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OPTICAL INVESTIGATIONS OF THE MAGNETIC PROPERTIES OF IRON NANOSTRUCTURES GROWN ON TUNGSTEN(110)

A thesis submitted to
THE UNIVERSITY OF DUBLIN
for the degree of
Doctor in Philosophy

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Trinity College
Dublin 2
Ireland

27th October 2006
DECLARATION

This thesis has been submitted to the University of Dublin for examination for the degree of Doctor of Philosophy by the undersigned.

This thesis has not been submitted as an exercise for a degree to any other university.

The work carried out in this thesis is entirely my own, except where assistance has been acknowledged in the text.

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Lee Carroll 27th October 2006

School of Physics,
University of Dublin,
Trinity College,
Dublin.
The structural and magnetic properties of ultra-thin Fe films and Fe nanostripes grown on vicinal W(110) are studied using Reflectance Anisotropy Spectroscopy (RAS), and the non-linear optic techniques of Second Harmonic Generation (SHG) and Magnetic Second Harmonic Generation (MSHG). Using Au as a capping material, it is possible to transfer the ultra-thin Fe films from the Ultra-high Vacuum (UHV) environment to the ambient laboratory atmosphere without destroying their magnetic properties, thereby allowing both in situ and ex situ investigations to be carried-out. The ex-situ investigations revealed significant MSHG contributions from Au-capped Fe nanostripes just 10 atoms wide (corresponding to a 0.25ML Fe film), thereby demonstrating the extreme magnetic sensitivity of non-linear optic techniques in probing surface magnetism. Measuring the temperature dependence of the MSHG contrast as a function of sample temperature allowed the Curie point of the surface magnetism to be determined, while measuring the MSHG signal as a function of applied field allowed the hysteresis loops of the surface magnetization to be deduced. The Curie point of the Au-capped 1ML Fe film was found to be 320K, indicating that the Au-capping layer significantly increases the Curie point above that of the uncapped Fe film [PRB 40(13)]. The Curie point is 270K for the Au-capped 30 atom-wide Fe nanostripes and 150K for the 10 atom-wide stripes. The hysteresis loop of the 1ML Fe Au-capped film is that of an almost perfectly hard ferromagnet, while those of the Au-capped Fe nanostripes are consistent with soft ferromagnetism. In some instances, the behaviour of the observed MSHG signal is consistent with premise that the surface magnetization varies across the face of the films and nanostripes. Specifically, the behaviour of the MSHG signal indicates that the surface magnetization in the region of the terrace-sites of the Fe nanostripes, $M^T(H,T)$, is not the same as the surface magnetization in the region of the step-sites of the nanostripes, $M^S(H,T)$. Given that the nanostripes are only one atom thick and tens of atoms wide, it does not seem reasonable that they could contain discrete terrace-region and step-region magnetic domains. Instead, it is possible that surface strain, nearest neighbour effects, and dimensionality considerations, produce a difference between the surface magnetization in the region of the mm2 terrace-steps and 1m step-sites.
Acknowledgements

I would like to acknowledge all the support given to me by the staff and students in the Surface and Interface Group of Prof. John F. McGilp over the many years it took to complete this research.

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Relevant publications


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<th>Description</th>
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<tbody>
<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>AOI</td>
<td>Angle-Of-Incidence</td>
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<tr>
<td>CEMS</td>
<td>Conversion Electron Mossbauer Spectroscopy</td>
</tr>
<tr>
<td>DFG</td>
<td>Difference Frequency Generation</td>
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<tr>
<td>HV</td>
<td>High Vacuum</td>
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<tr>
<td>LEED</td>
<td>Low-Energy Electron Diffraction</td>
</tr>
<tr>
<td>LN2</td>
<td>Liquid Nitrogen</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
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<tr>
<td>MOKE</td>
<td>Magneto-Optic Kerr Effect</td>
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<tr>
<td>MSHG</td>
<td>Magnetic Second Harmonic Generation</td>
</tr>
<tr>
<td>NI</td>
<td>Normal-Incidence</td>
</tr>
<tr>
<td>NRSSR</td>
<td>Nuclear Resonant Scattering of Synchrotron Radiation</td>
</tr>
<tr>
<td>OFHC</td>
<td>Oxygen-Free, High-Conductivity</td>
</tr>
<tr>
<td>ON</td>
<td>Off-Normal (incidence)</td>
</tr>
<tr>
<td>OPO</td>
<td>Optical Parametric Oscillator</td>
</tr>
<tr>
<td>PBN</td>
<td>Pyrolitic Boro-Nitrate</td>
</tr>
<tr>
<td>PEM</td>
<td>Photo-Elastic Modulator</td>
</tr>
<tr>
<td>PMT</td>
<td>Photo-Multiplier Tube</td>
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<tr>
<td>RA</td>
<td>Reflectance Anisotropy</td>
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</tr>
<tr>
<td>RI</td>
<td>Refractive Index</td>
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<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
</tr>
<tr>
<td>SP2ES</td>
<td>Spin-polarized 2-Electron Spectroscopy</td>
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<td>SPED</td>
<td>Spin-Polarized Electron Diffraction</td>
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<td>SP-STM</td>
<td>Spin-Polarized Scanning Tunnelling Microscopy</td>
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<td>SRVBPS</td>
<td>Spin-Resolved Valence Band Photoemission Spectroscopy</td>
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<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
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<td>THG</td>
<td>Third Harmonic Generation</td>
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<td>TOM</td>
<td>Torsion Oscillatory Magnetometry</td>
</tr>
<tr>
<td>TSP</td>
<td>Titanium Sublimation Pump</td>
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<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
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<td>UVFS</td>
<td>Ultra-violet Fused Silica</td>
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<td>VASE</td>
<td>Variable Angle Spectroscopic Ellipsometry</td>
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Introduction

1.0 Perspective

Modern international material-science is squarely focused on nanoscale science and technology. Exploiting self-assembly and preparation conditions to manipulate surfaces and interfaces, scientists can now develop designer materials optimised for both technological and research applications. Within the nanoscale research community, there exist a large and growing number of researchers investigating nanoscale magnetism. No doubt, this interest has been motivated, in part, by the successful incorporation of academic research from the field into commercially viable technology. Globally, extensive research is now being carried-out to help better understand the properties of the magnetic clusters, stacks, surfaces, films, nanostripes, and nanowires that will lead to improved technology in the future. Increasingly, the properties of these nanoscale magnetic structures are being investigated using optical techniques, such as Reflectance Anisotropy Spectroscopy (RAS), Magnet-Optical Kerr Effect (MOKE) and Magnetic Second-Harmonic Generation (MSHG). Unlike tradition electron spectroscopies, these optical probes can continuously monitor the properties of these future nanoscale magnetic devices, from their initial preparation in the Ultra-High Vacuum (UHV) environment, to their final ambient technological application.
1.1 Magnetism in ultra-thin films

Observations of ferromagnetism date-back to antiquity, but it is often forgotten that many other types of bulk magnetism were discovered comparatively recently. Antiferromagnetism was first experimentally observed in 1939[1], ferrimagnetism in 1951[2], and helimagnetism as recently as 1959[3]. Today's students of nanoscale magnetism should take a moment to reflect on this - new types of bulk magnetism were probably still being discovered while their supervisors were students. The discovery of several different types of magnetism in the early half of the 20th century was no coincidence; their discovery coincided with the advent of quantum physics, and with it, the concept of spin. Using this notion of quantum-spin, theoreticians could, for the first time, model experimental observations that had stubbornly resisted classical analysis for years. From these models, came suggestions for further experiments, and from these experiments came new data to further test the models. This constant feedback between newly developing theory and experimental observations resulted in an explosion of new and profound insights into the field of magnetism - the era of modern magnetism had been born.

