22}\) in terms of known physical parameters. Through
algebraic manipulations of Eqs. (2.28) and (2.29), one can obtain
\[ \epsilon_{22} = A\eta_{11} + B\sigma_{33}, \]
where \[ A = 1 + \frac{c_{12}c_{33} - c_{13}^2}{c_{11}c_{33} - c_{13}^2} \approx 1.18, \]
and \[ B = \frac{c_{13}}{(c_{13}^2 - c_{11}c_{33})} \approx -0.00233 \text{ GPa}^{-1}. \] (2.32)

The ‘1’ in \( A \) reflects the fact that the internal strain in the \( y \)-direction is equal to the internal strain in the \( x \)-direction, and the second term is due to increased strain in the \( y \)-direction from stress in the \( x \)-direction through Poisson’s ratio. The effect of the stress in the \( z \)-direction, \( \sigma_{33} \), is fairly weak (using stress values from reference [31], the overall affect on \( \epsilon_{22} \) is about 10\( \times \) weaker than that of the lattice expansion in the \( x \)-direction, the \( A\eta_{11} \) term). Therefore, only the \( A\eta_{11} \) term will be included in this analysis.

The value of \( \eta_{11}(T) \) represents the change in the \( a \) lattice parameter without applied stress relative to some reference point. It clearly varies with temperature through the coefficient of thermal expansion. For convenience, the reference point is chosen to be the lattice parameter at 40\( ^\circ \)C, \( i.e., \eta_{11}(40^\circ \text{C}) \equiv 0; \) in the thin film system used here, the elastic strain is nearly zero at 40\( ^\circ \)C. The temperature dependence of \( \eta_{11}(T) \) is then just determined by the coefficient of thermal expansion in the \( x \)-direction \( \gamma_x \), so \( \frac{d\eta_{11}}{dT} = \gamma_x \).

Depending on the source [30, 31], values for the coefficients of thermal expansion vary by \( \sim 10\% \); values of \( \gamma_x(\alpha) = -1.1 \times 10^{-4}/^\circ \text{C} \) and \( \gamma_x(\beta) = 6.3 \times 10^{-5}/^\circ \text{C} \) for the \( \alpha \) and \( \beta \) phases will be used here. Thermal expansion of the GaAs substrate may change the lattice parameters of the MnAs film, thus affecting the above results. The coefficient of thermal expansion of GaAs is \( 5.8 \times 10^{-6}/^\circ \text{C} \). Since it is much less than that for MnAs, it can be ignored.

In bulk MnAs, the sudden fractional increase in the \( a \) lattice parameter is \( \Delta \eta_{11} \sim 0.0092 \) [30]. This, along with the coefficients of thermal expansion given above, define \( \eta_{11}(T) \) for bulk samples. For thin films, \( \eta_{11}(T) \) should match bulk values for \( T > 40^\circ \text{C} \) and for \( T < 10^\circ \text{C} \). Between these temperatures, \( \eta_{11}(T) \) should transition smoothly. It is not immediately clear what form \( \eta_{11}(T) \) should take in this region; \( \sigma_{11} \) varies approximately linearly with temperature in reference [31], although no fit is given. A linear dependence will be assumed here. This gives the temperature dependent strain \( \epsilon_{22}(T) \) as shown in Fig. 2.3.

There are two possible forms in which strain may influence SHG in a material which possesses inversion symmetry: an inhomogeneous strain breaks the inversion symmetry,
Figure 2.3: Calculated strain vs. temperature using known values of the coefficients of thermal expansion and elastic constants.

thus allowing electric dipole SHG; or a homogeneous strain will change the electronic orbitals at the surface and in the bulk, which will modify the existing surface electric dipolar SHG, and bulk electric quadrupolar SHG. The strain is expected to be homogeneous in the direction of the surface normal for these films because the top region of the film cannot uniformly expand or contract relative to the bottom of the film. In the coexistence phase there is a periodic component of the strain; this could in principle produce diffracted orders of SHG, but will not affect the SHG yield in a reflection geometry. The penetration depth for both the fundamental and second harmonic light is $\sim 17$ nm (see section 2.4). This gives an effective $e^{-1}$ escape depth of any bulk SHG contributions of $\sim 6$ nm, therefore bulk quadrupolar SHG is expected to be weak. Strain-induced SHG is therefore assumed to originate from a modified surface electric dipole source.

The contribution of the strain to SHG is given by a rank-5 nonlinear photoelastic tensor $\mathbf{p}$, so $\chi_{ijklm}^{\text{eff}} = \chi_{ijklm}^{0} + p_{ijklm}\epsilon_{lm}$ [48] where $\chi_{ijkl}^{0}$ and $\chi_{ijkl}^{\text{eff}}$ are the unperturbed, and total effective SHG tensors respectively. Since the only nonzero component of the spatially averaged strain $\tau$ at the surface is $\epsilon_{22}$, hereafter simply $\epsilon_{s}$, this can be written as

$$\chi_{ijkl}^{\text{eff}} = \chi_{ijkl}^{0} + \epsilon_{s}\chi_{ijkl}^{s},$$

(2.33)

where $\chi_{ijkl}^{s}$ must contain the same symmetry as the MnAs.

It is not practical or especially useful to try to evaluate all the components of $p_{ijklm}$ or $\chi_{ijkl}^{s}$; instead, the effect of strain on SHG will be quantitatively investigated for a particular polarization combination: p-in, and p-out. Given the 2-fold rotational symmetry of MnAs films with the c-axis in-plane, the radiated second harmonic E-field may contain
an isotropic and 2-fold component:

\[
\frac{E^{2\omega}}{(E^{\omega})^2} \propto (a_0 + \epsilon_s(T)a_s) + (b_0 + \epsilon_s(T)b_s) \cos (2\phi),
\]

(2.34)

where \(a_0\) and \(b_0\) are constants related to \(\chi^0_{ijk}\), and \(a_s\) and \(b_s\) are constants related to \(\chi^s_{ijk}\). The intensity as a function of azimuthal rotation angle \(\phi\) is

\[
\frac{I^{2\omega}}{(I^{\omega})^2} = \left[ |a_0 + \epsilon_s(T)a_s|^2 + \frac{|b_0 + \epsilon_s(T)b_s|^2}{2} + 2\text{Re} \left( (a_0 + \epsilon_s(T)a_s)(b_0 + \epsilon_s(T)b_s)^* \right) \cos (2\phi) + \frac{|b_0 + \epsilon_s(T)b_s|^2}{2} \cos (4\phi) \right].
\]

(2.35)

\(I^{2\omega}\) is insensitive to global phase factors for the coefficients, and so without loss of generality \(a_0\) is taken to be real and positive. Furthermore, since \(I^{2\omega}\) is unchanged when all constants are changed to their complex conjugates, the imaginary part of \(a_s\) is taken to be positive. As Eq. (2.35) suggests, there may be 0th, 2nd and 4th Fourier elements to the \(\phi\)-dependent SHG intensity. These three values may be determined from measurements of \(I^{2\omega}(\phi)\) for several values of \(\phi\).

Since the strain is negligible at 40°C and grows with decreasing temperature, the \(a_{0/s}\) and \(b_{0/s}\) coefficients can be determined as follows. The magnitude of \(b_0\) may be found through a measurement of the 4th Fourier element with no strain present, then the magnitude of \(a_0\) can be obtained through the 0th Fourier element with no strain. The phase of \(b_0\) (relative to \(a_0\)) may be found through a measurement of the 2nd Fourier element with no strain. With high strain (i.e., at low temperatures), the 4th Fourier element is determined by the magnitude of \(b_s\) (when it dominates \(b_0\)). For intermediate strain, the interference term between \(b_s\) and \(b_0\) affects the 4th Fourier element, thus the phase of \(b_s\) may be found (where the sign of the component of \(b_s\) out of phase with \(b_0\) is arbitrary, but is ambiguous). Similarly, the magnitude of \(a_s\) may be found from the 0th Fourier element (once \(b_s\) is known), and the sign ambiguity is removed by the 2nd Fourier element. This illustrates that each of the complex coefficient can be uniquely determined, but rather than doing so in the manner suggested, it is much more practical to use a curve-fitting method to extract them.

It is worth emphasizing, however, that the actual values of the \(a_{0/s}\) and \(b_{0/s}\) parameters are not very important. The main point is that the SHG yield varies with temperature in a manner which can be fully explained by the temperature dependence of the strain \(\epsilon_s(T)\). Once the \(a_{0/s}\) and \(b_{0/s}\) parameters have been determined by measuring the SHG as a function of temperature under equilibrium conditions, it is then possible to use those
parameters to measure the strain using SHG as a probe after the MnAs film has been optically excited on an ultrafast timescale.

2.4 Heat Diffusion

Two experiments are carried out on MnAs, SHG and linear optical diffraction. Both experiments are carried out under both equilibrium conditions (i.e., at a constant temperature) and following ultrafast excitation from an optical pulse. Immediately following ultrafast excitation, electrons are excited to higher energy states and then quickly thermalize to a Fermi–Dirac distribution. MnAs does not have a band gap, and there are many states near the Fermi energy [54]. This gives MnAs its metallic characteristics, including short optical penetration depth and fast electron-lattice thermalization. The hot carriers are therefore expected to transfer energy to the lattice through electron-phonon interactions on a timescale of a few picoseconds. Since SHG is sensitive to strain, and the diffraction is sensitive to the grating amplitude, the lattice temperature is an important parameter for both experiments. The evolution of the temperature throughout the film and substrate is then determined by the heat diffusion equation. This process is described below.

It is first necessary to find the optical penetration depth of MnAs at 775 nm (used in both experiments). These are obtained from values given in reference [36]:

\[
\epsilon_\alpha^o = -6 + 19i \quad \text{and} \quad \epsilon_\beta^o = -1 + 23i
\]

which give give

\[
n_\alpha^o = 2.6 + 3.6i \quad \text{and} \quad n_\beta^o = 3.3 + 3.5i.
\]

These are the ordinary indices (designated ‘o’) in the \(\alpha\) and \(\beta\) phases; the extraordinary indices are similar and will not be used. These give a penetration depth of

\[
\delta = \frac{\lambda}{\pi \Im(n)} \sim 17 \text{ nm}.
\]

It is worth noting that from other references [35], one obtains

\[
n = 2 + 2.8i,
\]

which yields \(\delta = 22 \text{ nm} \), but the value 17 nm is used here.

In this calculation, the effects of ballistic electrons have been ignored. In good metallic films such as gold, the energy deposition depth into the lattice can reflect ballistic electron motion as well as optical penetration depth [55] with ballistic effects increasing the effective absorption depth by \(\sim 100 \text{ nm} \). This is not expected to be the case in MnAs where the carrier momentum scattering time is only \(\sim 5 \text{ fs} \) [56]. If a Fermi velocity of \(\sim 10^6 \text{ m/s} \) [57] is assumed, this gives a mean free path of only \(\sim 5 \text{ nm} \).

The thermal constants of MnAs vary with temperature, especially near the phase transition temperature. Bulk MnAs has a temperature-dependent heat capacity \(C_m\) (where \(m\) indicates MnAs, as opposed to the GaAs substrate) of \(\sim 50–70 \text{ J mol}^{-1} \text{ °C}^{-1} \).
near room temperature with a singularity at the phase transition temperature, and a latent heat of 7.5 kJ kg\(^{-1}\) \[58\]. Due to the existence of the coexistence phase in thin film MnAs, the latent heat is distributed between 10–40\(^{\circ}\)C. This makes a numerical model of heat diffusion driven by a short laser pulse much more complex. For example, if the film is initially at 10\(^{\circ}\)C, and if bulk parameters are used, an incident laser pulse may have enough energy to increase the temperature at some depth to 30\(^{\circ}\)C. However, because of the existence of the coexistence phase, it is not clear how much of that energy may be lost to latent heat effects. Furthermore, the existence of stripes is known only under equilibrium conditions. After laser-excitation, the top surface is immediately heated, and there is a large temperature gradient. Under these conditions, it is not known what form the stripes will take or how their parameters will vary throughout the film, and so it is not clear how to incorporate latent heat into a thermal model. Despite the presence of the stripes, the model described here is taken to be 1-dimensional, so the temperature is averaged in the \(x\)-direction. It is also not necessarily true that the total latent heat and specific heat of thin film MnAs are the same as those of bulk MnAs. They may be affected by, for example, the magnetocaloric effect or the energy stored as elastic strain. The thermal model described below must therefore include reasonable approximations to deal with latent heat, and ultimately, the calculated results can only be considered in view of this approximation. Nonetheless, they serve as a reasonable reference point for discussions of heating effects.

The energy density of bulk MnAs as a function of temperature, \(Q(T)\), is given in reference \[59\]; this is the function whose derivative is the heat capacity, \(C = \frac{\partial Q}{\partial T}\), and the magnitude of a discontinuity is the latent heat. The values of \(Q(T)\) must be converted to volumetric units to be applicable here; this is done using a unit cell volume (which contains 2 sets of MnAs) of \(6.8 \times 10^{-29}\) m\(^3\) \[7\]. Hence, 1 J mol\(^{-1}\) is equivalent to \(4.9 \times 10^{4}\) J m\(^{-3}\). The energy density is approximately linear with temperature for \(T < 10^{\circ}\)C and \(T > 40^{\circ}\)C, and presumably (values are given in steps of 20\(^{\circ}\)C) becomes nonlinear near 40\(^{\circ}\)C (where the heat capacity starts to increase), and has a step at 40\(^{\circ}\)C. Except for \(10^{\circ}\)C < \(T < 40^{\circ}\)C, this is assumed to apply for thin film MnAs as well. The values for \(Q(T)\) for \(10^{\circ}\)C < \(T < 40^{\circ}\)C will be obtained simply by assuming that \(Q(T)\) is linear between 10\(^{\circ}\)C and 40\(^{\circ}\)C. This is shown in Fig. 2.4.

The evolution of the temperature, \(T\), over time, \(t\), is governed by the heat diffusion
Figure 2.4: Energy density of MnAs as a function of temperature. Data points are given in reference [59]. The blue curve shows a sudden jump at 40°C corresponding to the latent heat of a bulk phase transition. The red curve shows the effect of the distributed latent heat expected for thin film MnAs. The heat capacity may be extracted from the slope: \( \sim 64 \text{ J mol}^{-1} \text{ °C}^{-1} \) for \( T < 10 \text{°C} \), and \( \sim 56 \text{ J mol}^{-1} \text{ °C}^{-1} \) for \( T > 40 \text{°C} \)

equation,
\[
\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial y^2},
\] (2.36)

where \( \kappa \) is the thermal diffusivity, and \( y \) corresponds to the surface normal. Equation (2.36) is subject to the boundary condition, \( \frac{\partial T}{\partial y} |_{y=0} = 0 \), which physically means no heat is transferred to the air. The initial energy density, \( Q(y, t = 0) \) is determined by the optical penetration depth \( \delta \); \( Q(y, 0) = Q_0 + T_{12} F \delta^{-1} \exp(-y/\delta) \), where \( T_{12} \) is the intensity transmission coefficient (which depends on angle of incidence and polarization), \( F \) is the optical fluence, and \( Q_0 \) is the energy density of the film before excitation. For a particular initial temperature, \( T_0 \), before excitation, \( Q_0 \) may be read directly from Fig. 2.4. Immediately after excitation, the temperature of the film at a particular depth may be found from \( Q(y, 0) \) using Fig. 2.4.

The thermal conductivity, \( K_m \), of MnAs varies with temperature [60], but does not exhibit any significant changes near the phase transition temperature. Values for thin film MnAs are therefore assumed to be the same as for bulk MnAs. These values are in the range 2–3 W m\(^{-1} \) °C\(^{-1} \) for most of the temperature range of interest. The thermal diffusivity is given by \( \kappa = \frac{K}{C_v} \), where \( C_v \) is the volumetric heat capacity. For bulk manganese arsenide, \( \kappa_m \sim 8 \times 10^{-7} \text{ m}^2 \text{ s}^{-1} \) [60] with a large decrease near the phase transition temperature due to the increase in heat capacity and latent heat effects. For
thin films where the latent heat is distributed, the same form should apply, but \( \kappa_m(T) = K_m(T)(\partial Q/\partial T)^{-1} \).