In 1968, the effect of antiferromagnetism was observed in the Low-Energy Electron Diffraction (LEED) pattern of the NiO(100) surface[4]. Since the mean-free path of the electrons is less than 1nm in NiO, the antiferromagnetism evident in the LEED image must exist in the top three or four atomic layers of the surface – the first observation of nanoscale magnetism had been made. Ferromagnetic surface magnetism studies of Fe, Co, Ni and other rare-earth metals soon followed, exploiting the phenomenon of spin polarization of field-emitted electrons from the surface[5]. In addition to studying the surfaces of magnetic crystals, contemporary advances in surface science permitted scientists to prepare their own clean and well-characterised magnetic surfaces, by depositing ultra-thin ferromagnetic films onto non-magnetic substrates[6]. With this approach, it has been possible for the dependence between surface-magnetization and ultra-thin film thicknesses to be determined[7, 8]. Such studies have revealed oscillatory behaviour, never before observed. The use of different planar, vicinal, and facetted surfaces as the non-magnetic substrates for film growth, allowed the effects of long-
range order in surface-magnetism to be investigated[7, 9-12]. In particular, it was discovered that sub-monolayer deposition of ferromagnetic material onto a vicinal substrate, followed by annealing, can lead to the formation of nanostripes of ferromagnetic material[13]. Very recent studies have even shown that single-atom chains of Co grown in this way on the Pt(997) surface are ferromagnetic[14-16]. Studies have also demonstrated that the behaviour of the nanoscale surface magnetism can be modified very significantly, by depositing a non-magnetic film on top of the ferromagnetic film[17-19]. The composition and thickness of this capping-layer often has an important impact on the behaviour of the underlying ferromagnetic film[20].

In investigations of magnetism in ultra-thin films, many combinations of ferromagnetic films and non-magnetic substrates have been investigated. Some particular combinations have emerged as model systems for investigation, because of their thermodynamic stability and rich magnetic behaviour. Perhaps the most extensively studied ultra-thin film system is that of Fe on W(110). The magnetic properties of ultra-thin Fe films grown on the W(110) surface have been investigated since the 1980s, using a variety of techniques including Conversion-Electron Mossbauer Spectroscopy (CEMS)[21]; Torsion Oscillatory Magnetometry (TOM) [22]; Spin-Polarized Electron Diffraction (SPED)[18, 23]; Scanning Tunnelling Microscopy (STM)[24, 25]; MOKE[13, 24, 26, 27]; Spin-Polarized Scanning Tunnelling Microscopy(SP-STM)[28]; Spin-Resolved Valence-Band Photoemission Spectroscopy (SRVBPS)[29]; Nuclear Resonant Scattering of Synchrotron Radiation (NRSSR)[30]; and Spin-Polarized 2-Electron Spectroscopy (SP2ES)[31]. Recent computational and theoretical investigations of the magnetic behaviour in ultra-thin Fe films on the W(110) surface have been equally extensive. Some models successfully predicting the experimentally observed effects include *ab-initio* full-potential linear muffin-tin orbital calculations[32]; the tight-binding method with Hartree-Fock approximation within the Hubbard Hamiltonian[33]; spin excitations studied using a nine band itinerant model[34, 35]; and local density functional calculations[36]. These parallel investigations, of both theory and experiment, have given rise to a large volume of high-quality and detailed scientific literature, describing the magnetic properties of the Fe W(110) interface.
Naturally, not all of the information regarding the Fe W(110) interface available from these studies is relevant to the optical investigations carried out in this thesis. The following is a brief summary of the most important properties of the Fe W(110) interface:

1. After suitable annealing to 800K, well-ordered pseudomorphic films are formed by the deposition of Fe onto the planar or vicinal W(110) surface, up to 2 Mono-Layers (ML)[13].
2. When Fe is deposited and annealed on a vicinal W(110) surface, with surface-steps running in the $<$110$>$ direction, step-flow growth is not observed and poorly aligned Fe nanostripes are formed[37].
3. When Fe is deposited and annealed on a vicinal W(110) surface, with surface-steps running in the $<$001$>$ direction, step-flow growth is observed and Fe mono-atomic height nanostripes are formed[13].
4. Fe nanostripes formed on this vicinal W(110) surface (with surface-steps running in the $<$001$>$ direction) are ferromagnetic and exhibit uniaxial magnetic anisotropy with an easy axis in the film-plane, along the $<$110$>$ direction[13, 25, 27].
5. Each of the Fe nanostripes grown on this vicinal W(110) surface is divided into “full stripe width spin-blocks with alternating sign of magnetization, and a length which continuously increases with decreasing temperature’[13].
6. It is principally the exchange interaction between these spin-blocks that results in the ferromagnetic-state of the nanostripes[13].
7. Fe films between 1.2ML and 1.48ML thick, formed on the vicinal W(110) surface, with surface-steps running in the $<$001$>$ direction, have an out-of-plane easy axis in the $<$110$>$ direction[24].
8. Modern micro-magnetic calculations predict this change in easy axis orientation as the result of exchange interaction between the 1st pseudomorphic Fe(110) layer and the double-layer stripes.
9. The Curie point of the ultra-thin Fe films grown on both planar and vicinal W(110) surfaces increases with the thickness of the film[18, 23].
10. The Curie-point of the underlying ultra-thin Fe films grown on both planar and vicinal W(110) surfaces are modified by the epitaxial adsorption of non-magnetic material[18, 21, 25].

11. Certain capping materials may even change the direction of the easy axis for the underlying ultra-thin Fe films[38].

1.2 Linear optical analysis of ultra-thin films

Using ellipsometry, Drude pioneered the optical investigations of ultra-thin films, in the mid 19th century. Modern Variable-Angle Spectroscopic Ellipsometry (VASE) is now a well-established linear optic technique, used extensively by both industry and research groups to determine the dielectric function and thickness of optically thin films, most notably in the field of semiconductor research[39-41]. Although VASE has exhibited monolayer sensitivity in very special cases[42], it is not an inherently surface-sensitive technique, and therefore has limited relevance when applied to the study of ultra-thin films. Elementary calculations show that VASE measurements are very unlikely to detect the presence of an ultra-thin Fe film, sandwiched between a metallic capping layer, and W(110) substrate. Given these limitations, the role of VASE in the analysis of capped ultra-thin films is modest. VASE measurements are used to determine the thickness and dielectric function of the capping layer. These measurements, even when only approximate, are useful aids in the interpretation of RAS results.

Like VASE, RAS is a spectroscopic linear optic technique that is used extensively to characterize surfaces and interfaces[43-45]. While VASE is essentially a bulk sensitive technique, RAS exhibits a high degree of surface sensitivity. Using the Aspnes-type RAS geometry, it is routinely possible to measure the optical anisotropy of a surface to better than one-part in a thousand[46]. The high-sensitivity of this geometry is realized through the application of a lock-in technique, and the absence of moving parts in the geometry. RAS is so sensitive that it has proven capable of measuring the differences in optical anisotropies between different low-index faces of the same crystal[47]; detecting step-induced anisotropy of vicinal surfaces[48]; and detecting the deposition of sub-monolayer films on surfaces[49, 50]. In a laboratory where non-linear optic techniques
are also used, RAS spectra have another use – they provide an indication of the energy at which SHG measurements should first be made. The reasoning behind this approach is the expectation of an equivalence between large linear optic anisotropies and large non-linear optic anisotropies, as suggested by the Miller relation[51, 52].

In principle, both VASE and RAS can be used to make Spectroscopic MOKE measurements from ferromagnetic samples. However, due to its lack of surface sensitivity, VASE-MOKE measurements are typically only successful when significant bulk ferromagnetism exists in the sample. For planar surfaces, it is easily shown that first-order RAS-MOKE measurements can only be made when the ultra-thin film under investigation exhibits a polar magnetization[53]. In principle, when sub-monolayer films are grown on a vicinal surface, the nanostripes may exhibit first-order RAS-MOKE signals for both polar magnetization and in-plane magnetization perpendicular to the steps, but, for the case of in-plane magnetization, the RAS-MOKE signal is expected to be very small, scaling as the tangent of the vicinal off-cut.

Instead of modifying techniques such as VASE and RAS to make MOKE measurements, custom experimental geometries are normally employed to investigate the magnetic properties of ultra-thin films. The principle behind these MOKE geometries differs little to those originally used by Kerr in the late 19th century. However, the combinations of modern modulated laser light-sources, semi-conductor photodiode detectors, and digital lock-in techniques, have massively boosted the sensitivity of today’s MOKE measurements. Contemporary MOKE measurements can now measure the magnetization of sub-monolayer ferromagnetic films[13]. It must be remembered, however, that MOKE is not a surface sensitive optical probe – it only achieves these high surface sensitivities when the ferromagnetic films are grown on non-magnetic substrates. In addition to measuring hysteresis, MOKE can be used to determine the Curie point of ultra-thin films, and to investigate their magnetic critical behaviour[26]. MOKE measurements have even been employed to investigate the effect of vicinal surfaces on the magnetic properties of ultra-thin films [9-12]. While these investigations have demonstrated that variations in surface step-density play an important role in the behaviour of surface-magnetism, they have not uniquely identified
the individual parts played by the step- and terrace-site contributions to the surface-magnetization of the ultra-thin films. To make such a determination, it is necessary to use a non-linear optical analysis, such as Second Harmonic Generation, where the increased number of tensor elements associated with a full description of such a high-order process permits the unambiguous separation of step- and terrace contributions.

1.3 Non-linear optical analysis of ultra-thin films

In 1754, the Italian composer and violinist Giuseppe Tartini published the treatise, *Trattato di musica secondo la vera scienza dell’armonia*, on the subject of music theory. This treatise contains the first known recorded observation of the non-linear harmonic-mixing of waves. Lord Rayleigh, in *The Theory of Sound*, elegantly summarizes this observation of Tartini:

"If two notes, at the interval for example of a Major Third, be sounded together strongly, there is heard a grave sound in addition to the two others. In the case specified, where the primary sounds, or generators, as they may conveniently be called, are represented by the numbers 4 and 5, the combination-tone is represented by 1”

Today, the phenomenon observed by Tartini is recognized as an acoustic example of Difference Frequency Generation (DFG) – just one of many second-order non-linear processes now known to occur. In this example, the DFG occurs because the vibrating parts of the ear are driven past their elastic limit by the strongly sounded tuning forks, causing the tissue to vibrate at frequencies other than those of the forks. In the classic undergraduate optics text, *Concepts of classical optics*, published in 1958, the author J. Strong[54] remarks that the phenomenon of harmonic-mixing “represents a complexity from which we are happily free in optics”. Unfortunately, this happy situation was not to last - the first observation of optical Second Harmonic Generation (SHG) was made just three years later[55]. Unsurprisingly, this observation of SHG coincides with the invention of the laser. For although a strongly sounded tuning fork may provide sound waves of sufficient amplitude to drive the human ear into a non-linear response, it is
only with the huge intensities available with laser-light that analogous non-linear optical behaviour can be observed. Within a short period, of the laser's invention, observations of optical DFG, sum frequency generation (SFG), and third harmonic generation (THG) were also reported[55].

Early investigations of optical SHG were conducted using uniaxial birefringent crystals such as KDP. With these crystals it is possible to set-up phase-matching conditions that result in a very high conversion-efficiency of fundamental photons to SH photons. The same is not true of centrosymmetric crystals, where inversion symmetry prohibits electric-dipole contributions to SHG, permitting only the weaker electric-quadrupole contribution to be made[56]. While this is a disadvantage to those interested in producing very high SHG signals, it is a great boon to surface scientists. At the surface, the inversion symmetry of the centrosymmetric crystal is broken, permitting electric-dipole contributions to the SHG signal from this region. The total SHG signal from a centrosymmetric crystal is therefore composed of the coherent superposition of a strong electric-dipole contribution from the surface region, and a weak electric-quadrupole contribution from the bulk. Unfortunately, because the volume of the surface region is far smaller than the bulk-region probed by optical radiation, there is no guarantee that the surface contribution is dominant in the measured SHG signal. However, for metal surfaces, the screening effects are often strong enough to guarantee that the bulk contribution is indeed small.