The thermal diffusivity of GaAs is \( \kappa_g = 3.1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \), and the thermal conductivity of GaAs is \( K_g = 55 \text{ W m}^{-1} \circ\text{C}^{-1} \). The temperature variation of these quantities is ignored here because the temperature of the GaAs substrate does not vary by more than \( \sim 5\circ\text{C} \) from its equilibrium value in any of the experiments.

For short times, the above description is sufficient, but on a timescale of several nanoseconds it is necessary to include the finite thickness of the MnAs film and heat diffusion into the GaAs substrate. The temperature evolution is then fully described by the following set of equations:

\[
\begin{align*}
Q(y, 0) &= Q_0 + T_{12}F\delta^{-1}\exp(-y/\delta) \\
\frac{\partial T_m(y, t)}{\partial t} &= -\kappa_m(T) \frac{\partial^2 T_m(y, t)}{\partial y^2} \quad \text{for } y < d_m \\
\frac{\partial T_g(y, t)}{\partial t} &= -\kappa_g \frac{\partial^2 T_g(y, t)}{\partial y^2} \quad \text{for } y > d_m \\
K_m(T) \frac{\partial T_m(d, t)}{\partial y} &= K_g \frac{\partial T_g(d, t)}{\partial y} \\
\frac{\partial T_m(y, t)}{\partial y} &= 0 \quad \text{at } y = 0
\end{align*}
\]

where \( T_m(y, t) \) and \( T_g(y, t) \) represent the temperature at time \( t \) and depth \( y \) into the MnAs \( (m) \) or GaAs \( (g) \), and \( d_m \) is the MnAs film thickness. The fourth equation forces the flow of heat out of the MnAs to be the same as the flow of heat into the GaAs.

These equations are modeled numerically using a finite difference method. The MnAs film and GaAs substrate are modeled as \( N_m \) and \( N_g \) discrete ‘pixels’ of size \( \Delta y_m = d_m/N_m \) and \( \Delta y_g = d_g/N_g \), and time occurs in steps of \( \Delta t \). On the timescales where any change to the diffraction/SHG is significant (\( \lesssim 2 \mu\text{s} \) which will be shown later), it is sufficient to simply treat the substrate as having a finite depth of \( d_g = 5 \mu\text{m} \). Then, Eqs. (2.37)
become:

\[
Q(y, 0) = Q_0 + T_{12} F \delta^{-1} \exp(-y \Delta y_m / \delta)
\]

\[
T_{m}^{y,t} = T_{m}^{y-1,t-1} - \frac{T_{m}^{y-1,t-1} - 2T_{m}^{y-1,t-1} + T_{m}^{y+1,t-1}}{(\Delta y_m)^2} \Delta t \quad \text{for} \quad 1 < y < N_m
\]

\[
T_{g}^{y,t} = T_{g}^{y-1,t-1} - \frac{T_{g}^{y-1,t-1} - 2T_{g}^{y-1,t-1} + T_{g}^{y+1,t-1}}{(\Delta y_g)^2} \Delta t \quad \text{for} \quad 2 < y < N_g
\]

\[
K_m \frac{T_{m}^{1,t} - T_{m}^{N_m,t}}{\Delta z_m} = K_g \frac{T_{g}^{2,t} - T_{g}^{1,t}}{\Delta z_g}
\]

\[
T_{m}^{0,t} = T_{m}^{1,t}
\]

(2.38)

where the fourth equation is used to solve for the top ‘pixel’ of GaAs, and the final equation creates a pixel immediately above the MnAs film, and forces the temperature gradient at the surface to be zero. The parameters \(\kappa_m\) and \(K_m\) are evaluated at the relevant temperatures.

For the simulations here, \(\Delta t = 1\) ps, \(\Delta y_m = 2\) nm and \(\Delta y_g = 16\) nm. The larger value of \(\Delta y_g\) is necessary for numerical stability, and acceptable because the larger thermal diffusivity of GaAs implies that the thermal gradient is always much less than in the MnAs. The temperature may then be calculated over any time interval for the MnAs/GaAs system.

The temperature as a function of depth into the substrate and time after optical excitation is shown in Fig. 2.5. In this simulation, the sample is held at 8°C, the fluence is 2.1 mJ/cm², and \(T_{12} = 0.51\). This is one of the cases examined in the diffraction experiment. The surface temperature reaches 214°C. It is clear from these graphs that the increase in temperature at the surface drops to half its initial value in \(\sim 300\) ps. After this, the temperature change decreases much more slowly, with the temperature increase being 10% of the peak increase after \(\sim 10\) ns, and 1% after \(\sim 100\) ns. This slow decay is because of the \(T \propto 1/\sqrt{t}\) behavior typical to 1-dimensional diffusion problems. After about 50 ns, the temperature throughout the film is nearly homogenous, and the temperature evolution is governed mostly by the diffusivity of the GaAs. There is a kink visible in the surface temperature evolution at about 2 ns. This is because the temperature has decayed to 40°C, after which point the heat capacity, and hence thermal diffusivity is reduced. Therefore, the temperature decay rate is reduced. In all cases, there are kinks at 10°C and 40°C, because within this range, the rate of thermal diffusion is lowest.
Figure 2.5: Left: Numerically calculated temperature as a function of depth in a 150 nm MnAs film after optical excitation. The sample is initially at 8°C. The incident laser pulse fluence is 2.1 mJ cm$^{-2}$, the high fluence case used in the diffraction experiment. Right: Temperature at the top surface of the MnAs film, and at the MnAs/GaAs interface. The upper plot is logarithmic in the time axis and shows the slow decay out to 1 µs; the lower plot has linear scales and shows the fast decay at the surface over the first few hundred picoseconds.

The temperature after $\sim 100$ ns may appear to have decayed to close enough to its equilibrium value that further change is of little significance. But small differences can be important depending on the experimental conditions. In this case for example, the film temperature decays to 10°C after $\sim 200$ ns. Therefore it is only after this time that the stripes should completely disappear. The long-time behavior may also appear important near the upper stripe limit of 40°C. If the equilibrium temperature is just under 40°C, then it may take several hundred nanoseconds for the temperature to decay to 40°C, and hence for the stripes to reappear. As will be shown in practice, however, the long time behavior is also apparent when the equilibrium temperature is further away from the 10°C/40°C limits because the magnitude of the pump-induced change is larger.
2.5 Diffraction Theory

Grating diffraction occurs when light is reflected (or in some cases, transmitted) from a structure which has a periodically modulating height profile or index of refraction, or both. When films of MnAs grown on GaAs are in the striped temperature region (\(\sim 10–40^\circ C\)), there is a known height modulation as illustrated in Fig. 1.3. The different phases have slightly different indices of refraction [36], which can also contribute to the diffraction. Before considering measurements of the diffraction under equilibrium and ultrafast conditions, it is worth investigating how the index modulation and height modulation combine to give diffraction, and approximately how much light is diffracted.

A full calculation of the diffraction efficiency from a simple grating is complicated, and the detailed structure of the MnAs film gratings is not clear. The height profile is not sinusoidal or square, and has many Fourier elements [32]. Kaganer et. al. derive a Fourier representation of the displacement in the surface normal direction, \(u_y(x, y)\), based on free energy minimization [32]:

\[
u_y = \frac{\eta}{1 - \nu} \left[ (1 - \xi) y + \sum_{n=1}^{\infty} c_n \frac{(-1)^n}{\pi n} \sin(\pi n \xi) \cos \left( \frac{\pi n x}{\Lambda/2} \right) \right],
\]

where

\[
c_n = a_n \exp \left[ - (1 - y) \frac{\pi n}{\Lambda/2} \right] - \frac{\Lambda/2}{\pi n} \exp \left[ -y \frac{\pi n}{\Lambda/2} \right],
\]

and

\[
a_n = 2 + 4 (1 - \nu) \frac{\Lambda/2}{\pi n} \left( 3 - 4 \nu \right) \frac{\Lambda/2}{\pi n} + 2 \exp \left[ -\frac{\pi n}{\Lambda/2} \right] + 2y \left( \exp \left[ -\frac{\pi n}{\Lambda/2} \right] - 1 \right),
\]

(2.39)

where \(\eta\) is the difference between the internal strain in the \(\alpha\) and \(\beta\) phases, \(\eta = \eta_{\alpha xx} - \eta_{\beta xx}\), \(\nu\) is the Poisson ratio, \(\xi\) is the filling fraction of the \(\alpha\) phase, and \(\Lambda/2\) is half the grating period (this is denoted as \(\lambda\) in reference [32]). The displacement \(u_y\) is normalized to the film thickness. However, the stripes are not even homogenous on a 10 \(\mu m\) scale (as seen in section 3.2.2); there are bifurcations and other irregularities in the stripe structure. It is also not clear if the index of refraction varies smoothly or abruptly between the \(\alpha\) and \(\beta\) regions. Indeed, the indices have only been studied for homogenous films, and it is not known if the index of refraction of \(\alpha\)-MnAs is the same if it is part of a striped film, or as a homogenous film. These diffraction calculations are therefore only intended to provide order of magnitude estimates for the diffraction efficiency, and indicate under what conditions the diffraction efficiency will increase or decrease.
Chapter 2. Theory

If light with wavevector \( \mathbf{k} \), or wavelength \( \lambda \), is reflected from a medium with a position-dependent reflection coefficient \( r(x) \), then the E-field, \( \mathbf{E}_{\text{out}} \) of the outgoing wave immediately above the surface is given by

\[
\mathbf{E}_{\text{out}}(x, y) = \mathbf{E}_0 e^{i k x} e^{i k y \cos \theta} r(x),
\]

where \( \mathbf{E}_0 \) is the amplitude of the incoming light, and \( \theta \) is the angle of incidence. The surface is assumed to be at \( y = 0 \) and the light propagates in the \( x-y \) plane. The reflectivity coefficient \( r(x) \) is assumed to include both the Fresnel coefficients and phase shifts resulting from a height modulation. Since the incident light is assumed to be a plane wave, \( \mathbf{E}_{\text{out}}(x, y) \) is infinite in extent.

If \( r(x) \) is periodic with period \( \Lambda \), then it can be written as a Fourier series,

\[
r(x) = \sum_{j=-\infty}^{\infty} r_j e^{i 2 \pi j x},
\]

where \( r_j \) are the various Fourier coefficients.

The relevant quantity in terms of diffraction is the angle (of which there are generally many) of the outgoing beam which is mathematically obtained using a k-space representation of \( \mathbf{E}_{\text{out}} \). The \( z \)-component is zero, and the angle of the outgoing beam can be obtained from \( k_x \) alone, so it is sufficient to calculate the outgoing field in terms of \( k_x \) at the surface:

\[
\mathbf{E}_{\text{out}}(k_x, k_z = 0, y = 0) \propto \int \mathbf{E}_{\text{out}}(x, z) e^{i k x} dxdz.
\]

The outgoing k-vector can be written in terms of the angle of the outgoing light, \( k_x = k \sin \theta_{\text{out}} \). Putting Eqs. (2.40) and (2.41) into Eq. (2.42) gives

\[
\mathbf{E}_{\text{out}}(k_x) \propto \mathbf{E}_0 \sum_{j=-\infty}^{\infty} r_j \delta(\Lambda(\sin \theta_{\text{in}} + \sin \theta_{\text{out}}) + \lambda j).
\]

This is normalized to a delta function because the incoming wave is infinite in extent. In practical terms, the normalization can be determined by examining the case of a plane surface, where \( r_0 \) is the only nonzero element and is the reflection coefficient. In this case, \( \mathbf{E}_{\text{out}} = r_0 \mathbf{E}_0 \), so the actual normalization is unity. The delta function simply determines the well-known relation between the incoming and outgoing angles, and the period of the grating.

The MnAs films in the coexistence phase can be approximated as rectangular gratings. This may not be accurate, but if Eq. (2.39) were changed such that \( c_n = 1 \), then the
resulting equation would represent a rectangular grating. In particular, the filling fraction dependence (i.e., \(\sin(\pi n\xi)\)) is the same as that for a rectangular grating. It is also not clear how the index of refraction transitions between the two phases, but a rectangular structure is assumed here. Mathematically, \(r(x) = r_a\) for \(0 < x < \xi \Lambda\), and \(r(x) = r_b\) for \(\xi \Lambda < x < \Lambda\), where \(\xi\) is the filling fraction of the \(\alpha\) phase and \(r_a\) and \(r_b\) are the reflection coefficients for each component of the stripes. The Fourier series for \(r(x)\) can be easily computed:

\[
r_j = \frac{1}{\pi j} e^{-\pi j n}(r_a - r_b) \sin(\pi j \xi),
\]

\[
r_0 = r_a \xi + r_b (1 - \xi).
\] (2.44)

This gives reflected intensities of

\[
I(j = 0) = I_{in} |\xi r_a + (1 - \xi) r_b|^2,
\]

\[
I(j = 1) = I_{in} \left| \frac{r_a - r_b}{\pi} \right|^2 \sin^2(\pi \xi),
\] (2.45)

where \(I_{in}\) is the incident intensity. The \(j = 0\) case simply shows that the specular reflection is determined by the average reflectivity, and the \(j = 1\) case is what is measured in the following experiments.

There are three relevant values for \(r_a\) and \(r_b\) that one can imagine occurring: \(r_{\alpha,0}\) is the reflectivity coefficient for \(\alpha\)-MnAs at the surface \(y = 0\); \(r_{\beta,-\Delta d}\) corresponds to \(\beta\)-MnAs at a position \(y = -\Delta d\); and \(r_{\beta,0}\) corresponds to \(\beta\)-MnAs at a position \(y = 0\). Under equilibrium conditions, \(r_a = r_{\alpha,0}\) and \(r_b = r_{\beta,-\Delta d}\). Under highly non-equilibrium conditions after ultrafast heating however, it is possible that the entire film can be converted to \(\beta\)-MnAs before the height modulation relaxes. In this case, \(r_a = r_{\beta,0}\) and \(r_b = r_{\beta,-\Delta d}\). These values use the standard Fresnel reflection coefficients, with an additional factor of \(e^{4\pi \cos(\theta_{in}) \Delta d / \lambda}\) corresponding to twice the propagation distance \(\Delta d\) (this follows from Eq. (2.6) in section 2.2.1).

The indices of refraction can be extracted from reference [36]: \(n_\alpha = 1.9 + 2.9i\) and \(n_\beta = 2.1+3.1i\) (these are for 387 nm light which is used to measure diffraction, rather than for 775 nm light, which is used to excite the samples). Data for the height modulation are not consistent, and vary depending on the reference [4]; a value of \(\Delta d = 4 \text{ nm}\) is used here. This is consistent with atomic force microscope measurements shown in section 3.2.2. If the angle of incidence is 45° (as used in these experiments), the peak diffraction
efficiencies are

\[
\frac{I(j = 1)}{I_{in}} = \frac{|r_{\alpha,0}^s - r_{\beta,-\Delta d}^s|}{r_{\beta,0}^s - r_{\beta,-\Delta d}^s} = \frac{2.7 \times 10^{-4}}{\pi^2} \text{ with index modulation,}
\]

\[
= \frac{5.6 \times 10^{-4}}{\pi^2} \text{ with no index modulation. (2.46)}
\]

This should be a reasonable order of magnitude estimate for the diffraction efficiency. It is interesting to note that the lower value, which corresponds to a height modulation without an index modulation is larger than the upper value, which corresponds to both a height modulation and index modulation. This means that if the phase were to change before the height modulation has time to relax, i.e., on an ultrafast timescale after optical excitation, the diffraction would actually increase for a brief period.
Chapter 3

Experiment

3.1 Overview

In this chapter, some of the important properties of the particular MnAs and C-film samples are measured and described, as well as the experimental techniques used to measure the second harmonic generation and diffraction. Section 3.2 describes the samples, in particular how they are made, and measurements used to characterize them using well-established techniques. Section 3.3 details the experimental setups used to measure SHG and stripe-induced diffraction, including the laser sources and measurement techniques.