The surface sensitivity of SHG from centrosymmetric materials is now well established, having been first demonstrated over twenty years ago[57]. SHG has proven itself sensitive enough to detect the deposition of ultra-thin films[58, 59]; the adsorption of gases[59]; different surface reconstructions of semiconductors[60]; and step-induced anisotropy on vicinal surfaces[61]. Detailed phenomenological models have been developed dealing with the surface electric-dipole and bulk electric-quadrupole contributions to the SHG signal from planar and vicinal cubic centrosymmetric crystals[56, 60, 62-64]. These models show that the use of vicinal surfaces can help the surface and bulk contributions to be identified. As a result, SHG investigations are often carried-out on vicinal surfaces. Performing these at Normal-Incidence (NI) greatly
enhances the sensitivity of SHG to the step-induced anisotropies of the vicinal surface, since it is easily shown that the SHG signal measured in the NI geometry is composed of approximately equal coherent contributions from the step- and terrace-sites of the surface. Because it is a high-order optical process, the full phenomenological models describing SHG from centrosymmetric crystals are necessarily highly detailed, dealing with transformations of third- and fourth-order optical susceptibility tensors. Even with the help of the symmetry relations and Fourier analysis provided in these detailed models, it is often difficult to extract quantitative information from SHG data, without performing a great many independent measurements, using different polarization and azimuthal alignments, and different angles of incidence. These difficulties have encouraged the development of simplified bond-hyperpolarizability models of SHG, where simple assumptions about the non-linear polarizability of bonds allows a radical simplification in the interpretation of results to be made[51, 52]. Although these models have proved successful in describing the SHG signal from some surfaces, there is mounting evidence that they lack the scope to be generally applicable[65].

The fact that the magnetization of a centrosymmetric crystal induces additional electric-dipole contributions to the SHG signal at the surface, while leaving those of the bulk unchanged, was first recognized in 1987[66]. Theoretical models indicating that these magnetization-induced surface electric-dipole contributions were sufficiently large to observe experimentally soon followed[67]. In fact, these calculations showed that the magnitude of these magnetization-induced terms are up to 10% that of the non-magnetic crystallographic terms. This figure is approximately three orders of magnitude greater than that observed in the linear magneto-optic response of surfaces. Experimental observations of MSHG soon followed, from the surface of magnetic crystals[68]; ultra-thin films on non-magnetic substrates[69]; capped ultra-thin films[70-72]; and magnetic multilayers[73]. These observations confirmed the predicted ratio of magnetization-induced terms and crystallographic terms, verifying that extremely large Kerr rotations in the non-linear response do, in fact, occur. Not only did MSHG investigations confirm existing observations regarding surface magnetization, they soon began to uncover new and exciting magnetic behaviour in ultra-thin films, as has been reviewed by Rasing[74] and Kirilyuk[75]. Often, these discoveries were made from samples composed of
capped ultra-thin films of ferromagnetic material grown on a non-magnetic substrate. Such samples are resistant to electron spectroscopy investigations, because of the very short mean free-path associated with electrons in the condensed matter of the cap. Before the advent of MSHG, the magnetic properties of these capped ultra-thin films could only be investigated with MOKE, but, as has already been mentioned, this linear optic technique lacks true surface sensitivity. Phenomenological models of MSHG have already been developed for simple surfaces[76]. But, as yet, no model describing the MSHG from ultra-thin films grown on vicinal substrates has been published.

1.4 Motivations for Epioptic investigations of Fe on W(110)

The crystallographic and magnetic properties of capped and uncapped ultra-thin Fe films grown on the vicinal W(110) surface are well-studied, using a variety of techniques. As a result, the interfaces represent an ideal experimental platform on which to perform a range of new Epioptic [77] investigations:

- RAS measurements of the clean vicinal W(110) surface will complement existing RAS measurements of the clean planar W(110) surface[78], thereby allowing the effect of the surface steps on the surface optical anisotropy to be determined.
- RAS investigations of Fe nanostripes grown on the vicinal W(110) surface will also determine if the nanostripes have an optical anisotropy signal that depends in well-defined manner on the stripe width. The observation of such a ‘finger-print’ would be very useful for future work, where it would allow an optical determination of Fe film thickness.
- Normal incidence (NI) SHG measurements of the clean vicinal W(110) surface will determine if a well-defined 1m non-linear hyper-polarizability is associated with surface steps.
- NI SHG measurements of Fe nanostripes grown on the vicinal W(110) surface will determine if a well-defined 1m non-linear hyper-polarizability is associated with the stripes, and if this hyper-polarizability depends sensitively on the stripe width.
• The regularity of the well-defined Fe nanostripes grown on the vicinal W(110) surface motivate the development of a new phenomenological MSHG model to accommodate the different MSHG contributions made by the 1m step-sites and mm2 terrace-sites regions of the stripes.

• Because of the step-flow growth exhibited by the Fe nanostripes on the vicinal W(110) surface, stripes of between 40 atoms and 1 atom in width can be grown. Access to such narrow nanostripes, approaching nanowires, will test the practical limits of MSHG as a tool for probing surface magnetism.

• Monitoring the MSHG signal of the Fe nanostripes as a function of temperature will allow their Curie point to be determined. If the Curie point for a range of different nanostripes is measured in this way, then it can be determined if their Curie point varies monotonically with stripe width, or exhibits oscillatory behaviour[79].

• Monitoring the MSHG signal of the Fe nanostripes as a function of applied magnetic field will allow their hysteresis loops to be determined. The shape of these hysteresis loops will make it possible to determine if the nanostripes are ferromagnetic or super-paramagnetic.


Non-linear optic analysis

2.0 Overview

A simple phenomenological model describing the MSHG contribution to the SHG-signal from ultra-thin ferromagnetic films and nanostripes grown on a vicinal surface is developed. This model breaks-down the contributions made by the mm2 terrace-sites and lm step-sites of the films and nanostripes to the overall SHG-signal. The model is applied to common SHG experimental geometries, providing a framework with which experimental MSHG results may be interpreted. It is shown that the temperature dependence of the MSHG contrast may be proportional to the temperature dependence of the surface magnetization. Different approaches to extracting the crystallographic and magnetization-induced electric-field contributions to the SHG signal are investigated. A new approach to extracting the surface magnetism hysteresis loops from MSHG data is developed. Simulations are developed that predict 1) The temperature dependence of the MSHG contrast; 2) The MSHG-derived hysteresis loops; from films and nanostripes exhibiting a surface magnetization gradient across their faces.
2.1 Phenomenology of SHG

When it is incident at an optical material, the oscillating electric-field \( E \) of EM radiation induces an oscillating polarization \( P \) in that material. \( P \) acts both as the source of further transmission of \( E \) into deeper layers of the material, and as the source of the EM radiation reflected from the surface layers. When the magnitude of \( E \) is modest, a linearity between \( E \) and \( P \) is observed. However, when the magnitude of \( E \) is very great, the electronic-configuration of the material cannot rearrange itself sufficiently to maintain the linearity between \( P \) and \( E \). At these high intensities, \( P \) becomes a non-linear function of \( E \). It is quite simple to infer some important properties regarding \( P \) without knowing the exact details of the divergence from linearity.

Assuming monochromatic, linearly polarized EM radiation, and applying a Taylor expansion we have:

\[
P(E) = aE + bE^2 + cE^3 + ...
\]

\[
P(E) = a\left(E_0 \cos \omega t\right) + b\left(E_0 \cos \omega t\right)^2 + c\left(E_0 \cos \omega t\right)^3 + ...
\]

\[
P(E) = P(0; t) + P(\omega; t) + P(2\omega; t) + P(3\omega; t) + ...
\]

\[
P(0; t) = \left\{ \frac{b}{2} E_0^2 + \ldots \right\}
\]

\[
P(\omega; t) = \cos \omega t \left\{ aE_0 + \frac{3c}{2} E_0^3 + \ldots \right\}
\]

Where:

\[
P(2\omega; t) = \cos 2\omega t \left\{ \frac{b}{2} E_0^2 + \ldots \right\}
\]

\[
P(3\omega; t) = \cos 3\omega t \left\{ \frac{c}{2} E_0^3 + \ldots \right\}
\]

It is apparent from this expansion that components of \( P \) oscillate, not only at the frequency of the incident EM radiation, but also at integer harmonics of that frequency. It is clear that the magnitude of these harmonics scales as integer powers of the magnitude of \( E \); odd harmonics as odd powers of \( E \), even harmonics as even powers of \( E \). Although this Taylor expansion demonstrates the general behaviour of \( P \), for high magnitude of \( E \), it does not provide any insight into the physical origin of the effect.

Shen[1] applies a rigorous classical treatment to the problem of non-linear polarization,
using a perturbation expansion of a second-order non-linear harmonic-oscillator. From this analysis, the electric-dipole second-harmonic (SH) $P$ can be deduced in terms of the properties of the oscillator:

$$P(2\omega; t) = \frac{-Naq^3 E_0^2 e^{-2\omega t}}{m^2 (\omega_0^2 - \omega^2 - \omega^2 - 4\omega^2 - i2\omega\Gamma)}$$  \hspace{1cm} E2.1.5

Where the standard naming conventions used in E2.1.5 are explained in reference [1]. In addition to verifying the proportionality of $P(2\omega; t)$ to the square of the magnitude of $E$, predicted by the Taylor expansion, the analysis of Shen reveals the dispersion of the SH response. It is clear that the magnitude of $P(2\omega; t)$ may become very large when the frequency of the EM radiation is close to a resonant frequency of the system. This phenomenon is known as resonant enhancement and is often exploited in experimental observations of SHG.

To analyse the properties of $P(2\omega; t)$ in single crystals, it is insufficient to consider only the number-density ($N$) of the oscillator sites contributing to the polarization - the spatial orientation of these sites must also be taken into account. This is achieved by substituting the scalar $N$ with $\tilde{N}$, a tensor containing, in some way, information regarding the symmetry-class of the crystal. In a widely held convention, the dispersion terms in E2.1.5 are convolved into $\tilde{N}$, to form another tensor $\gamma^c(2\omega)$, designated the crystallographic electric-dipole second-harmonic susceptibility tensor. Using dyadic multiplication, the $P(2\omega; t)$ induced in a crystal can then be expressed in the following shorthand expression:

$$P(2\omega; t) = \gamma^c(2\omega) \cdot E(\omega; t)E(\omega; t)$$  \hspace{1cm} E2.1.6

Alternatively, and perhaps more usefully, $P(2\omega; t)$ can be expressed using the assumed-summation notation:

$$P_j(2\omega; t) = \chi_{ij}^c(2\omega)E_j(\omega, t)E_i(\omega, t)$$  \hspace{1cm} E2.1.7
The number and type of symmetry operations \( (\Sigma^{(n)}) \) supported by the point-group of a crystal determine the number of independent non-zero elements in \( \chi^{C}(2\omega) \). Neumann's principle requires all properties of a crystallographic system to share, at the very minimum, all of the symmetry operations of the crystal itself. Consequently each tensor element of \( \chi^{C}(2\omega) \) must satisfy the following condition:

\[
\Sigma^{(n)} \circ \chi_{ijk}^{C} = \chi_{ijk}^{C}
\]

E2.1.8

Where:

\[
\Sigma^{(n)} \circ \chi_{ijk}^{C} = T_{ii'}^{(n)} T_{jj'}^{(n)} T_{kk'}^{(n)} \chi_{i'j'k'}^{C}
\]

E2.1.9

\( T_{ii'}^{(n)} \) being elements of the axial transformation-matrix of the symmetry operation \( \Sigma^{(n)} \).

Frequently, E2.1.9 is only satisfied when \( \chi_{ijk}^{C} = 0 \). In this instance, the element \( \chi_{ijk}^{C} \) is said to be symmetry-forbidden. Since the crystal bulk and surface support different symmetry operations, they will have different numbers of such symmetry forbidden elements. It is readily demonstrated that \( \chi_{ijk}^{C} = 0 \) \( \forall \ i, j & k \) for the crystal bulk-region of centrosymmetric species. This is the origin of the surface sensitivity of SHG - no electric-dipole \( P(2\omega) \) originates from the bulk region of centrosymmetric crystal, but at the surface or interface, where the inversion-symmetry is broken, electric dipole contributions are permitted. In addition to the symmetry-conditions imposed on \( \chi^{C}(2\omega) \) by the point-group of the surface, electric-dipole SHG has an internal symmetry giving \( \chi_{ijk}^{C} = \chi_{ikj}^{C} \), and further reducing the number of independent tensor elements in \( \chi^{C}(2\omega) \). When it can be applied, Kleinmann symmetry may also reduce the number of independent tensor elements in \( \chi^{C}(2\omega) \).

### 2.2 Phenomenology of MSHG

When an applied-field \( H \) causes the magnetization \( (M(H)) \) of a crystal, additional contributions to \( P(2\omega) \) may be induced. These magnetization-induced contributions are governed by \( \chi^{M}(2\omega) \), the magnetization-induced electric-dipole second-harmonic
susceptibility tensor. The total \( P(2\omega) \) from the magnetized crystal is given by the linear superposition of the crystallographic and the magnetization-induced contributions:

\[
P(2\omega; t, M(H)) = \chi^C(2\omega): E(\omega; t)E(\omega; t) + \chi^M(2\omega): E(\omega; t)M(H)
\]

\[P(2\omega; t, M_L(H)) = \chi^C(2\omega)E_j(\omega; t)E_k(\omega; t) + \chi^M(2\omega)E_j(\omega; t)E_k(\omega; t)M_L(H)
\]

Like the elements of \( \chi^C(2\omega) \), the elements of \( \chi^M(2\omega) \) must satisfy the symmetry conditions asserted by Neumann’s principle. Because \( \chi^M(2\omega) \) depends on \( M \), a polar vector, the application of symmetry conditions to \( \chi^M(2\omega) \) is slightly different to the application to \( \chi^C(2\omega) \):

\[
\Sigma^{(n)} \chi^M_{ijkl} = \chi^M_{ijkl}
\]

Where:

\[
\Sigma^{(n)} \chi^C_{ijkl} = T^{(n)}_{ii'} T^{(n)}_{jj'} T^{(n)}_{kk'} S^{(n)}_{LL'} \chi^C_{i'j'k'L'}
\]