3.2 Samples

Both graphene and MnAs thin films have been the subject of intense research, so methods to produce and characterize them are continually being discovered. This section outlines the production details and some characteristics for the graphitic and MnAs samples. SHG from thin film systems is clearly dependent on the film thickness. For C-films, this is explained in chapter 2; for MnAs films, SHG from the GaAs substrate would give a thickness-dependent SHG to the MnAs for sufficiently thin films. Therefore, particular emphasis is placed on measuring film thickness before doing the SHG or diffraction experiments.
3.2.1 Exfoliated Graphene and Graphite

Graphene is a single sheet of carbon atoms arranged in a hexagonal pattern. Natural graphite consists of many such layers loosely bonded together, through van der Waals interaction, usually in a Bernal (AB) arrangement. The first ‘graphene’ that was produced, epitaxial graphene, was generated through heating a material such as silicon carbide so as to remove the silicon near the top surface [14]. This leaves several atomic carbon layers bonded to the surface. The properties of these films are similar to those of graphene even though they are many layers thick; this is due to decoupling between adjacent layers which are not stacked in the usual hexagonal-Bernal arrangement [50]. Aside from the issue of whether or not this is truly graphene, it is not suitable for the SHG measurements presented here because of the irregular stacking arrangement, it is difficult to get an exact (e.g., one or two) number of layers, and the bottom layer next to the substrate is strongly doped [61]. For this work, micromechanical exfoliation [2] is used. This involves peeling layers off bulk graphite and depositing them on a substrate (for reasons discussed below, the substrate is 300 nm SiO$_2$ on (001)Si). This results in an easily measurable number of layers; 1–4 layers can usually be measured exactly but thereafter there is an uncertainty that roughly scales with the number of layers. These films are only weakly bonded to the substrate, and since they are derived from natural graphite, the stacking arrangement is generally hexagonal-Bernal. The process of making these samples is very easy and involves mostly simple materials, but it is extremely time-consuming and generates films that are usually no more than 20 $\mu$m across. Although this method has been very fruitful for fundamental physics research, it is not likely to ever be used in commercial devices. Other methods have very recently been discovered to generate graphene of various quality, notably chemical vapor deposition, but at the time that these experiments were done, micromechanical exfoliation was the most reliable method to produce high quality graphene. In continuing the convention introduced in chapter 2, graphene means a single atomic hexagonal layer of carbon, and C-film means a film of one or more layers of graphene.

The natural graphite flakes were acquired from Asbury Carbons, and have a purity of 99.59% carbon. To make exfoliated C-films, several flakes are placed on a piece of scotch tape. The tape is then folded over, exposing both surfaces of the flakes to the tape, and then peeled back to cleave the graphite, and expose smoother surfaces. This process is repeated several times to make many freshly cleaved graphite spots on the tape. The
Figure 3.1: Approximate colour and luminance of C-films vs. thickness (number of layers). For thin samples (< 5 layers), the luminance drops nearly linearly with thickness allowing an exact determination of the number of layers. Thereafter, the colour is used to approximate the thickness.

tape is then pressed onto the substrate using a vice, and then removed, leaving pieces of graphite and glue debris on the substrate. When examined under an optical microscope, occasional pieces of graphene and few-layer C-films are found.

Graphene absorbs \(~ 2\%\) of near-infrared and visible light, making it difficult to detect optically. When placed on a layered substrate (e.g., 300 nm SiO\(_2\) on Si as is used here), interference effects make few-layer C-films visible [18, 62], and the number of layers may be determined exactly for sufficiently thin samples. Furthermore, for thicker samples, it is possible to approximately measure the number of layers from the colour of the C-film. The reflectance spectrum from the thin film system may be calculated using the transfer matrix formalism described in chapter 2. This spectrum may then be converted
Figure 3.2: Raman spectra of various C-films. Spectra are shifted vertically for clarity.

to colours that can be printed or displayed on a computer monitor, but this last step is very approximate because it depends on the observer and viewing conditions; there is no one-to-one correspondence between a (red, green, blue) triplet and a full colour spectrum.

The theoretical C-film colours were calculated by Ryan Newson [63], and are used here. The approximate colour and luminance are shown in Fig. 3.1. The luminance is a measure of approximately how bright a film appears to the eye.

Raman spectroscopy is commonly used to distinguish between 1-layer, 2-layer and 3-layer samples [19, 20, 21]. Raman spectroscopy involves inelastic light scattering from a material at wavelengths near the exciting wavelength. This probes vibrational and rotational modes of the crystal structure, which are qualitatively different for 1-layer, 2-layer, and 3-layer C-films. For C-films thicker than 3 layers, the Raman spectrum becomes indistinguishable from that of bulk graphite. A Horiba Jobin Yvon LabRam Raman system with a 532 nm Excel 1000 laser excitation source is used to characterize
Figure 3.3: Microscope image of a typical C-film sample. This sample has 1-layer (graphene) and 2-layer regions. The graph shows the intensity along the indicated path. The picture shows the full colour (RGB) composite, whereas the graph shows the magnitude of the ‘G’ component only.

The C-films. Several Raman spectra are shown in Fig. 3.2.

The review paper by Dresselhaus et al. [21] outlines the thickness-dependence of Raman spectra from few-layer C-films. The most notable features in the Raman spectra are the G-band, occurring at about 1580 cm$^{-1}$ and G’-band occurring at about 2700 cm$^{-1}$. The G-band corresponds to the optical vibration mode of two neighboring carbon atoms on a layer. The G’-band, which is found in all sp$^2$ carbon materials, results from a double resonance process whereby an electron is scattered from the K point to the K’ point, and back again, creating two phonons with opposite wave-vectors. For graphene, the G’-band is a single band, whereas for multilayer C-films, the G’-band consists of two closely spaced bands (G’$_1$ and G’$_2$). For graphene, the G’ band has $\sim 4\times$ higher intensity.
than the G-band; for 2-layer C-films, they are nearly the same intensity; and for 3 or more layers, the G-band has higher intensity. Furthermore, the shape of the G’ band changes with the number of layers.

From the features of the Raman spectra, it is easy to unambiguously determine if a C-film is graphene. Then, the optical microscope images can be calibrated by comparing the bare substrate to graphene (i.e., to determine the drop in measured intensity for each layer), to accurately measure up to ~ 5 layers. Figure 3.3 shows a C-film sample and a plot of the intensity drop from 1- and 2-layer samples. For thicker samples, the colour of the C-film gives an approximate thickness measurement. This procedure is followed to characterize the C-films used in these experiments.

### 3.2.2 MnAs Films

Bulk MnAs crystals may be made by direct reaction of the elements [30], but thin films may be grown epitaxially on a substrate, giving them different properties depending on the substrate and orientation used [7]. One of the most commonly studied systems is (1100)MnAs on (001)GaAs where MnAs[0001] ∥ GaAs[110]. Such samples are used in this work. These samples were grown by David Rench and colleagues in Professor Nitin Samarth’s group at Pennsylvania State University.

Two sets of MnAs samples with different thickness were used in this work. The film thickness was accurately measured using cross-sectional scanning electron microscopy (SEM) with a Hitachi model S-5200. Images of the samples taken with SEM are shown in Fig. 3.4. From these images (and others at different sample positions), the thicknesses are found to be 150 and 190 nm, with variations of ~ 5 nm.

As discussed in section 1.3, when the sample is held at a temperature between 10°C and 40°C, the ferromagnetic and paramagnetic phases are known to coexist in a stripe-like pattern [8, 4]. The coexistence phase reflects the significant role played by strain [32]. There is a well-defined relationship between the film thickness $d$ and the stripe period, $\Lambda$: $\Lambda \approx 4.8d$ [4]. Therefore, a measurement of the stripe period helps to confirm the thickness measurement, and is also important for diffraction measurements. This may be done for example, using atomic force microscopy (AFM) or magnetic force microscopy (MFM). Both of these measurements are performed on the samples, but AFM gives clearer results; one such image is shown in Fig. 3.5.

As is clear in the AFM picture, the stripes are not regular, but frequently expand and
bifurcate, therefore the stripe period and profile are not constant, but may be described by a distribution about an average. The average period may be found through the 2-dimensional spatial Fourier transform of the AFM image. This is shown in Fig. 3.5. The Fourier transform image is the k-space representation of waves; the positions of the peaks in k-space correspond to the center spatial frequency (i.e., the average stripe period), and the width of the peaks correspond to the spread in spatial frequency (i.e., the variation in stripe period). As shown in Fig. 3.5, the distance between adjacent peaks is $1 \mu m^{-1}$, which corresponds to a period of 1000 nm for the 190 nm sample. The average stripe period for the 150 nm sample is found to be 740 nm. The width of the peaks in the Fourier transform profile, is $\sim 50\%$ of the peak separation, indicating that the variation in the stripe period is also about 50%. This can be seen in Fig. 3.5; there are stripes which are twice as large as other stripes, especially near where they bifurcate. Although the variation in stripe period is relatively large, the uncertainty in the mean stripe period (related to the uncertainty in the distance between the peaks) is much less. Through measurements of the separation between several sets of peaks, the uncertainty in the average stripe period is found to be $\sim 10\%$.

Given the measured thickness values of 150 and 190 nm, and the formula $\Lambda \approx 4.8d$, this should give stripe periods of 720 nm and 912 nm. These are within the uncertainty of the measured values.
Figure 3.5: Left: AFM image of the 190 nm sample over a 10 µm × 10 µm area. Top-right: 2-dimensional Fourier transform of the AFM image. This shows the spatial frequency of the stripes. The direction of the stripes is indicated by the black line. Bottom-right: Profile of the Fourier transform along the black line indicated. The peaks correspond to the various Fourier orders of the stripes.

3.3 Laser Sources and Experimental Setup

Three separate sets of experiments are performed, each with its own setup: SHG on MnAs films (under equilibrium and ultrafast excitation conditions), SHG on C-films, and ultrafast optical diffraction from MnAs films.

3.3.1 Second Harmonic Generation from MnAs

This experiment involves measuring SHG from thin films of MnAs on GaAs in two cases: 1) under equilibrium conditions where the sample is held at various fixed temperatures, and; 2) after the sample is excited with another laser pulse. Both experiments use exactly the same setup, except in the first case the excitation pulses are blocked. Both the fundamental probe and pump pulses are generated by an amplified Ti-sapphire laser system (Clark-MXR CPA-2001), which provides 1 mJ, 200 fs laser pulses at a center wavelength of 775 nm, with a 1 kHz repetition rate. Figure 3.6 shows the experimental setup. The probe pulses are focused onto the sample at an angle of incidence of 60° with a 22 cm focal length lens, and the SHG emission is collected with a 5 cm focal length lens.
A large angle (60°) was chosen so the three lenses (see Fig. 3.6) and their translation stages could physically fit in the space available, and in related SHG work, similar angles (∼60°) were found to give the highest SHG intensity [39]. The pump pulses follow the same beam path in the opposite direction, and are therefore focussed with the 5 cm lens. Both lenses are defocussed by 2 mm (the probe lens away from the sample and pump lens toward the sample) to generate a probe spot size of 220 μm × 40 μm (FWHM) and pump spot size of 300 μm × 180 μm. The ellipticity is due to the large angle of incidence and focussing conditions.

While several pump pulse energies are used for the experiment, most of the data reported makes use of two: 0.64 and 1.28 μJ per pulse. This energy and pump spot area give peak incident fluences of ∼1 and ∼2 mJ cm⁻². Because the probe spot is comparable in size to the pump spot, the effective fluence is better approximated by multiplying the pump intensity with the square of the probe intensity (since the SHG is measured), and integrating the result over the spot size. This normalization factor incorporates effects where parts of the probe spot probe the sample where the pump intensity is lower than the peak value. This gives effective fluences of 0.9 and 1.8 mJ cm⁻²; hereafter they are simply called low and high fluence. The probe fluence (≲1 mJ cm⁻²) is kept as high as possible to generate a strong signal without inducing any non-quadratic behavior. Pump and probe powers are monitored with separate biased silicon photodiodes, not shown in Fig. 3.6.

The probe pulse may increase the sample temperature slightly, but this would not affect the lattice temperature over the course of the 200 fs pulse, and any probe-induced change of the sample is unimportant as long as the SHG yield scales quadratically with the probe. The 387 nm probe SHG light is separated from the fundamental pump and probe light with a dichroic mirror, optically filtered, and measured using a cooled photomultiplier tube (model Burle C31034) with photon counting electronics (Stanford Research Systems SR400). The photon counter is gated to a 5 ns window centered on the probe pulse to effectively eliminate room light and dark counts. The pump beam contains a delay arm to introduce delays up to 700 ps. A linear polarizer and half-wave plate are used to control the polarization of the fundamental probe beam, and another polarizer is used as an analyzer. The pump beam is kept s-polarized to avoid interference effects with the probe beam.

Samples are mounted on a computer-controlled rotational mount to measure the SHG intensity as a function of azimuthal angle of rotation, ϕ, about the surface normal.
Figure 3.6: Diagram of the SHG setup. The pump beam arm is only used in the ultrafast excitation experiment on MnAs. LP=linear polarizer, HWP=half wave plate, PMT=photomultiplier tube, BS=beam splitter.

Additionally, two more sets of translation stages are used; one pair is used to position a particular area of the sample at the axis of rotation, and another pair to place the axis of rotation in the laser beam. Thus the SHG is measured from a particular area on the sample for every angle of rotation. This is observed with a CCD camera positioned to image the sample surface using an LED to illuminate the sample. The samples are fixed to a Peltier cooler, which is mounted on a water-cooled heat sink. An attached thermistor (LM35) is used to measure the sample (equilibrium) temperature, which, for the equilibrium (not pumped) scan, is kept in the -20 to 70°C range. The samples are enclosed in a dehumidified chamber to prevent condensation. A polyurethane sheet (from a shower curtain) is used to enclose the sample area. Dry nitrogen gas is pumped through to keep the humidity level, as measured with a hygrometer, less than 0.1%. Any condensation on the sample is immediately visible with the CCD camera.

For the equilibrium experiments, the temperature of the sample is constantly monitored through the thermistor, and the current through the Peltier element is regularly adjusted to maintain the desired temperature. After the sample reaches equilibrium (∼2 minutes after setting the temperature), a rotational scan is performed, and the number of photons is counted over a 10 second interval at 4° increments.

For the pump–probe experiment, the sample is kept at a constant initial temperature,
and the number of photons is counted at various probe delay times from $< 0$ (excitation pulse arrives after the probe pulse) to 700 ps. This is then repeated as the sample is rotated in $4^\circ$ increments.

3.3.2 Second Harmonic Generation from Graphene

This experiment involves measuring SHG from graphene and few-layer graphite. The laser pulses are generated by a Coherent Mira model 900 Ti:sapphire oscillator, which provides 1 nJ, 150 fs laser pulses with a center wavelength of 800 nm, at a 80 MHz repetition rate. Apart from the laser source, the experimental setup is nearly identical to that used for the MnAs SHG experiment shown in Fig. 3.6, minus the pump arm and temperature control. Because of the small area of the graphene flakes (varied, but generally $< 100 \mu m$ across), a 0.12 numerical aperture microscope objective is used to focus the laser pulses, generating elliptical focal spot sizes of approximately $7 \mu m \times 10 \mu m$; the samples are placed in the focus of the laser beam. The laser pulses are attenuated to $\sim 0.06 nJ$ to avoid damaging the samples. Samples are regularly checked for damage using an optical microscope after scans, and the SHG yield is found to be quadratic with the fundamental intensity up to the intensities used (at higher intensities that cause damage, the measured SHG appears non-quadratic and generally irregular).

Because of the high repetition rate, the photon counter is not gated, and simply measures the number of photons for a set interval (as high as 30 seconds depending on the measured intensity). The dark count/background light is also regularly measured by blocking the laser pulses.

Through various trials, it was found that the rotation mount has a small degree of irregular motion (i.e., deviation from perfect circular motion about a fixed center) which makes the position of the axis of rotation well-defined only to within about $5 \mu m$. Because of this, and the finite size of the focal spot, only C-films which contain a circular area of at least $20 \mu m$ diameter are used to avoid situations where the laser spot might partially wander off the sample.

3.3.3 Stripe-Induced Diffraction

This experiment involves measuring the diffraction efficiency from a stripe-induced grating on MnAs films in cases where the sample is held at fixed temperatures, and some time after the sample is optically excited with another laser pulse. The pump–probe
experiment consists of two types of measurements: one with high time resolution but limited to short delays (a few nanoseconds), and one with unlimited delays but poor time resolution (a few nanoseconds). To measure the grating over a few nanoseconds after the pump pulse with sub-picosecond resolution, a delayed probe pulse is used to measure the diffraction. This technique is limited to probe delays of a few nanoseconds because of walk-off effects associated with a few meters of extra path length. To measure the grating over unlimited timescales, a separate continuous-wave laser is used, and the time-resolved diffraction is observed with an oscilloscope. In this case, the temporal resolution is limited by the electronics to $\sim 10$ ns.

The Clark laser system is used to generate both pump and probe pulses for the high time-resolution experiment. Because diffraction angles are most accessible with a laser wavelength slightly less than the grating period, the laser output is frequency doubled (to 387 nm) with a BBO (beta barium borate) crystal to measure the diffraction. The fundamental 775 nm is used to optically excite the samples.

The equation governing diffraction is $\Lambda (\sin(\theta_{\text{out}}) + \sin(\theta_{\text{in}})) = m\lambda$, where $\theta_{\text{in}}$ and $\theta_{\text{out}}$ are the angles of the incoming and outgoing light, $\Lambda$ is the grating period, $\lambda$ is the light wavelength, and $m$ is the diffraction order. For the 150 nm film which has a measured stripe period of 740 nm, and the 190 nm film which has a stripe period of 1000 nm, the first order diffraction exists ($i.e.$, $-1 < \sin(\theta_{\text{out}}) < 1$) for any angle of incidence. With an angle of incidence of $45^\circ$, the 740 nm period grating gives an outgoing angle of $\sim -10^\circ$, and the 1000 nm period grating gives an outgoing angle of $\sim -18^\circ$.

An angle of $45^\circ$ is used for both pump and probe, where the pump beam propagates in the opposite direction as the probe beam. This angle simplifies alignment and is a good compromise in allowing enough space for the necessary translation stages, while minimizing aberrations in the laser spot which occur for large angles. The setup is shown in Fig. 3.7. The probe arm contains a $\sim 415$ mm delay stage capable of introducing probe delays up to $\sim 5$ ns.

A 15 cm focal length lens is used to focus the probe beam, and 10 cm lens for the pump beam. The probe beam is focussed onto the sample, generating a spot size of 60 $\mu$m $\times$ 50 $\mu$m FWHM. The pump beam is defocussed by 8 mm to generate a spot size of 450 $\mu$m $\times$ 310 $\mu$m FWHM. The diffracted probe light is collected and focussed onto a photomultiplier tube (model Hamamatsu R928) with a 7 cm focal length lens with a diameter of 7.5 cm; a nearly hemispherical shape is necessary due to the large divergence of the diffracted light which is related to the stripe irregularity as discussed in section
Chapter 3. Experiment

Figure 3.7: Diagram of the diffraction setup. The pump beam arm is blocked in the equilibrium temperature experiment. The lens used to image the sample onto the CCD is used for alignment, but removed during experiments. PMT=photomultiplier tube, BS=beam splitter.

3.2.2. Although this high numerical aperture spherical lens causes various aberrations, this is irrelevant to this experiment; the only disadvantage is that a significant fraction of the light is likely lost due to spurious reflections and aberrations. Because the diffracted light is not much stronger than scattered light, an iris is placed before the photomultiplier tube to block most of the scattered light. The lens and detector are placed at different positions depending on the sample (stripe period) used. For each sample, they are positioned to maximize the measured diffraction power. The diffraction power is monitored with a lock-in amplifier (Stanford Research Systems SR830), while chopping the probe beam (not shown in Fig. 3.7); this reduces noise from room light and scattered pump light.

Two pump pulse energies are used for most of the experiments: 3.2 and 1.6 $\mu$J. These correspond to peak fluences of 2.1 and 1.05 mJ cm$^{-2}$, hereafter simply called high and low fluence. For this experiment, the pump spot is $\sim 6\times$ larger than the probe spot, so finite spot size effects are ignored. The pump pulses are p-polarized, and the probe is
s-polarized.

For the longer time delay experiment, a Coherent Vioflame (GaN based) laser is used as a CW probe. This generates $\sim 30$ mW of 409 nm light. Since the wavelength is similar to that used in the high time-resolution experiment, the same optics are used at the same positions, and a separate mirror is added to inject the probe beam along the same path. The signal from the photomultiplier tube is amplified with a DC-300 MHz amplifier (Stanford Research Systems SR440), and measured with an oscilloscope (Tektronix TDS220). To eliminate noise from various sources, the probe beam is periodically blocked and unblocked, the signal is measured in both cases, and the difference between the two is calculated. This is repeated several times, and the results averaged.

A CCD and lens are used to image the sample surface, using an LED for illumination, at normal incidence and to find pump/probe overlap. This lens is removed during measurements because the diffracted light is also near normal incidence. The sample equilibrium temperature is monitored and maintained in exactly the same way as the SHG experiment. The pump and probe power (for both pulsed and CW cases) are monitored with separate photodiodes (not shown in Fig. 3.7).
Chapter 4

C-Film SHG: Results and Analysis

4.1 Overview

As discussed in chapter 2, second harmonic generation is measured from C-films of various thickness using several different polarization combinations. The end result of the analysis is to resolve the nonlinear tensor elements. However, much of the physics involved in SHG from C-films, as well as thin film systems in general can be studied through four particular samples: the bare substrate (as a reference), graphene, bilayer C-films, and bulk graphite with a single polarization combination. These cases are examined in section 4.2. Section 4.3 shows examples of measurements for various other polarization combinations and film thicknesses, and finishes with the extraction of the nonlinear tensor elements.

4.2 Symmetry of Graphene and C-films

The experimental procedure is described in chapter 3, whereby the SHG is measured from a particular sample as a function of azimuthal rotation angle $\phi$. The results from several of these measurements are shown in Fig. 4.1; these are measurements taken from the bare substrate (SiO$_2$ on (001)Si), graphene, a bilayer C-film, and bulk graphite. In all four cases, the incident light is p-polarized and the p-polarized second harmonic light is measured.

In chapter 2 it is shown that the SHG intensity from the bare substrate must show 4-fold rotational symmetry (that being the symmetry of (001)Si), and from symmetry considerations alone, the presence of graphene can only add an isotropic contribution.
Chapter 4. C-Film SHG: Results and Analysis

Figure 4.1: Left: Normalized SHG signal from the SiO$_2$/(001)Si substrate (red squares) and graphene (black circles) as a function of azimuthal angle. Both data sets are fit to Eq. (4.1) (solid curves). The absolute angle is arbitrary, but corresponds to the same physical orientation for both data sets. Right: SHG signal from a bilayer C-film (black circles) and from bulk graphite (red squares) as a function of azimuthal angle. Both data sets are fit to Eq. (4.2) (solid curves). The absolute angle is arbitrary for both curves. All data sets are normalized such that the mean SHG intensity from the substrate is unity.

This may be given as

$$\frac{I^{2\omega}(\phi)}{(I^\omega)^2} \propto A_0 + A_4 \cos(4\phi), \quad (4.1)$$

where $A_n$ are phenomenological constants corresponding to the $n$th elements of a Fourier decomposition of the azimuthal pattern. In principal, it is the E-field which has 4-fold rotational symmetry, therefore the intensity could contain an 8th Fourier element, but as Fig. 4.1 shows, such a contribution is negligible. Equation (4.1) is used to fit the data for the bare substrate and graphene in Fig. 4.1.

For the bare substrate the anisotropy parameter $A_4/A_0 = 0.13 \pm 0.03$ whereas for the graphene/SiO$_2$/(001)Si, $A_4/A_0 = 0.08 \pm 0.03$. As Fig. 4.1 also indicates, the normalized SHG intensity from the graphene system is slightly higher than that of the bare substrate. These differences are related to differences in the linear optical properties of both systems or a possible contribution of the graphene layer to isotropic SHG. Over the course of several measurements, it was found that the SHG from graphene and the substrate is at best marginally stronger than that from the bare substrate. However, I did not attempt to extract tensor information from these results because the experimental uncertainty
The SHG signal from a bilayer C-film sample on the substrate shows a qualitatively different azimuthal pattern than that from graphene on SiO$_2/(001)$Si. Indeed, the pattern is now dominated by a 3-fold symmetry as shown in Fig. 4.1. In chapter 2, it is shown that for a multilayer C-film on a SiO$_2/(001)$Si substate, the $\phi$-dependent signal has several (0,1,3,4,6,7,8) nonzero Fourier elements (Eq. (2.27)). But as the data from the bilayer sample in Fig. 4.1 shows, only the 0th and 3rd Fourier elements strongly contribute. This suggests an equation of the form

$$\frac{I^{2\omega}(\phi)}{(I^\omega)^2} \propto A_0 + A_3 \cos(3\phi), \quad (4.2)$$

where $A_n$ are phenomenological constants. This equation is used to fit both the data for the bilayer sample, and the bulk graphite sample. The SHG signal from bilayer C-films is shown to fit well with Eq. (4.2) as the figure indicates. The degree of anisotropy from the bilayer graphene dominates that from the substrate with anisotropy parameter $A_3/A_0 = 0.6 \pm 0.1$. For the bulk graphite sample, the 3-fold symmetry dominates but now with $A_3/A_0 = 0.5 \pm 0.1$.

In section 2.2 it was suggested that an inversion symmetry argument could be applied to graphene, which would forbid SHG, but such an argument would similarly have to apply to bilayer C-films. The presence of an extremely strong SHG yield from bilayer C-films shows that an inversion symmetry argument cannot be applied to thin films. Furthermore, it can be noted by comparing the signal from bilayer graphene to that from the bare substrate that the average signal (0th Fourier element) is not enhanced by the presence of the C-film. This is in agreement with the symmetry-based analysis used in section 2.2.2; in the zero-thickness limit, the isotropic contribution (0th Fourier element) from the C-film approaches zero because the SHG from the two surfaces cancel, leaving an entirely anisotropic (3rd Fourier element) response. It is interesting to note that the anisotropic response from bilayer C-films is much stronger than that from bulk (001)Si. This is partially because the silicon only has one surface available for SHG, whereas the C-film has two; and also because surface dipole SHG cannot show 4-fold rotational symmetry, but can show 3-fold rotational symmetry. It may be surprising that the signal from bilayer C-films is significantly stronger than that from bulk graphite; this supports the assumption that any bulk quadrupolar SHG from the graphite is weak, and that it is the surfaces rather than the bulk which generate the bulk of the signal.
4.3 Tensor Element Analysis

This section summarizes SHG measurements from C-films of various thickness using several polarization combinations: (pp), (sp), (ps), (ss), and (ds), where the first letter is the incident, and the second letter is the outgoing polarization (‘d’ means diagonal). The aim is to extract all nonlinear tensor elements associated with surface SHG. The values themselves are not very physically important; the important point is to determine whether a set of nonlinear tensor elements can account for all of the results.

Results for (ps) SHG are shown in Fig. 4.2 for a bilayer and ∼ 15-layer C-film sample. It is clear that the 6th Fourier element decreases with layer number. Results for (ss) polarization combinations are qualitatively similar. Two data sets from a ∼ 5-layer sample are shown in Fig. 4.2, one with (pp) and one with (ds). The 3rd Fourier element always has the same phase between (pp) and (sp) combinations, and inverted negative for (ps) and (ss) combinations as shown in table 2.3, but is evidently shifted with diagonal polarization.

Although for each sample and polarization combination the SHG intensity is measured...
for many angles $\phi$, the only useful parameter values that may be extracted are the first few elements in the Fourier series of $I^{2\omega}(\phi)$. Because the 4-fold contribution from the substrate is much weaker than the 3-fold contribution from the C-film, only the 0th, 3rd and 6th elements are consistently larger than the noise. In cases where there is a large 3rd element ([(pp), (sp), (ds) polarization combinations), the 6th element is too weak to be seen. This pattern is comparable to that from bare (001)Si/SiO$_2$: when the isotropic contribution is polarization-suppressed, an apparent 8-fold symmetry arises due to the 4-fold symmetric E-field squared, but when the isotropic contribution is allowed, the interference between the (strong) isotropic and (weak) 4-fold E-field contributions gives a 4-fold symmetric signal with an unmeasurably weak 8-fold component. Finally, with the weak Si contribution neglected, the signal from the (ss) and (ps) combinations is of the form $\cos^2(3\phi)$, so the 0th and 6th elements provide the same information. Therefore, the most important Fourier elements of the data are shown in Fig. 4.3. The intensity is normalized such that the 0th (isotropic) Fourier element from the substrate is unity.

When multiple samples of the same thickness were available, the average is used, and the error bars represent the variation. A few data points vary significantly from the fit, and likely result from sample imperfections where too few samples of the same thickness are available to average over. In some cases, outlying data points may be caused by samples with regions of ABC stacking as described in section 1.2 because this stacking arrangement possesses a different surface symmetry than AB stacking. It is known [9], that C-films can contain regions with both AB and ABC stacking domains, but the ABC arrangement accounts for only $\sim 15\%$ of few-layer C-films. In these cases, the azimuthal dependence of the SHG, including the apparent symmetry, would vary significantly depending on the position on a particular sample. This would also be the case if a C-film sample contained multiple crystal domains. Such inconsistent measurements were occasionally found, and those samples were not used for further analysis. It is therefore unlikely that alternate stacking arrangements or multi-domain crystals are a significant source of error for these experiments.

The trends in the data confirm those suggested in Fig. 4.2. The strongest anisotropic SHG occurs for bilayer C-films and generally decreases with increasing C-film thickness. The isotropic contribution behaves in a similar manner for most polarization combinations. This is in agreement with the theoretical predictions which assume surface SHG sources on both surfaces of the C-film.

The data is fit to the parameters shown in table 2.3 for the four complex parameters
\( \partial_x \). This effectively involves choosing values for all four \( \partial_x \) to minimize the difference between the theoretical and experimental Fourier components \( f_{gh}^m \). These nonlinear tensor elements are

\[
\begin{align*}
\partial_{11} &= 0.6 + 2.4i, \\
\partial_{15} &= 0.2 - 0.7i, \\
\partial_{31} &= -0.5 + 5.2i, \\
\partial_{33} &= -0.17 + 0.19i.
\end{align*}
\] (4.3)

These values are normalized such that the (pp) SHG signal generated from the SiO\textsubscript{2}/(001)Si substrate is unity, the phase of \( \beta_{pp} \) is chosen to be zero, and the constant \( |F^2| = 1 \) in Eq. (2.27). For all values the radius of the uncertainty circle in the complex plane is estimated to be about 25\% of the modulus of the coefficient.

It is worth emphasizing that the use of the four nonlinear tensor elements associated with the dipolar contribution from a single graphene/air interface is sufficient to account for the trends in the data. It is particularly interesting that, as in the case of linear optical propagation, no material constants have to be changed in going from 2 layers to bulk; only the C-film thickness needs to be changed in the calculations. If a bulk quadrupolar contribution from the C-films exists, it must be weak and, in any event, does not seem to be needed to account for the variation of the SHG signal with number of layers. Variation in the SHG signal with number of layers is mainly accounted for by linear light propagation effects, once multilayer interference is taken into account.
Figure 4.3: Fourier elements of $I^{2\omega}(\phi)$ for various polarization combinations: (top-left and right: 0th and 3rd element for (pp); second from top left and right: 0th and 3rd element for (sp); 3rd from top left: 6th element for (ps); right: 6th element for (ss); bottom-left and right: 0th and 3rd element for (ds) where the phase of the 3rd Fourier element is plotted as well). The SHG intensity is normalized to the square of the incident intensity, and normalized such that the isotropic contribution from the substrate is unity. The curves are fits using the equations in table 2.3.
Chapter 5

MnAs: Results and Analysis

5.1 Overview

Chapter 3 describes the experimental methods used to measure optical second harmonic generation and first order linear optical diffraction from thin films of MnAs. The results of those experiments are presented here, along with some analysis with the aim of better understanding the phase transition on an ultrafast timescale. This analysis makes use of the theoretical calculations shown in chapter 2.