Here, \( T^{(n)}_{ii'} \) are elements of the axial transformation-matrix of the symmetry operation \( \Sigma^{(n)} \), while \( S^{(n)}_{LL'} \) are elements of the polar transformation-matrix of the same operation, \( \Sigma^{(n)} \). For a given symmetry operation, the axial and polar transformation-matrices are different. For example, the axial and polar transformation matrices for the mirror-plane operation \( \sigma_x \) are given by:

\[
\bar{T}(\sigma_x) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \bar{S}(\sigma_x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}
\]

For the bulk region of centrosymmetric crystal, \( \chi^M_{ijkl} = 0 \ \forall \ i, j, k & L \). This is the origin of the surface sensitivity of MSHG - no magnetization-induced electric-dipole contributions to \( P(2\omega) \) originate from the bulk region of centrosymmetric crystal, even when it is magnetized. At the surface or interface, where the inversion-symmetry is broken, both magnetization-induced and crystallographic electric dipole contributions
are permitted. Typically, the ratio of the magnetization-induced tensor elements to the crystallographic tensor elements, is 10%[2].

2.3 MSHG tensor elements of the vicinal surface

Broadly speaking, a semi-infinite crystal is composed of two regions - the bulk and the surface. If its surface-normal is close to a low-order Miller-plane, then the crystal is said to have a vicinal surface. Such a vicinal surface is often composed of regular arrays of atomic-steps separated by surface-terraces. In general, the bulk, terrace, and step regions of a crystal support different point-groups, implying that any process governed by a tensor (\(\mathcal{T}\)), behaves differently in the bulk (\(\mathcal{T}_b\)), terrace (\(\mathcal{T}_t\)), and step (\(\mathcal{T}_s\)) regions.

For the case of the vicinal BCC crystal illustrated in F2.3.1, the point-groups and relevant symmetry operations are given T2.3.1.

![Figure F2.3.1: Schematic of the vicinal surface of a crystal, with an off-cut of \(\alpha\), shown with both the surface (\(K\)) and optic (\(K'\)) co-ordinate systems](image)

---

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Table T2.3.1: Point-group and symmetry operations supported by the different regions of a vicinal BCC crystal

<table>
<thead>
<tr>
<th>Region</th>
<th>Point-group</th>
<th>Symmetry operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal bulk</td>
<td>43m</td>
<td>$\sigma_x, \sigma_y, \sigma_z$</td>
</tr>
<tr>
<td>Surface terraces</td>
<td>mm2</td>
<td>$\sigma_x, \sigma_y$</td>
</tr>
<tr>
<td>Surface steps</td>
<td>1m</td>
<td>$\sigma_y$</td>
</tr>
</tbody>
</table>

The non-zero elements of the crystallographic tensors $\gamma^C_S$ and $\gamma^C_T$ are given in table T2.3.2, and the non-zero elements of the magnetization-induced tensors $\gamma^M_S$ and $\gamma^M_T$ are given in table T2.3.3 (as previously discussed, $\gamma^C_B = \gamma^M_B = 0$). To aid clarity of later formulations, each element of $\chi^C_{ijk} = ijk$ is assigned a unique upper-case letter of the Roman alphabet, while each elements of $\chi^M_{ijkl} = ijkL$ is assigned a unique lower-case letter. Each tensor element is suffixed with a superscript, denoting either terrace ($T$) or step ($S$) origination.

Table T2.3.2: Non-zero elements of $\gamma^C_S$ and $\gamma^C_T$ and the naming convention of their elements

<table>
<thead>
<tr>
<th>$\gamma^C_S$</th>
<th>xxx=$A^S$, xyy=$B^S$, xzz=$C^S$, xzx=xxx=$D^S$, yyz=yyz=E^S, yxy=yyx=F^S, zxx=zzz=$G^S$, zyx=zzz=$H^S$, zzz=zzz=$I^S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma^C_T$</td>
<td>xzx=xxz=$D^T$, yyz=yyz=$E^T$, xzx=xxz=$G^T$, zyy=zzz=$H^T$, zzz=zzz=$I^T$</td>
</tr>
</tbody>
</table>
Table T2.3.3: Non-zero elements of $\mathbf{T}^M_s$ and $\mathbf{T}^M_t$ and the naming convention of their elements

| $\mathbf{T}^M_s$ | $M_0$ | $xyzX=xyzX=d^s$, $xxyX=xyxX=g^s$, $yxxX=f^s$, $yyxX=k^s$, $yzyX=m^s$, $yzxX=yzxX=p^s$, $zzyX=zzyX=v^s$, $zxyX=zxyX=w^s$, $xzyX=xzyX=w^s$ |
| $M_1$ | $xxxX=xxX=a^t$, $xxyX=xxyX=b^t$, $xzyX=xzyX=c^t$, $yyxX=yyX=f^t$, $yyzX=yyzX=g^t$, $yyyX=k^t$, $zzxX=zzX=s^t$, $zzyX=zzzX=r^t$, $zzzX=zzzX=q^t$, $zzyX=zzyX=p^t$, $zzyX=zzyX=t^t$, $zxyX=zxyX=q^t$, $zzyX=zzyX=t^t$, $zzyX=zzyX=p^t$ |

$\mathbf{T}^M_t$

| $M_0$ | $xyxX=xyxX=f^t$, $yxzX=yxzX=g^t$, $yyzX=yyzX=h^t$, $yzyX=i^t$, $yyzX=yyzX=g^t$, $yyyX=k^t$, $zzxX=zzxX=q^t$, $zzzX=zzzX=r^t$, $zzzX=zzzX=q^t$, $zzyX=zzyX=p^t$, $zzyX=zzyX=t^t$, $zzyX=zzyX=p^t$, $zzyX=zzyX=t^t$, $zzyX=zzyX=p^t$ |

The wavelength of light is far greater than the width of an individual terrace, meaning that individual steps and terraces cannot be probed. This fact is important for two reasons; firstly, the SHG signal observed from the vicinal surface will depend on the coherent superposition of $\mathbf{T}_s^C$ and $\mathbf{T}_t^C$; secondly, the reflection of light from the vicinal surface occurs from the gross surface-plane, not the atomically flat terrace-plane. To deduce the observed crystallographic electric-dipole second-harmonic susceptibility tensor ($\mathbf{T}_o^C$), it is necessary to transform the superposition of $\mathbf{T}_s^C$ and $\mathbf{T}_t^C$ from the surface co-ordinate system (K) to the optic co-ordinate systems (K'):

$$\mathbf{T}_o^C = \mathbf{T}(K \rightarrow K') \circ (\mathbf{T}_s^C + \mathbf{T}_t^C)$$  \hspace{1cm} E2.3.1

Where:

$$\mathbf{T}(K \rightarrow K') = \begin{pmatrix} 1 & \alpha & 0 \\ -\alpha & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$  \hspace{1cm} E2.3.2