There are essentially four distinct sets of experimental results: SHG and optical diffraction, both of which were measured under equilibrium conditions and after optical excitation. The SHG is intended to probe the MnAs in a spatially averaged sense, i.e., it is only sensitive to the spatially averaged surface strain, $\epsilon_s$, and is not affected by other Fourier components of stripe properties. These results are shown in section 5.2. The first order, linear diffraction experiment is sensitive to the first Fourier component of the stripe amplitude and dielectric constant variation. These results are shown in section 5.3. Both of these experiments must be interpreted together to form a full picture of the ultrafast dynamics of the MnAs film; this is given in section 5.4.

5.2 Second Harmonic Generation from MnAs

The first part of this experiment involves measuring SHG from MnAs films under equilibrium conditions, i.e., while being held at a fixed temperature. The aim of the analysis of this data is to show that the SHG yield depends on strain, including its temperature dependence. This can then be used as a calibration for the second part of the experiment,
where the sample is excited by another laser pulse. The instantaneous strain $\epsilon_s(\tau)$ can then be measured through SHG at various times $\tau$ after the excitation pulse.

### 5.2.1 Equilibrium Conditions

As described in section 3.3, the SHG is measured from the MnAs samples as a function of azimuthal rotation angle $\phi$. This is done for a range of sample temperatures from $-20^\circ$C to $70^\circ$C. For these measurements, and all further SHG measurements on MnAs, the incident 775 nm light is p-polarized, and the p-polarized second harmonic light is measured. This combination was found to give the strongest and most consistent measurements.

Some results from these measurements on a 150 nm MnAs film are shown in Fig. 5.1. It can be seen that the SHG yield is 2-fold rotationally symmetric; specifically, the signal is unchanged when the sample is rotated by $180^\circ$. Such a pattern is expected because of the 2-fold rotational symmetry of (1100)MnAs. The SHG yield can be decomposed in a manner similar to the graphene experiments; i.e.,

$$I^{2\omega}(\phi) \propto \sum f^n \cos n\phi.$$ 

The largest Fourier element visible to surface SHG is the third, so because of the 2-fold symmetry here, there may be 0th and 2nd Fourier elements in the E-field. The intensity may therefore have $f^0$, $f^2$, and $f^4$ nonzero elements. For each temperature, the black curve shows a fit to the data using only these three Fourier elements. Since the full plot of SHG yield vs. temperature and $\phi$ is unwieldy for analysis, and the only important values are these three Fourier elements, they are each plotted as a function of temperature in Fig. 5.2.

In the discussion above, a bulk quadrupolar SHG source term is neglected. Such a source could give a 4th Fourier element to the E-field. This would give rise to other Fourier elements in the intensity, such as a $\cos(8\phi)$ term, which is not apparent from the signal/noise of the experiment.

Figures 5.1 and 5.2 show data from a 150 nm MnAs film on GaAs. Measurements are also made from 190 nm films; these are shown in Fig. 5.3. The trends are qualitatively the same for both films. This is because the optical penetration depth ($\sim 17$ nm) is much less than the film thickness, so both films are essentially bulk as far as these measurements are concerned. The normalization constants are slightly different between the films, and also vary depending on the position on a particular film. This is likely because of slightly different surface properties, for example, from being exposed to air for extended periods. Therefore, only the set of data from the 150 nm film, all from the same position, is
Figure 5.1: Measured SHG intensity of a 150 nm MnAs film as a function of rotation angle $\phi$ and temperature. The angle $\phi = 0$, where the SHG is at a minimum, is associated with the (0001) direction being perpendicular to the plane of incidence. The SHG intensity is normalized such that the peak zeroth Fourier element has the value unity. The black curves show fits using 0th, 2nd, and 4th elements in a $\cos(n\phi)$ expansion.

discussed here with the understanding that the same considerations apply to the 190 nm film.

The data in Fig. 5.2, specifically the 0th Fourier element, shows the expected trends based on the theory for strain-induced SHG presented in section 2.3. The SHG yield is lowest at 40°C, increasing rapidly with decreasing temperature down to 10°C, and continues increasing with decreasing temperature. In this temperature range, the sample expands, and strain increases while it is cooled, first because of the phase transition, and then because of the negative coefficient of thermal expansion. Above 40°C, the SHG yield increases much more slowly. In this region the strain also increases slowly because of a positive coefficient of thermal expansion which increases the strain. In section 2.3 it is shown that the strain in the $y$-direction is proportional to the stress in the $x$-direction (with a negative proportionality constant). Indeed, the plot of the 0th Fourier element
Figure 5.2: Fourier elements of the 150 nm MnAs film SHG intensity vs. temperature (at left) and strain (at right). The inset for the 0th Fourier element shows the increasing SHG intensity past 40°C. The curves are fits based on strain-induced SHG. The error bars have the same magnitude for all three Fourier components, and are only clearly visible for the 2nd and 4th Fourier elements.

of the SHG yield has the same features as the plot of stress (specifically, $\sigma_{11}$) in reference [31].

SHG can also be induced by magnetization. It is therefore worthwhile to investigate whether the trends in Figs. 5.2 and 5.3 might be caused by magnetization rather than strain. Indeed, there are several reasons to believe that magnetization-induced SHG is negligible.

Magnetization-induced SHG is mathematically described by a second harmonic polarization of the form $P(2\omega) = \chi^{(3)}_{\text{mag}}E(\omega)E(\omega)M$, where $\chi^{(3)}_{\text{mag}}$ is a rank-4 pseudotensor and $M$ is the magnetization [64]. The magnetization is zero in the paramagnetic phase, and increases as the MnAs film is cooled through the coexistence phase, and further increases (depending on the applied field) as the sample is further cooled below 10°C [65]. The experiments described above are not performed under the influence of a magnetic
field (aside from Earth’s magnetic field). Therefore, as the sample is cooled from 40°C and ferromagnetic regions form, there is no preferred direction for the magnetization, and ferromagnetic domains are expected with sizes on the order of a few microns [66]. Because of the ferromagnetic domains, the spatially averaged value of $M$ over regions as large as the laser spot approaches zero. Therefore, the net magnetization-induced SHG should be negligible. The possibility of magnetization-induced SHG was further explored by measuring the SHG after exposing the sample to a strong magnetic field ($\sim 0.2$ T) from a neodymium magnet to align the domains, as well as with the sample mounted directly on the magnet. This field strength should nearly saturate the magnetization [65, 66]. In both cases the measured SHG remained unchanged relative to measurements performed without magnetic fields, thus indicating that magnetization-induced SHG is negligible for the experiments shown here. Furthermore, any magnetization-induced SHG would be insignificant and constant at temperatures $\gtrsim 40°C$ when the film is entirely paramagnetic. As shown in Figs. 5.2 and 5.3, the SHG intensity actually starts to in-

Figure 5.3: Fourier elements of the 190 nm MnAs film SHG intensity vs. temperature (at left) and strain (at right). The data and fits are constructed in the same manner as for the 150 nm film.
crease again above $\sim 40^\circ$C. This behaviour is consistent with strain-induced SHG, but not magnetization-induced SHG.

In section 2.3, the strain $\epsilon_s(T)$ is calculated from various elastic and lattice parameters; this is plotted in Fig. 2.3. The right side of Fig. 5.2 shows the SHG yield Fourier components as a function of calculated strain, $\epsilon_s(T)$, rather than temperature. It is shown in Eq. (2.35) that the three Fourier components of the SHG yield depend on $\epsilon_s(T)$ and four parameters ($a_0$, $b_0$, $a_s$ and $b_s$) associated with nonlinear tensor elements, and that these parameters could be extracted using fits to the data. The curves in Fig. 5.2 show these fits. They agree reasonably well with all Fourier components, validating the assumption that the modified SHG signal is due to spatially averaged surface strain. As mentioned earlier, the actual values of the $a$ and $b$ fit parameters are not important. The important point is that the theory matches the data well enough to use SHG as a probe to measure $\epsilon_s$.

According to the theory presented in section 2.3, the fourth Fourier element of the SHG yield must always be positive. This is because it arises from the magnitude squared of the E-field, which has a second Fourier element. The plot of the fourth Fourier element in Fig. 5.2 shows that the fourth Fourier element goes below zero by more than the uncertainty shown. This must be caused by another source of SHG, possibly bulk quadrupolar, which can contain a fourth Fourier element in the field. But this effect is only slightly beyond the uncertainty of the data, about 0.01 in the normalized units. Given that the intensity of the zeroth Fourier element is $\sim 0.3$ to 1.0 in these units, this effect can safely be ignored.

### 5.2.2 Ultrafast Excitation

In the previous section, it was shown that SHG can be used to probe the spatially averaged strain, $\epsilon_s$. Since the pulses used to measure SHG are $\sim 200$ fs long, this method can also be used to probe the instantaneous strain after the sample has been excited by another laser pulse. The experimental details for this experiment are given in section 3.3, and the results are shown here.

The SHG measurements for this part of the experiment are taken as a function of time delay $\tau$ up to 700 ps after optical excitation by the pump pulse, as well as rotation angle $\phi$. The equilibrium sample temperature, $T_0$, is maintained at a fixed value for each experimental run. The pump fluence is also kept fixed at 1.8 mJ cm$^{-2}$ (high fluence)
and 0.9 mJ cm\(^{-2}\) (low fluence). Three experimental situations are investigated: 1) low fluence starting at -20\(^\circ\)C, where the MnAs should stay in the \(\alpha\) phase; 2) high fluence starting at -20\(^\circ\)C to investigate a situation where the film starts in a homogeneous phase, but is pumped with sufficient energy to reach the coexistence phase; and 3) high fluence starting at 20\(^\circ\)C, where the film starts in the coexistence phase.

Figure 5.4 shows the SHG yield vs. delay time in the second case, where \(T_0 = -20\(^\circ\)C\), with high pump fluence. This is the situation which shows the largest pump-induced change. The intensity in Fig. 5.4 has been decomposed into the three relevant Fourier elements in the same way as for the equilibrium experiment, only as a function of time delay rather than temperature. The zeroth Fourier element shows a clear decrease over the first tens of picoseconds. This is qualitatively consistent with a decrease in strain, or increase in temperature. The zeroth Fourier element then decays back toward the equilibrium value on a timescale of hundreds of picoseconds up to nanoseconds. The second, and especially the fourth Fourier element are largely dominated by noise, but suggest the same trend. The curves shown in the plots involve a fit using heat diffusion which is discussed below; they are drawn here to show that the three Fourier elements show the strain in the same manner as in the equilibrium experiment. Since the zeroth Fourier element shows the most clear trends, it is used for further analysis.

It is shown in Fig. 5.2 that there is a one-to-one correspondence (neglecting situations where the temperature is > 40\(^\circ\)C) between the strain or temperature in the MnAs film, and the zeroth order Fourier element of the SHG intensity. This can also be done as a function of time delay. Figure 5.5 shows the extracted strain after optical excitation in the low fluence case starting from \(T_0 = -20\(^\circ\)C\). The strain clearly experiences a sudden drop after excitation, but stays above 0.015, indicating that the top part of the sample does not reach the coexistence phase. It might be thought that the temperature can, in principle, be determined from the strain; this is shown in Fig. 5.5 at right. However, the correspondence between strain and temperature is only well-understood under equilibrium conditions. It is not immediately clear if the same relation should hold after ultrafast excitation, where the temperature changes quickly over time and as a function of depth into the film, and whether temperature alone determines the strain. In the coexistence phase, the correspondence between strain and temperature is even less clear under non-equilibrium conditions; this issue is re-examined later.

In section 2.4, a computational model was proposed to simulate heat diffusion in MnAs films on GaAs. In particular, this is used to find the expected temperature as a
Figure 5.4: Zeroth, second, and fourth Fourier elements of the SHG intensity from a 150 nm MnAs film after being optically excited. This case shows a situation where the sample is held at -20°C, and is pumped with a high fluence. The error bars have the same magnitude for all three Fourier components, and are only shown for the 2nd and 4th Fourier elements. The red curves are a fit using a heat diffusion model discussed in the text.

function of depth at various times after optical excitation. It was noted that, because of the phase transition dynamics, this simulation could best be seen as a reasonable but simplistic approximation. The simulated surface temperature as a function of time delay is shown in Fig. 5.5 for the relevant experimental conditions. The only parameter in the heat diffusion simulation for which it is difficult to assign a value is the time taken for the strain to reach a minimum (consistent with a higher temperature) after optical excitation. This time is likely a combination of the carrier–lattice thermalization time, and the time taken for the sample to vertically contract as a result of a different equilibrium lattice parameter; this is further discussed in section 5.4. A value for this strain development time, hereafter called $\tau_1$, of 5 ps is used here, but more accurate values are extracted below.
Figure 5.5: Extracted strain (top) and corresponding temperature (bottom) as a function of time delay after optical excitation. The sample is held at -20°C, and is pumped with low fluence. The blue points represent values extracted from the data; the black curves show values derived from the heat diffusion model using bulk thermal parameters; and the red curves use a model with modified thermal parameters to best fit the data.

The black curves in Fig. 5.5 show the simulated temperature and strain based on the bulk parameters (specific heat and thermal conductivity). These curves clearly show the same trends as the data, but it appears that the sample doesn’t heat up as much as the model predicts, or equivalently, the strain doesn’t drop as much as the thermal model predicts. There are several possible reasons for this to do with experimental issues (e.g., imperfect pump–probe overlap), or factors intrinsic to the sample (e.g., thermal parameters are different in thin film form). Most experimental issues, such as an imperfect pump–probe overlap, or the effect of a finite sized pump will act to decrease the temperature rise as is seen here. The thermal properties of thin film MnAs may or may not be different from the bulk; this is not something that can easily be experimentally measured, and is difficult to investigate theoretically. Before discussing these possibilities, it is worth investigating whether or not the strain/temperature decay possibly follows a
different thermal diffusion model, one with modified thermal parameters relative to the bulk; and also how well the model matches the SHG data under different experimental conditions.

To keep the same type of approximations (i.e., a distributed latent heat), the following parameters are used: a multiplication factor for the specific heat, a multiplication factor for the thermal conductivity, and a strain development time, $\tau_1$ (the latent heat is not relevant for low fluence excitation with the sample initially at -20°C). These parameters are found by fitting the simulated temperature to the measured SHG data. This simulated temperature is shown in Fig. 5.5 by the red curves. The following parameters are obtained: the specific heat has been increased by $1.9 \times$, the thermal conductivity has been increased by $3.1 \times$, and the extracted $\tau_1$ time is 6 ps. Not surprisingly, these fit parameters give good agreement between the model and the data. This does not necessarily mean that the films have these modified thermal parameters, but the fitted parameters help to quantify the difference between the model and the data.

It is also possible that the deviation between the data and the thermal model could be explained by different optical, rather than thermal, properties. Based on the data from reference [36], the transmission coefficient only varies by $\sim 10\%$ between the $\alpha$ and $\beta$ phases. To ascertain that the theoretical intensity transmission coefficient ($T_{1,2} = 0.22$ for s-polarized light at 60°) is indeed accurate for the samples used here, the reflectivity was directly measured. Depending on the sample position, the reflectivity was found to be between $\sim 0.65$ and 0.75. This agrees with the theoretical value assuming $\sim 3$-13% of the incident light is scattered due to imperfections. It is therefore unlikely that different optical constants play a significant role in the deviation between the data and the thermal model. As calculated in section 2.5, the first order diffracted intensity is expected to be $2.7 \times 10^{-4}$, so the presence of the stripes is not likely to significantly affect the transmitted light.

The high fluence case with the sample initially at $T_0 = 20^\circ$C is shown in Fig. 5.6. The data is presented in the same manner as the previous case; the upper graph shows the extracted strain, and the lower graph shows the associated temperature. It is immediately clear from the data that the expected trends appear: the temperature increases over several picoseconds, and then returns toward equilibrium over hundreds of picoseconds to nanoseconds. However, it is also clear that $\tau_1$ is much larger; the strain is still decreasing after 100 ps. This is probably too long to be related to electron–lattice thermalization. The thermalization time should not significantly depend on which phase or combination
Figure 5.6: Extracted strain (top) and corresponding temperature (bottom) as a function of time delay after optical excitation. The sample is held at 20°C, and is pumped with high fluence. The blue points represent values extracted from the SHG data; the black curves show values derived from the heat diffusion model using bulk thermal parameters; and the red curves use a model with modified thermal parameters to best fit the data.

of phases are involved. Since this time is much longer when the sample is initially in the coexistence phase, it is likely related to the dynamics of the stripes; this is investigated in section 5.3.

The black curves use the temperature model based on the bulk thermal parameters, and the red curves use a model with modified thermal parameters as before. For consistency, the same thermal conductivity and specific heat are used that were found for the low fluence, low temperature data set. Whereas for the low temperature case, the measured heating was about $\sim 40\%$ less than bulk parameters suggest, for the 20°C case, the difference is about $5\times$. This shows that an experimental issue, such as imperfect pump–probe overlap, cannot be responsible for the mismatch between the thermal model using bulk parameters and the data; the MnAs film shows a strong resistance to a decrease in strain or increase in temperature on a picosecond to nanosecond timescale
near the phase transition temperature. The fitted curve uses a modified latent heat of 1.9$\times$ the bulk value.

The final set of data represents the low temperature, high fluence case where the MnAs film is initially in the $\alpha$ phase, but the fluence is sufficiently high to excite it just into the coexistence phase. This is shown in Fig. 5.7. Figure 5.4, shown at the beginning of this section, is based on the same data as is used here. The black curves show the temperature obtained from the thermal model using bulk parameters, and the red curves show the temperature using the modified thermal parameters obtained from the previous two data sets. The trends of the data and curves are similar to the previous situations; the measured temperature rise is $\sim 50\%$ lower than the thermal model predicts, but has the correct qualitative behaviour. The modified thermal model matches the data reasonably well. It is important to note that the thermal parameters are not fit to the data in this case; they are those obtained from the previous data sets. This illustrates that a single set of effective thermal parameters (except for $\tau_1$) accounts for all the behaviour observed.

5.3 Optical Diffraction from MnAs

Like the SHG experiment, the diffraction is initially measured as a function of temperature under equilibrium conditions. These results can then be used as a calibration for the diffraction after optical excitation. The diffraction is measured after optical excitation on short timescales at high resolution using delayed probe pulses, and on long timescales using a continuous probe beam. Diffraction is sensitive to the stripe periodicity, through possible contributions from both the alternating film height, and the index of refraction.

5.3.1 Diffraction from MnAs Under Equilibrium Conditions

In this experiment, the first order diffraction is measured from MnAs films as a function of temperature. The equilibrium data is taken concurrently with the pump–probe experiment to avoid changes to the alignment or other issues that would affect the calibration between the equilibrium and pump–probe data. Therefore, at various times the same data is taken using a probe pulse from the Clark laser system, and CW light from the Coherent Vioflame laser. In all cases, measurements are taken in order of decreasing temperature to avoid inconsistent results due to hysteresis effects. Figure 5.8 shows a plot of normalized diffraction intensity as a function of temperature over the relevant
Figure 5.7: Extracted strain (top) and corresponding temperature (bottom) as a function of time delay after optical excitation. The sample is held at -20°C, and is pumped with high fluence. The blue points represent values extracted from the SHG data; the black curves show values derived from the heat diffusion model using bulk thermal parameters; and the red curves use a model with modified thermal parameters obtained from previous data.

Temperature range. Data for this plot was taken using a 190 nm film, but the shape of the plot and temperature endpoints are nearly the same for the 150 nm film; this is in agreement with previous work [4].

The actual diffraction efficiency is measured using a power meter to measure the incident and diffracted power. A maximum diffraction efficiency of $\sim 3.7 \times 10^{-5}$ is found at the peak temperature ($\sim 25$°C) for the 190 nm film. This is somewhat lower than the expected value of $2.7 \times 10^{-4}$ calculated in section 2.5. However, this estimate makes use of several approximations (most notably, the actual surface profile shown in Fig. 3.5 is not rectangular, but possesses a significant degree of randomness; and the indices of refraction are based on homogenous films rather than striped films). The diffracted light is generated over a large range of angles (as shown in Fig. 3.7) making a large diameter,
Figure 5.8: First order normalized diffraction efficiency vs. temperature under equilibrium conditions from a 190 nm MnAs film. The points are measured data as the sample is cooled, and the curve is a $\sin^2(\pi \xi)$ fit as suggested by Eq. (2.45). The diffraction efficiency is normalized to give a maximum value of unity after background scattering effects have been subtracted.

short focal length lens necessary to collect it. It is difficult to estimate how much light is lost, either from missing the edge of the lens, or from not being properly focussed onto the power meter due to lens abberations. The actual diffraction efficiency is not used in further analysis; only the renormalized values are used.

It is known that for a sample of a particular film thickness, the stripe period is nearly constant, and the width of the $\alpha$ phase stripes, or equivalently the filling fraction $\xi$, decreases linearly with temperature throughout the transition region. The height profile may be approximated as a periodic rectangular grating, i.e., sudden jumps between the $\alpha$ and $\beta$ regions. The actual surface is smoother though as shown in Fig. 1.3; this deviation is discussed in section 2.5. Under equilibrium conditions, it is shown in section 2.5 that the first order diffracted intensity is $I_1 = I_0 \sin^2(\pi \xi)$, where $\xi$ is assumed to vary linearly from 1 at $\sim 10^\circ$C to 0 at $\sim 40^\circ$C and $I_0$ is the peak diffraction intensity. This fit is shown in Fig. 5.8. The endpoints of the transition are used as fitting parameters, but are always within $\sim 3^\circ$C of 10°C and 40°C. These fits show reasonably good agreement with the data for both film thicknesses. The factor $I_0$ is used to normalize the data. The original data has a large offset due to scattered light. This offset is subtracted from the data shown in Fig. 5.8, and then renormalized so that $I_0 = 1$. 


5.3.2 Ultrafast Excitation: Short Timescale Behaviour

In the previous section, it is shown that linear optical diffraction can be used to probe the stripes on MnAs films under equilibrium conditions. This section involves the same measurements performed shortly after the film has been optically excited by another laser pulse. The pump pulse is $\sim 200$ fs long, with a center wavelength of 775 nm and 1 kHz repetition rate. This is frequency-doubled to generate 387 nm probe pulses. These timescales imply that the best temporal resolution available is $\sim 200$ fs, and any effects introduced by the pump pulse which last more than 1 ms can accumulate over time. In section 2.4, it is shown that under these experimental conditions, the expected temperature change decreases to $< 1\%$ of the peak value within $\sim 1$ $\mu$s, so energy accumulation should not be an issue. The delay stage used for this experiment allows for pump–probe delays of up to 5 ns. Two pump fluences are used: 2.1 mJ cm$^{-2}$ (high fluence) and 1.05 mJ cm$^{-2}$ (low fluence) for most of the experiments, and samples are held at various equilibrium temperatures as before.

Figure 5.9 shows the measured diffraction efficiency vs. time delay for the 190 nm film. The graphs show cases starting at different equilibrium temperatures and fluence. All the data is normalized to the peak diffraction efficiency ($I_0$) obtained under equilibrium conditions. There are several trends in the data that are worth discussing. When the sample is initially within the coexistence phase, there are regular oscillations in the diffraction signal; before the diffraction intensity starts oscillating, there is often a fast increase to the signal that only lasts a few picoseconds; the signal always drops, nearly to zero in the high fluence case regardless of what the initial temperature is; and the signal increases very slowly after excitation, on a timescale of several nanoseconds or more.

Data was also taken with 150 nm films. A few sets of data from 150 nm films are shown in Fig. 5.10 using different fluences and initial temperatures. The diffraction efficiency data appears very similar for the 150 nm and 190 nm films; they both show oscillations and other increasing/decreasing diffraction trends on similar timescales. Most of the following discussion makes use of the data from the 190 nm films with the understanding that it also applies to the 150 nm films.

The oscillations are the most curious aspect of the signal. There are none in the SHG data (on the timescale shown, at least one full oscillation would have been apparent), and the temperature certainly does not oscillate. Clearly there is more to the dynamics than can be explained using thermal effects alone. The oscillations always occur when
Figure 5.9: First order normalized diffraction efficiency measured after optical excitation of a 190 nm MnAs film. The black curves are measured data. The red curves are based on theoretical calculations using bulk thermal parameters.
the sample is initially in the coexistence phase, and always have a phase such that a maximum occurs at zero time delay. They never occur if the sample is initially in the ferromagnetic phase. The oscillation period is nearly constant regardless of initial sample temperature or excitation fluence. However, it is different for the 150 and 190 nm samples. This is clearly shown in Fig. 5.11. It is $408 \pm 4$ ps for the 190 nm sample, and $335 \pm 4$ ps for the 150 nm sample. These values represent the mean and standard deviation of measurements with various temperatures and fluences.

In the coexistence phase, initially the film has alternating ferromagnetic ($\alpha$) and paramagnetic ($\beta$) regions with corresponding larger and smaller strains. Immediately after excitation, the magnetic properties may change at some rate but neither the SHG nor the diffraction experiment is directly sensitive to the magnetic properties. The strain, however, cannot immediately relax; this involves macroscopic rearrangement of the lattice. Before excitation, the lattice parameters vary periodically with the stripe period. This is a periodic density modulation, and can be thought of as a frozen-in acoustic wave. After excitation, the ‘equilibrium’ condition (in the sense of what the film would evolve to if
Figure 5.11: First order normalized diffraction efficiency measured after optical excitation for both film thicknesses and two initial temperatures. The vertical lines are regularly spaced based on the initial position of the peaks. The graph at left has a log scale to show the weak oscillations at later delays. All three sets of data were obtained with a high fluence excitation pulse.

held with the temperature profile following excitation) is such that the surface is flat, i.e., no density modulation. When a region of high density expands toward equilibrium, it necessarily overshoots the equilibrium state. The frozen-in acoustic wave evolves as a time-dependent acoustic standing wave; it does not simply decay toward a flat surface, but oscillates as a standing wave with a temporal period equal to the stripe wavelength, $\Lambda$, divided by the speed of sound. This description assumes a sufficiently high fluence that the whole film is out of the coexistence phase. Even if it’s not, the new ‘equilibrium’ state is different than the initial state, so the film will oscillate about the ‘equilibrium’ state starting from the initial state.

The speed of sound can be approximated from the elastic constants to verify that this hypothesis has some merit. It is worth noting first, however, that a solid material has several types of waves (longitudinal, transverse, as well as surface waves) with different speeds depending on the direction of propagation. The wave motion in MnAs films is likely a combination of these. A longitudinal wave results from a periodic compression/expansion of a material, and is likely associated with the periodic density modulation in MnAs films. Since the direction of compression is the $x$-direction, the speed is given by $c = (c_{11}/\rho)^{1/2}$. MnAs has a molar mass of 130 g/mol, and a unit cell volume (which
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contains 2 sets of MnAs) of $6.8 \times 10^{-29}$ m$^3$ [7]. This gives $\rho = 6.4 \times 10^3$ kg/m$^3$. From section 2.3, $c_{11} = 40$ GPa. This gives a longitudinal mode sound speed of 2500 m/s.

Transverse waves result from a periodic shear strain in the material, which also occurs in MnAs films and gives rise to the periodic height modulation. This type of wave has a speed given by $c = (G/\rho)^{1/2}$ where $G$ is the shear modulus and $\rho$ is the density. The shear modulus is the ratio of shear stress to shear strain, i.e., $\sigma_{12} = 2G\epsilon_{12}$, since the displacement is in the $y$-direction and the wave propagates in the $x$-direction (there is another shear modulus relating, for example, a strain in the $x$-direction to stress in the $z$-direction, but this is not important here). For a material with hexagonal symmetry, $G = (c_{11} - c_{12})/2$. This gives a transverse mode sound speed of 1600 m/s.

As shown in section 3.2, the 150 nm MnAs film has a measured stripe period of $740 \pm 70$ nm, and the 190 nm MnAs film has a measured stripe period of $1000 \pm 100$ nm. With measured oscillation frequencies of $335 \pm 4$ ps for the 150 nm sample and $408 \pm 4$ ps for the 190 nm sample, these give wave speeds of $2210 \pm 220$ m/s and $2450 \pm 250$ m/s. These are in agreement with the the speed of sound of longitudinal waves.

In these calculations, it is assumed that one full oscillation of the sound wave corresponds to one full oscillation of the diffraction signal. One might assume that the diffraction signal should oscillate with twice the frequency of the sound wave. The surface should start in a striped state (high diffraction), pass through a flat state (no diffraction), and reach a striped state with the opposite phase as the original state (high diffraction). This is one half of a sound wave cycle, but one full diffraction oscillation. In other words, for a standing wave, the diffraction should peak twice for every full oscillation cycle. However, for a weak fluence, even if the surface reaches the paramagnetic phase, most of the film is still in the coexistence phase, so the sound wave will remain frozen-in for most of the film. The surface profile therefore oscillates about an equilibrium state that has a surface modulation instead of being flat, and unless the oscillation is sufficiently strong, it never proceeds past a flat state while oscillating. Since the same diffraction oscillation period is seen regardless of fluence or initial temperature, this always seems to be the case.

Depending on the equilibrium temperature and pump fluence, there are $\sim 5$ clearly resolvable oscillations. However, in the cases where there are clearly more, the phase of the oscillations apparently changes. The phase change is shown in Fig. 5.11 where the evenly spaced vertical lines are initially at the peaks, but later in the troughs. This suggests two distinct but similar speeds of sound that give rise to a beating pattern in the
standing waves. For the 190 nm film, this appears to be after 2.0 ± 0.5 full oscillations, so the beat frequency (which corresponds to twice this time) is 250 ± 60 MHz. This suggests a difference in speeds of sound of ~ 220 ± 50 m/s. This difference likely corresponds to two different types of acoustic waves, such as longitudinal and transverse, both of which are close to the measured speed. The calculated theoretical values for the speeds differ by 900 m/s, so the actual waves are likely more complicated, i.e., a type of wave specific to the near-surface region.

If the film is initially between 10°C and 40°C and is optically excited, the diffracted signal oscillates about some value. This value is always lower than the initial value. After several nanoseconds, the diffracted intensity starts to rise again if the initial temperature is sufficiently low. Except for a few picoseconds after excitation it always takes a few nanoseconds at minimum for the diffraction signal to reach the initial value again. This implies that the optical excitation can destroy the stripes quickly (apart from the oscillations), but cannot create stripes on a timescale less than a few nanoseconds. For example, if a sample is initially at 8°C, just below the coexistence phase, the diffraction signal remains within noise of zero for at least 3 nanoseconds, as shown in Fig. 5.9. After this, the diffraction signal appears to start to climb, although barely beyond the noise. If the stripes obeyed strictly thermal behaviour, the stripe-induced diffraction would increase immediately after excitation when the sample is initially near the 10°C transition point. Instead, there appears to be a delay of ~ 5 ns for the stripes to form.