Both K and K' are illustrated in F2.3.1. If the surface magnetization is constant across the entire film or nanostripe, then E2.3.1 may be applied to the magnetization-induced electric-dipole second-harmonic susceptibility tensor ($\mathbf{T}_o^M$)
However, if a variation in the surface magnetization exists across the film or nanostripe, such that the surface magnetization in the region of the mm\textsuperscript{2} terrace-sites, $M^T$, is different to that of the surface magnetization in the region of the lm step-sites, $M^S$, then $\gamma^M_o \neq \tilde{T}(K \rightarrow K') \circ (\gamma^M_S + \gamma^M_T) M$, and it is necessary to include the contributions of $M^T$ and $M^S$ separately:

$$\gamma^M_o M^o = \tilde{T} \circ (\gamma^M_S M^S + \gamma^M_T M^T)$$

Such a gradient in the surface magnetization might occur for several reasons. For the case of pseudomorphic nanostripes, spatial variation in the magnetization could arise from\[3\]:

1) The reduced co-ordination of the ferromagnetic atoms at the edge of the stripe (lm) with respect to those at the centre of the stripe (mm\textsuperscript{2})

2) The different stresses experienced by the ferromagnetic atoms at the edge of the stripe with respect to those at the centre of the stripe.

3) The different dimensionality of the ferromagnetic atoms at the edge of the stripe (quasi-1D) and at the centre of the stripe (2D).

In fact, there are two distinct edges to each pseudomorphic nanostripe; the edge in contact with the step-site of the substrate from which the step-flow growth progresses, and the edge that grows out onto the terrace of the substrate. However, since both edges share the same lm symmetry, it is not possible to distinguish between their different contributions using MSHG. The observed surface magnetization in the region of the lm step-sites, $M^S$, is an intractable superposition of these two contributions,
The non-zero elements of \( \gamma^C \), and their dependence on the elements of \( \gamma^S \) and \( \gamma^T \) are given in table T2.3.4, while the non-zero elements of \( \gamma^M M^O \), and their dependence on \( \gamma^M M^S \) and \( \gamma^M M^T \) are given in table T2.3.5.

**Table T2.3.4: Non-zero elements of \( \gamma^C \) and their relationship to the elements of \( \gamma^S \) and \( \gamma^T \)**

<table>
<thead>
<tr>
<th>( \gamma^C )</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( A = A^S + \alpha(2D^S + G^S + 2D^T + G^T) )</td>
</tr>
<tr>
<td>B</td>
<td>( B = B^S + \alpha(H^S + H^T) )</td>
</tr>
<tr>
<td>C</td>
<td>( C = C^S + \alpha(-2D^S + f^S - 2D^T + I^T) )</td>
</tr>
<tr>
<td>D</td>
<td>( D = D^S + \alpha(-A^S + C^S + f) + D^T )</td>
</tr>
<tr>
<td>E</td>
<td>( E = E^S + \alpha f^S + E^T )</td>
</tr>
<tr>
<td>F</td>
<td>( F = F^S + \alpha(E^S + E^T) )</td>
</tr>
<tr>
<td>G</td>
<td>( G = G^S + \alpha(-A^S + 2f^S) + G^T )</td>
</tr>
<tr>
<td>H</td>
<td>( H = H^S - \alpha B^S + H^T )</td>
</tr>
<tr>
<td>I</td>
<td>( I = I^S + \alpha(-2f^S - C^S) + I^T )</td>
</tr>
<tr>
<td>J</td>
<td>( J = J^S + \alpha(-D^S - G^S + f^S - D^T + G^T + I^T) )</td>
</tr>
</tbody>
</table>

In addition to changing the value of observed tensor elements through a rotation of the co-ordinate system, the off-cut, \( \alpha \), also plays a role in determining the relative-population of the step- and terrace-sites at the vicinal surface[4]. Where \( \alpha \) is small and measured in radians, the number of step-sites scales as \( \alpha \), while the number of terrace sites scales as \( (1 - \alpha) \), Therefore, the ratio of step- to terrace-sites scales approximately as \( \alpha \). This is an important factor in determining the relative step- and terrace-site contributions to \( \gamma^C \) and \( \gamma^M M^O \). For example, accounting for the relative populations of the step- and terrace-sites, \( \gamma^C = (\alpha \gamma^S + \gamma^T) \). This means that significant step-site contributions to the SHG signal will only be observed in an experimental geometry in which the terrace-site contributions are somehow reduced by a factor comparable to \( \alpha \)-factor. Fortunately, such geometries exist; the simplest example being the polarization-rotation geometry in the NI-geometry.
<table>
<thead>
<tr>
<th>Table T2.3.5: Non-zero elements of $\gamma^M o M^o$ and their relationship to the elements of $\gamma^T y M^T$ and $\gamma^S S M^S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_y$</td>
</tr>
<tr>
<td>$a_{M_y} = (a^S + 2a^S + a^S)M_y + (a^T)M_y^T$</td>
</tr>
<tr>
<td>$b_{M_y} = (b^S + a^T)M_y + (b^T)M_y^T$</td>
</tr>
<tr>
<td>$c_{M_y} = (c^S + 2a^S + a^T)M_y + (c^T)M_y^T$</td>
</tr>
<tr>
<td>$f_{M_y} = (f^S - a^S + a^S + a^S)M_y + (-a^T + a^T + a^T)M_y^T$</td>
</tr>
<tr>
<td>$o_{M_y} = (o^S - a^S)M_y + (-a^T)M_y^T$</td>
</tr>
<tr>
<td>$r_{M_y} = (r^S + a^S)M_y + (r^T)M_y^T$</td>
</tr>
<tr>
<td>$s_{M_y} = (s^S - a^S + 2a^S)M_y + (-a^T + 2a^T)M_y^T$</td>
</tr>
<tr>
<td>$t_{M_y} = (t^S - a^T)M_y + (-a^T)M_y^T$</td>
</tr>
<tr>
<td>$u_{M_y} = (u^S - 2a^S - a^S)M_y + (-2a^T - a^T)M_y^T$</td>
</tr>
<tr>
<td>$x_{M_y} = (x^S - a^S - a^S + a^S)M_y + (x^T)M_y^T$</td>
</tr>
<tr>
<td>$d_{M_y} = ((f - a^S + a^S)M_y + (-a^T + a^T)M_y^T$</td>
</tr>
<tr>
<td>$g_{M_y} = (g^S + a^S + a^S)M_y + (g^T)M_y^T$</td>
</tr>
<tr>
<td>$i_{M_y} = (i^S + 2a^S)M_y + (i^T)M_y^T$</td>
</tr>
<tr>
<td>$k_{M_y} = (k^S + k^S)M_y + (k^T)M_y^T$</td>
</tr>
<tr>
<td>$m_{M_y} = (m^S - 2a^S)M_y + (m^T)M_y^T$</td>
</tr>
<tr>
<td>$p_{M_y} = (p^S + a^S + a^S)M_y + (-a^T + a^T)M_y^T$</td>
</tr>
<tr>
<td>$v_{M_y} = (v^S - a^S - a^S)M_y + (v^T)M_y^T$</td>
</tr>
<tr>
<td>$y_{M_y} = (y^S - a^S + a^S)M_y + (-a^T + a^T)M_y^T$</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>$\gamma^M o M^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_x$</td>
</tr>
<tr>
<td>$e_{M_x} = (e^S - a^S + a^S)M_x + (-a^T + a^T)M_x^T$</td>
</tr>
<tr>
<td>$h_{M_x} = (h^S + a^S + a^S)M_x + (h^T)M_x^T$</td>
</tr>
<tr>
<td>$f_{M_x} = (f^S + 2a^S)M_x + (f^T)M_x^T$</td>
</tr>
<tr>
<td>$l_{M_x} = (l^S + l^S)M_x + (l^T)M_x^T$</td>
</tr>
<tr>
<td>$n_{M_x} = (n^S - 2a^S)M_x + (n^T)M_x^T$</td>
</tr>
<tr>
<td>$q_{M_x} = (q^S - a^S + a^S)M_x + (-a^T + a^T)M_x^T$</td>
</tr>
<tr>
<td>$w_{M_x} = (w^S - a^S - a^S)M_x + (w^T)M_x^T$</td>
</tr>
<tr>
<td>$z_{M_x} = (z^S - a^S + a^S)M_x + (-a^T + a^T)M_x^T$</td>
</tr>
</tbody>
</table>