There are several possible causes for the delayed stripe formation. The most obvious is that it simply takes time for the lattice within the entire depth of the film to rearrange itself from a uniform excited state to a well-ordered state with the phases organized into stripes. Shortly after excitation, when a significant volume of the sample cools to a temperature consistent with stripes, islands of α-MnAs may start to form in the β-MnAs. These islands may then group together to self-organize into stripes, a process which must take some time. Another possible cause of the long delay for stripe formation is the large temperature gradient. Stripes are known to exist under equilibrium conditions where the film has a uniform temperature. The stripe period is related to the film thickness, and the fact that the film has uniform properties. If the film properties depend on the depth, as would be the case near the phase transition temperature if there is a large thermal gradient, this would affect the stripe period. Therefore, as the film is quickly heated and cools, it continually tries to reach a different stripe period. There is no evidence in these measurements of a different stripe period, but it would not be surprising that this effect
slows down the stripe formation.

Although it is clear that aspects of the stripe dynamics do not obey thermal behavior on a timescale of a few nanoseconds, the diffraction can still be compared with a thermal model to show what aspects of the stripe dynamics do obey thermal behavior. Even if the stripes could respond instantaneously to the local lattice temperature, it is not clear how the thermal gradient, which is always present after optical excitation, would affect the stripes. One reasonable approximation is that the stripe amplitude follows the known temperature dependence, and the temperature is a function of depth. Then the net stripe amplitude is the integral of the stripe amplitude over all depths. So, for example, if the top surface is at a temperature > 40°C and the bottom surface is at a temperature < 10°C, there is a region in between that is in the coexistence phase, and this will lead to a weak stripe amplitude. The red curves in Figs. 5.9 and 5.10 show the results of the thermal model.

Whenever the model predicts a rise in the stripe amplitude within a few nanoseconds of excitation, the actual response always lags. However, when the model predicts a decrease after excitation, the measured amplitude does decrease (ignoring the oscillations). Both the model and the data show the rise in stripe amplitude observed after 2–3 nanoseconds when the equilibrium temperature is below ∼ 24°C. At higher temperatures (≥ 24°C with high fluence, or ≥ 32°C with lower fluence), both the data and the model show that stripes do not significantly start to reform within the time frame available. The model and experimental values do not always start at the same position (before time zero). The equilibrium diffraction efficiency (before time zero) changes slightly between experimental runs. It is known from previous experiments that the stripe amplitude, which varies with temperature, shows hysteresis [32]. When the sample is optically excited through the phase transition one thousand times per second, it is not surprising that the hysteresis might somehow affect the diffraction. This effect is generally unavoidable, but the normalized equilibrium diffraction efficiencies don’t usually vary by more than ∼ 0.2.

The final aspect of the diffraction experiments available on these timescales is the fast increase of the diffracted signal immediately after excitation, barely visible in Figs. 5.9 and 5.10. This is typically most apparent when the sample is initially at temperatures ≥ 24°C and with higher fluence. Figure 5.12 shows the diffraction near zero time delay. Interestingly, the fast increase in diffraction efficiency occurs for initial temperatures from ∼ 20°C to 40°C. This effect cannot be explained through the thermal model given
Figure 5.12: Diffraction efficiency over the first few picoseconds after optical excitation of an MnAs film at various equilibrium temperatures. Black lines are actual data, and the red curves are guides to the eye. These data are taken with a 190 nm film, at high fluence, although similar patterns occur for lower fluence and 150 nm films.

above for two reasons: the stripe amplitude should never increase when heated from temperatures \( \gtrsim 25^\circ C \), i.e., the temperature corresponding to the peak diffraction; and the diffraction amplitude increases above the maximum value encountered under equilibrium conditions. The latter reason is not immediately clear because the magnitude of this fast increase is small compared to noise and systematic errors; but because it is observed throughout most of the temperature range, it also exists at the temperature of the peak diffraction, \( \sim 25^\circ C \). In all cases, this fast effect occurs on a timescale of 3–4 picoseconds, reaching a maximum in 6–8 picoseconds. This is clearly much faster than the timescale associated with an acoustic wave.

In the discussion of the diffraction data above, the actual cause of the diffraction was ignored. As indicated in section 2.5, diffraction is caused either by a modulating index of refraction, or a modulating height profile, or both. It is shown that the index and height modulation affect the diffraction efficiency, but not in a simply additive way. When only the height modulation is included, the diffraction efficiency is found to be \( \sim 2\times \) greater than if both the height and index modulation are included.

An optically induced modification to the index of refraction does not require the lattice
to rearrange, and may therefore happen on a few-picosecond timescale. Immediately after excitation, the index of refraction may increase as the lattice heats up. This timescale is much less than the oscillation period caused by acoustic waves, so the height modulation has not had time to change. This may therefore be the second situation described in Eq. (2.46); there is only a height modulation but the index modulation has disappeared (or at least decreased).

This situation was predicted to give rise to a \(\sim 2\times\) greater diffraction efficiency, but the measured increase is only \(\sim 30\%\). This discrepancy may be because the index modulation is not as thought, or because the height modulation is reduced over this \(\sim 5\) ps timescale. These possibilities are further discussed in section 5.4.

### 5.3.3 Ultrafast Excitation: Long Timescale Behaviour

The previous section outlined the results and the most important features of the diffraction experiment with a sub-picosecond time resolution, but limited to \(\sim 5\) ns delays. With the use of a continuous wave probe and oscilloscope, it is possible to measure the pump-induced diffraction on an unlimited timescale, but with a resolution of \(\sim 10\) ns, limited by electronics. For this experiment, the same pump laser is used for optical excitation (\(\sim 200\) fs pulses with a center wavelength of 775 nm and 1 kHz repetition rate), and a Coherent Vioflame (409 nm light) is used as a probe. On this timescale, the lattice oscillations are not resolvable, but the long timescale behavior can be measured.

Some typical plots of diffraction vs. time delay after optical excitation on a 150 nm sample are shown in Fig. 5.13 using a low pump fluence, and Fig. 5.14 using a high pump fluence. Some of the plots are shown in pairs: a medium timescale plot up to 400 ns, and a long timescale plot up to 2 \(\mu\)s. On these timescales, the stripes behave in a manner somewhat consistent with diffusion processes such as thermal diffusion. If the sample is initially near the 10°C threshold, or even slightly below, stripes form on a timescale of \(\sim 10–20\) ns, and then decay on a timescale of up to 100 ns. If the sample is initially at \(\sim 20°C\), the stripes are destroyed within \(\sim 2\) ns after excitation, especially with a high fluence pump, as seen earlier. The stripes then reform and, depending on the initial temperature, reach a higher diffraction amplitude than under equilibrium conditions. They then decay toward the equilibrium value on a timescale of \(\sim 100\) ns. If the sample is initially at higher temperatures, especially near the 40°C threshold, the stripes are completely destroyed, and take longer to reappear. This is because it can take \(\sim 100\) ns
(depending on the fluence and initial temperature) before the temperature has decayed to \(\sim 40^\circ C\). In these cases, the stripes are still visibly reforming even up to \(2 \mu s\).

Quantitatively, the temperature and stripes can be modeled in the same way as before with bulk parameters. A stripe amplitude is calculated as a function of depth based on the temperature at that depth, and then the net stripe amplitude is the integral of this amplitude. This model may not be physically accurate, but as noted in section 2.4, after \(\sim 100\) ns, the temperature at the front and back surfaces are nearly the same to within \(\sim 1^\circ C\). After this time, the model simply describes a film with a nearly uniform temperature. The temperature model has the same features as the data in most cases. The model reproduces the time that it takes for the stripes to return to equilibrium values. The model is also consistent with those cases wherein the stripes are reduced after excitation, but reform to a higher amplitude than equilibrium. In many of the cases, however, the theory and experimental values do not start at the same diffraction efficiency. This is the same systematic error encountered before; the equilibrium diffraction value changes slightly between experimental runs, probably because of hysteresis effects. In some cases the model does not give the same time dependence as the data shows, for example in many cases for the first \(\sim 400\) ns, the stripes reform slower than the model predicts. This is likely due to some of the nonthermal effects discussed in the previous section.

It was previously found that when a film is excited from \(8^\circ C\), stripes do not form to any significant degree within the first 5 ns after optical excitation. Figure 5.14 shows that stripes eventually do form after \(\sim 20\) ns, although barely observable from the diffraction data, and only clearly in the high fluence case. It is also worth investigating whether stripes can be created when starting further away from the striped temperature range, i.e., \(< 8^\circ C\). A few data sets were taken starting at temperatures down to \(0^\circ C\), with higher fluence. In this case, the fluence is \(2 \times\) the high fluence case used before, or \(4.2 \text{ mJ cm}^{-2}\). These are shown in Fig. 5.15.

It is clearly much more difficult to generate ‘non-equilibrium’ stripes starting from temperatures near \(0^\circ C\), even with very high fluence. Fluences higher than \(4.2 \text{ mJ cm}^{-2}\) are not practical because this is close to the damage threshold of MnAs films. With this fluence, stripes can be created with an amplitude barely observable with diffraction starting from a temperature of \(0^\circ C\). In these high fluence, low temperature cases, the thermal model is consistent with the timescale over which the stripes exist, but underestimates the amplitude of the stripes. This is in agreement with results from the previous section;
Figure 5.13: Diffraction efficiency over hundreds of nanoseconds after optical excitation from various equilibrium temperatures using low pump fluence from a 150 nm film. Black lines are experimental data, and red curves are based on theoretical values as discussed in the text. Some graphs which show different timescales with the same experimental conditions are shown side by side.
Figure 5.14: Diffraction efficiency over hundreds of nanoseconds after optical excitation from various initial temperatures using high pump fluence from a 150 nm film. Black lines are experimental data, and red curves are based on theoretical values as discussed in the text. Some graphs which show different timescales with the same experimental conditions are shown side by side.
Figure 5.15: Pump-induced diffraction from a 150 nm film using 2× the high fluence at lower temperatures. Black lines are experimental data, and red curves are based on theoretical values as discussed in the text.

stripes do not form immediately after optical excitation. Furthermore, their properties may be a complicated function of heat distribution in the film.

All the data shown in Figs. 5.13, 5.14, and 5.15 were taken using 150 nm MnAs films. Data was also taken using 190 nm films. These are shown in Fig. 5.16. For the most part, the data for the two film thicknesses are very similar. They both show increasing stripe amplitude if the sample is initially at a low temperature, decreasing stripe amplitude when starting from high temperatures, and a decrease followed by an increase when starting at intermediate temperatures. The magnitudes of the changes are similar as well. The most obvious difference is that if the sample is initially below 10°C, the 190 nm film does not form stripes to the same extent as the 150 nm film. This is true for any fluence and may be related to the difference in temperature across the film. Shortly after optical excitation, the top and bottom surfaces of the MnAs film are at different temperatures (i.e., the thermal gradient discussed earlier); this effect is larger for thicker films.
Figure 5.16: Pump-induced diffraction from a 190 nm film using various fluences and initial temperatures. Black lines are experimental data, and red curves are based on theoretical values as discussed in the text. Some graphs which show different timescales with the same experimental conditions are shown side by side.
It was suggested earlier that a strong thermal gradient could inhibit stripe formation. If that is the case, this effect would be even stronger for a higher fluence excitation. In comparing Figs. 5.14 and 5.15, it can be seen that when the sample is initially at 8°C, there is not a large difference between the high fluence and 2× high fluence cases. The peak stripe amplitude is nearly the same in both cases, and decays slightly slower in the 2× high fluence case. This can easily be explained if the thermal gradient slows stripe formation. On short timescales for the 2× high fluence case, more of the material is in a temperature region which can have stripes (indicated by higher stripes in the thermal model), but this is countered by the higher thermal gradient. After ~100 ns, the heat deposited in the high fluence case has diffused enough to make most of the film below the coexistence phase temperature region, whereas with 2× the high fluence, enough energy has been deposited that the film is still within the coexistence phase region.

5.4 Perspectives of MnAs Phase Transition

The previous sections show results from SHG and optical diffraction on short and long timescales after optical excitation. Although both of these experiments probe slightly different properties (essentially the zeroth and first order Fourier components of the stripes), all these results must be taken together to properly formulate the dynamics of the phase transition on the relevant timescales. The aim of this section is to propose a model which describes the dynamics of MnAs films which is consistent with all the data presented above. It should be noted again though that none of these experiments probe the magnetic properties directly. The only aspects of the phase transition which are probed here are related to the changing lattice parameters and index of refraction.

The results of the SHG experiment show that the sample effectively heats up on a timescale of \( \tau_1 \sim 6 \text{ ps} \) when initially in a homogenous ferromagnetic phase at \(-20\)°C, even when the fluence is low enough to keep the sample mostly in the ferromagnetic phase. This means that the \( \sim 6 \) ps time constant is related to the lattice contraction in the \( y \)-direction (normal to the surface) as a result of heating. This time constant is much less than the oscillation period in the \( x \)-direction because the region over which the film must contract is the optical penetration depth, \( \sim 17 \text{ nm} \) rather than the stripe period \( \sim 1000 \) nm. In principle, the lattice could oscillate vertically as a result of this sudden change in the lattice parameter. This is clearly not seen in the data. Two possible reasons for the lack of oscillations are: 1) that the strain relaxation/oscillation time is comparable
to the electron/lattice thermalization time, so the equilibrium lattice parameter changes slower than oscillations could happen; and 2) the initial heat profile is exponential, which would act to smooth out any oscillations.

It is still possible to calculate a time constant associated with a deformation over a scale of 17 nm; this would be the period of oscillation if the deformation were sinusoidal, but because the deformation is exponential, it is only an approximate timescale associated with the relaxation. With an acoustic wave speed of 2330 m/s, and length scale of 17 nm, the resultant timescale is $\sim 7$ ps. This is in agreement with the measured time constant from the SHG data when starting from low temperatures. The $\sim 6$ ps time constant seen in the SHG experiments is consistent with the time taken for the diffraction to peak immediately after excitation when starting from within the coexistence phase. The fast peak in the diffraction is therefore likely due to a modified index of refraction because of lattice strain in the $y$-direction. In principle, the index of refraction could be changed by hot electrons alone, but this would show up as a changed diffraction or SHG within $< 1$ ps of excitation.

When the sample is in the coexistence phase, there is a periodic density grating. This is a result of a minimization of the free energy due to the mixture of phases and elastic energy considerations. The periodic density is like a frozen-in acoustic wave. After ultrafast heating, the equilibrium state is closer to a flat structure of homogenous paramagnetic MnAs. The frozen-in acoustic wave therefore evolves in time, and oscillates exactly as a standing acoustic wave.

The lattice oscillations are seen to start almost immediately following optical excitation. Mathematically, the first peak in the diffraction oscillation occurs at time zero. This is also seen in that when the diffraction increases suddenly after excitation, it starts to drop again within $\sim 10$ ps. The first minimum of the diffraction oscillation is then at $\sim 200$ ps after excitation. This implies that the force required to start the oscillation (i.e., the restoring force) starts at around the same time as the fast diffraction peak. In the notation used in section 2.3, the periodic modulation of the total strain $\epsilon_{11}$ has not had time to change within $\sim 5$ ns, but the internal strain $\eta_{11}$ has changed, and therefore the elastic strain $e_{11}$ (i.e., related to the restoring force) has also changed. Under equilibrium conditions, $\eta_{11}$ depends on the phase of the film, so this suggests that the phase transition, at least near the surface, happens within $\sim 10$ ps after excitation. It is not known from these experiments if the magnetic properties change at the same time, but under equilibrium conditions, the magnetic properties follow the lattice parameter when
changing phase in either bulk or thin film form.

In the SHG experiment, with the sample initially in the coexistence phase, the strain does not appear to decrease to the extent that it should, and it takes considerably longer ($\tau_1 \sim 100$ ps) to reach a minimum. This experiment is clearly only sensitive to the spatially averaged (zeroth Fourier element) strain, otherwise it would show nearly two full oscillations in the time frame available. One possible reason for the delayed/reduced drop in average strain in this case is that a considerable amount of the deposited energy is actually in the acoustic wave. It is not clear if one should think of the acoustic energy as being already present before the optical pulse, or deposited by the optical pulse. After optical excitation, the MnAs film has absorbed all the energy from the pulse, and within $\sim 10$ ps, the electrons and lattice are in thermal equilibrium at an increased temperature. After 100 ps, there is energy in the form of an acoustic wave which decays after $\sim 3$ ns. This energy must be converted to heat, further increasing the film temperature. Therefore, it makes sense from the perspective of conservation of energy to think of the optical pulse as depositing some of its energy into the film as heat, and the rest into the lattice in the form of an acoustic wave, which is then converted to heat after $\sim 3$ ns. When the sample is initially in the coexistence phase, it therefore takes more energy to increase the temperature by a fixed amount on a sub-nanosecond timescale than it would under equilibrium conditions. Experimentally, this would appear as an increased latent heat. This could be part of the reason that the latent heat appears higher when a film is rapidly heated with an optical pulse, and that the temperature appears to take longer to rise.

Although this energy loss in the acoustic wave must occur to some degree, it may not be the main cause of the reduced/delayed decrease in the spatially averaged strain. The temperature dependence of the spatially averaged strain is only well-understood under equilibrium conditions where the $\alpha$ and $\beta$ phases form regular stripes. Since the lattice is oscillating, it is clear that the lattice is in a non-equilibrium state, so there is no evidence that the spatially averaged strain should depend on the temperature in the same manner as is does under equilibrium conditions.

The lattice oscillation period is determined by the stripe wavelength, and hence the thickness of the film. There appear to be at least two types of waves with different speeds visible from the apparent beating in the diffraction signal. The speeds of these waves are similar to the longitudinal sound wave, but are likely affected by the surface nature of the waves. In all cases, the waves disappear in 5 ns or less depending on the fluence.
and initial temperature. It is not clear what determines this time constant. It may be related to energy redistribution in the films. Immediately after excitation, the stripe structure oscillates about a new equilibrium state. This equilibrium state evolves as the energy diffuses through the film on a few-nanosecond timescale. Because the temperature profile, and hence the equilibrium lattice parameter, changes drastically over the first 5 ns, the evolution of the wave is complex and cannot easily be modeled.

Apart from the oscillations, the stripes are generally reduced after excitation, and mostly destroyed when the sample is initially near 40°C, especially with high fluence. This may be partially due to thermal effects which act to convert the stripes into a homogenous β phase. But it may also be due to the large thermal gradient which affects the conditions necessary to support stripes of a particular wavelength. With the sample initially in the coexistence phase near 10°C, the stripes start to reform after ~ 3 ns, eventually reaching a higher amplitude than at equilibrium. However, with the sample initially in the homogeneous ferromagnetic phase at a temperature < 10°C, stripes do not form for ~ 20 ns. One possible reason for this is that even when they are excited from > 10°C, the stripes are destroyed at the surface, but may still exist deeper down in the film. This may make it easier for the stripes to form, e.g., from the bottom up in a nucleation-like process. With the sample initially at colder temperatures, the stripes have to form from a completely homogeneous state, which likely takes longer.

After ~ 100 ns, the film starts to behave as if it were near equilibrium conditions. In this time frame, the MnAs behaviour is likely determined mainly by thermal parameters and certainly by diffusion effects. The stripes reform or decay on a timescale consistent with thermal diffusion, which can take several microseconds.

The preceding discussion outlines a model for the evolution of MnAs films following optical excitation. Some important aspects of this model are summarized in Fig. 5.17. This particular case shows a sample which is initially near the peak of the coexistence phase (~ 25°C) with a low fluence excitation such that the stripes are not completely destroyed. However, similar dynamics and timescales apply for other fluences and initial temperatures.
0-200 fs: laser excitation
<1 ps: electron thermalization

100-2000 ns: film approaches equilibrium

~100 ns: temperature gradient disappears, film becomes homogeneous

~5 ns: stripes start to reform

<6 ps: lattice thermalization
6-100 ps: contraction in y-direction

~300 ps: oscillation period
~2 ns: oscillations decay

Figure 5.17: Evolution of an MnAs film, initially in the coexistence phase, following optical excitation. The top diagram shows the initial film configuration at the time of optical excitation. The timescales given are approximate, and vary depending on the initial temperature and fluence. Blue and yellow regions represent $\alpha$ and $\beta$ phases respectively, and mixed shades represent regions where aggregation and nucleation effects may be occurring.
Chapter 6

Conclusions

6.1 Summary of C-Film SHG

This experiment involves measuring optical second harmonic generation from exfoliated graphene, multilayered C-films, and bulk graphite. These samples are deposited on a SiO$_2$/(001)Si substrate, and the SHG is measured using a pulsed 800 nm laser. The SHG is measured as a function of azimuthal rotation angle, $\phi$, for samples of various thickness. For each sample, five different polarization combinations are used: p-in, s-out; p-in, p-out; s-in, s-out; s-in, p-out; and diagonal-in, s-out.

The most obvious qualitative difference is found between 1-layer and 2-layer C-films (often referred to as graphene and bilayer graphene) for p-in, p-out polarized light. Graphene is found to generate very little SHG light, and the angle-dependent signal is not significantly different from that from the bare substrate. This shows 4-fold symmetry, characteristic of the rotational symmetry of (001)Si. A bilayer sample is found to generate a qualitatively different angle-dependent signal. This signal is 3-fold rotationally symmetric rather than 4-fold. The strong SHG from bilayer C-films is understood in terms of their surface symmetry. Whereas graphene has 6-fold rotational symmetry, bilayer C-films have only 3-fold rotational symmetry at the surfaces because of the AB stacking arrangement. The reduced symmetry at the surfaces of > 1-layer samples allows more nonzero elements in the nonlinear susceptibility tensor responsible for SHG. These extra nonzero tensor elements are found to generate electric fields that add constructively at either surface of the C-film, thus producing strong 3-fold rotationally symmetric SHG. The nonzero tensor elements in graphene add destructively, thereby producing very weak SHG.
From bilayer C-films to bulk graphite, the SHG yield is found to vary quantitatively, but the rotational pattern is always 3-fold rotationally symmetric for p-in, p-out polarized light. Other polarization combinations are also found to vary quantitatively from bilayer to bulk, but maintain the same qualitative pattern. In general, the SHG yield from bulk graphite is \( \sim \frac{1}{2} \) the yield from bilayer C-films.

The thickness dependence of the SHG yield from bilayer C-films to bulk graphite is calculated theoretically assuming the SHG originates from the front and back surfaces of the C-film, as well as the (001)Si substrate. The front and back surfaces of the C-film are assumed to have the same nonlinear tensors which are independent of sample thickness. The total SHG yield is the sum of these sources, which add coherently. It is shown that, except for an overall phase factor, all of the nonzero tensor elements related to the C-film surface can be uniquely identified through SHG measurements of all 5 polarization combinations over several film thicknesses. The data is fit to the surface SHG model, and the nonlinear tensor elements are extracted.

Some nonlinear tensor elements are of opposite sign between the front and back surfaces for symmetry reasons; these are the only ones which are not symmetry forbidden in graphene. Because they switch sign, the generated E-fields add destructively, so the predicted SHG yield is nearly zero. Other tensor elements that do not switch sign are responsible for the 3-fold rotational symmetry of > 1-layer C-films. Therefore, the predicted SHG yield is strongest from bilayer C-films where the opposite surfaces are closest together and have a minimal attenuation between them. The fact that the measurements agree with these two predictions validates this model. This suggests that for surface SHG calculations from thin films, the opposite sides of the film can be treated as independent surfaces, even if the film is one or two atoms thick.

### 6.2 Summary of MnAs Experiments

Two experiments were performed on MnAs films grown on GaAs. The first is SHG, and the second is linear optical diffraction. These films undergo a phase transition between 10\(^\circ\)C and 40\(^\circ\)C, and in this intermediate temperature range, both ferromagnetic and paramagnetic phases coexist in a striped pattern. The SHG measurements are found to probe the spatially averaged normal component of the surface strain which is known to exist in MnAs films. The diffraction measurements probe the first Fourier element of the stripe profile. Both of these experiments are performed as a function of temperature.
under equilibrium conditions, and in pump–probe situations where the sample is first optically excited by a pump pulse.

Under equilibrium conditions, the SHG signal as a function of temperature is consistent with known values of strain as a function of temperature. The results from the equilibrium SHG experiment are therefore used as a calibration so the strain, or equivalently temperature, can be extracted from SHG measurements after optical excitation.

After optical excitation, the SHG signal is found to behave qualitatively (but not quantitatively) as expected based on a heat diffusion model using bulk thermal parameters. Within $\sim 10$ ps, the strain decreases, consistent with heating or an increased energy density in the film near the surface region. The strain then increases back toward the equilibrium value, reaching the halfway point in $\sim 500$ ps. However, the magnitudes of the changes to the extracted strain or temperature are below the calculated values. In the low fluence case, where the sample remains mostly in the $\alpha$ phase, this difference is $\sim 40\%$. When the sample is initially at higher temperatures or using a higher fluence such that part of the film undergoes the phase transition, it is found that the difference between the data and theoretical values is much greater; the extracted temperature increase is $\sim 1/5$ the value calculated. Although this experiment shows qualitatively thermal behaviour, the results from the diffraction experiment show distinctly nonthermal behaviour over the first few nanoseconds, especially when the sample is initially in the coexistence phase. The reason for the discrepancy between the SHG data and the model is likely due to this nonthermal behaviour.

The relation between the stripe structure and temperature is well-known for MnAs films. Under equilibrium conditions, the measured diffraction is shown to follow the expected trends. The actual magnitude of the diffracted signal is lower than the calculated value, likely because of the irregularity of the stripes.

When an MnAs film is optically excited from within the coexistence phase, the diffraction signal oscillates over the first $\sim 4$ ns. The oscillation period is consistent with one or more acoustic standing waves with a wavelength equal to the stripe period. Under equilibrium conditions, the periodic density/height modulation from the stripes may be seen as a frozen-in acoustic wave. The energy from the excitation pulse increases the temperature, so the new spatially equilibrium state has no stripes, or reduced stripes depending on the fluence. The frozen-in acoustic waves therefore evolve as standing acoustic waves.

Apart from the acoustic wave oscillations, the stripes can be destroyed within $\sim 3$ ns after optical excitation (depending on the excitation fluence). The stripes can not, how-
ever, form quickly. If the equilibrium temperature is near the middle of the coexistence phase region, the stripes can start to regrow after $\sim 3$ ns. If the equilibrium temperature is below the coexistence phase region (i.e., $< 10^\circ$C), no stripe growth happens within the first 5 ns available with the time-resolved pump–probe experiment. From the longer timescale data, it is shown that stripes do form after excitation from $< 10^\circ$C, although to a much lower degree than a thermal model predicts, and only after $\sim 20$ ns. Several causes for this behaviour are suggested. A large thermal gradient may prevent the stripes from forming as they usually occur under equilibrium conditions. Also, the stripes likely form in a nucleation-type process, where regions of $\alpha$-MnAs appear and disappear in the primarily $\beta$-MnAs surface. These regions must conglomerate into stripes, and when the initial state has no stripe structure, this must take time.

After $\sim 100$ ns, in most cases, the evolution of the stripes approximately follows a thermal trend, with the diffraction increasing or decreasing toward the equilibrium value. Depending on the equilibrium temperature and fluence, it can take several microseconds before the diffraction efficiency becomes indistinguishable from the equilibrium value.

### 6.3 Outlook

The unusual electronic and optical properties of graphene may make it of use in nano-electronic and photonic devices. But before graphene can reach its full potential, its fundamental properties must be fully investigated. The experiments reported in this thesis have investigated it through SHG. Since the work reported here was completed, other groups have followed up with related work. Theoretical studies on the origin of SHG in graphene have been reported [67, 68]. Direct electric current has been used to break the inversion symmetry to enhance SHG from graphene [69]. There have also been reports of other optical and optoelectronic effects in graphene [70].

It has been shown in this thesis that SHG is a useful tool for probing surface and symmetry properties, and is sensitive to the stacking arrangement in multilayer C-films. Similar experiments to those reported here may be performed on other types of graphene, such as CVD graphene or epitaxial graphene. The exfoliated graphene used here is most commonly used to generate low defect, highly crystalline graphene, albeit in small quantities. SHG could, for example, be used to probe the stacking arrangement of other forms of graphene, or compare them to exfoliated graphene in other respects. The strong SHG from bilayer films is due to the 3-fold rotational symmetry, which only occurs
because of the AB stacking arrangement. If multilayer C-films were fabricated in an AA stacking arrangement, the SHG may be reduced significantly.

These experiments were the first to measure SHG from very thin crystalline films of a known thickness. It was found that SHG from 2-atom thick films is stronger than that from bulk because of the 3-fold rotational symmetry. The model used to describe the SHG from graphene made use of identical nonlinear susceptibility tensors from opposite surfaces, even for films of one or two atomic layers. It would be worthwhile to investigate this behaviour in other materials with similar or completely different crystal structures. This would help determine if the model is universal, or only accurate for graphene where the atomic layers are only weakly bonded.

The other material system investigated in this thesis is manganese arsenide in the form of thin films. These have the potential for use in spintronic and magnetic applications \[4, 5\]. When MnAs undergoes the phase transition, it goes from paramagnetic to ferromagnetic, and two of the lattice parameters change by $\sim 1\%$. In thin film form, because of the substrate-induced strain, the films form alternating stripes of ferromagnetic and paramagnetic phases. If MnAs is to be used in real world applications, it is important to fully understand the magnetic phase transition that occurs near room temperature, especially on ultrafast timescales. The experiments in this thesis investigated the structural change through various optical effects.

Since the experiments performed in this thesis were carried out, the ultrafast dynamics of MnAs films have been studied using diffraction in a manner similar to that described here \[71\]. Those experiments involve a very limited set of experimental conditions (time delay range, fluence, and initial temperature) and so they could not observe most of the dynamics shown here. Not surprisingly, their conclusions are somewhat different than those described here, but because of the limited range of their experiments, it is not useful to try to compare their results and conclusions to those given here.

A natural extension to the diffraction experiments performed here would be to measure the angular dependence of the outgoing light. This would provide insight into the periodicity of the stripes including possible nonthermal behaviour such as a different stripe period caused by a strong thermal gradient. Such an experiment is impractical with the setup used here because of the large angular aperture of the collection lens and the physical constraints of having the necessary lenses close to the sample.

Given the highly nonthermal behaviour of MnAs films discovered here, it would be worthwhile to investigate the magnetic properties directly. Both the SHG and linear
optical diffraction measurements only probe the crystal structure, which may not follow the magnetic properties on ultrashort timescales. For example, the stripes indicate alternating bands of ferromagnetic and paramagnetic phases. When the stripes oscillate after optical excitation, it is not clear if the magnetic properties also oscillate. It may be possible to probe the magnetic properties optically using magneto-optical Kerr effect (MOKE) measurements. This involves observing changes to the polarization of reflected light due to magnetization. MOKE measurements may be difficult however, because MnAs films are known to be linearly birefringent, so it may be difficult to isolate effects due to magnetization alone. It should be possible to perform MOKE measurement in a pump–probe situation, like the experiments presented here.

Observing the magnetism of the stripes on an ultrafast timescale would be significantly more challenging. It would be difficult to focus an optical beam tightly enough to be able to resolve the stripes which are of the same scale as the wavelength of visible light. The magnetism of the stripes are commonly observed through magnetic force microscopy (MFM). Such measurements cannot, however, be easily performed in a time-resolved manner. Nonetheless, it is important to investigate the dynamics of the magnetic properties of MnAs films on ultrafast timescales if they are to be used for device applications.

The experiments described in this thesis provide insight into the ultrafast dynamics of the solid-to-solid phase transition in MnAs films. It would also be worthwhile to investigate the ultrafast dynamics in other materials. For example, strain plays a role in the phase diagrams of ferroelectric thin films [72], as well as that of certain superconductors [73]. The role of strain may be studied through SHG or other ultrafast optical techniques.
Bibliography


[60] Fujieda, S., Hasegawa, Y., Fujita, A. & Fukamichi, K. Thermal transport properties of magnetic refrigerants La(Fe$_x$Si$_{1-x}$)$_{13}$ and their hydrides, and Gd$_5$Si$_2$Ge$_2$ and MnAs. J. Appl. Phys. 95, 2429–2431 (2004).