2.4 Effect of Fresnel factors on MSHG

In the preceding analysis of $P(2\omega; M(\mathbf{H}))$, no thought was given to what relationship exists between the electric-field giving rise to the non-linear behaviour at the surface ($\mathbf{E}(\omega)$) and the electric-field of the EM radiation, $\mathbf{E}(\omega; \theta, \phi)$, incident at that surface. This relationship is governed by the fundamental Fresnel factors, $f_s(\theta)$, of the surface, where $\theta$ refers to the external Angle-Of-Incidence (AOI) of the fundamental beam, with respect to the surface. The Fresnel factors of centrosymmetric crystals are almost isotropic, with azimuthal variation typically below 1%. Although RAS can measure the
small departures from isotropy at surfaces and interfaces, assuming the Fresnel factors are isotropic when investigating SHG is a good approximation. Following the notation of Lüpke et al. [5], the possible values of $f_i(\theta)$ are given in Table T2.4.1.

**Table T2.4.1: Possible fundamental frequency and SH Fresnel factors of a centrosymmetric crystal**

<table>
<thead>
<tr>
<th>$F_i(2\omega; \theta)$</th>
<th>$f_i(\omega; \theta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\frac{\sin \theta}{n_o(2\omega)}$</td>
<td>$\frac{\sin \theta}{n_o(\omega)}$</td>
</tr>
<tr>
<td>$\sqrt{1 - \left(\frac{\sin \theta}{n_o(2\omega)}\right)^2}$</td>
<td>$\sqrt{1 - \left(\frac{\sin \theta}{n_o(\omega)}\right)^2}$</td>
</tr>
</tbody>
</table>

In T2.4.1, $n_o(\omega)$ and $C$ are the effective Refractive Indices (RI) of the substrate at the fundamental and SH frequencies, respectively. Where the dielectric constant, $\varepsilon$, of the substrate is complex at the frequencies of interest, $n_o(\omega)$ and $n_o(2\omega)$ are deduced using a complicated function of $\Im[\varepsilon]$, $Re[\varepsilon]$, and $\Im[\varepsilon][6]$. In choosing the necessary $f_i(\omega; \theta)$ factors to be applied to $E(\omega; \theta, \varphi)$ in order to determine $E(\omega)$, the motivation is the satisfaction of the boundary conditions of the enforced by Maxwell equations. These selection rules are discussed in detail by Lupke et al. [5]. Clearly, at NI both $F_i(2\omega; \theta)$ and $f_i(\omega; \theta)$ converge to values of to either 0, or 1.

Accounting for the $f_i(\omega; \theta)$ factors allows the crystallographic and magnetization-induced contributions to $P(2\omega; M(H))$ may be expressed in terms of $E(\omega; \theta, \varphi)$:

\begin{align*}
P_i^C(2\omega; \theta, \varphi) &= \chi_{iik}^C(2\omega) f_i(\omega, \theta) f_k(\omega, \theta) E_j(\omega; \theta, \varphi) E_k(\omega; \theta, \varphi) \quad \text{E2.4.1} \\
P_i^M(2\omega; \theta, \varphi, M_k(H)) &= \chi_{ijkl}^M(2\omega) f_i(\omega, \theta) f_j(\omega, \theta) E_k(\omega; \theta, \varphi) E_l(\omega; \theta, \varphi) M_k(H) \quad \text{E2.4.2}
\end{align*}
The electric-field vector of the SHG arising from these polarization field contributions may be deduced by applying the SH Fresnel factors, \( F_i(\theta) \), which are also given in Table T2.4.1:

\[
E_i^C(2\omega; \theta, \phi) = F_i(2\omega, \theta)P_i^C(2\omega; \theta, \phi)
\]

\[
E_i^M(2\omega; \theta, \phi, M_L(H)) = F_i(2\omega, \theta)P_i^M(2\omega; \theta, \phi, M_L(H))
\]

The intensity of this SH EM radiation is determined from the magnitude of its Poynting vector. The intensity of SH EM radiation, polarized along the \( i \) axis is given by:

\[
|\mathbf{S}_i(2\omega; \theta, \phi, M_L(H))|^2 = \frac{E_i^C(2\omega; \theta, \phi) + E_i^M(2\omega; \theta, \phi, M_L(H))}{2}
\]

From centrosymmetric crystals, the value of \( |\mathbf{S}_i(2\omega; \theta, \phi, M_L(H))| \) is so small that it is usually measured using a photon-counting technique. Instead of converting the photon-counts into an actual intensity, a widely held convention is to use a normalized intensity \( \widetilde{I}_i \), quoting the SHG signal in photon-counts per second (Hz):

\[
\widetilde{I}_i(2\omega; \theta, \phi, M_L(H)) = \left| E_i^C(2\omega; \theta, \phi) + E_i^M(2\omega; \theta, \phi, M_L(H)) \right|^2
\]

### 2.5 MSHG experimental geometries

Two configurations are commonly used to investigate the SHG-signal from interfaces and surfaces:

- **Sample-rotation geometry:** Sample-rotation investigations involve selecting input- and output-polarizations of high symmetry (typically s- and p-polarization), and measuring the SHG-signal as the azimuthal angle of the sample is varied by rotation about the sample normal. To extract the maximum amount of information, the SHG
measurement is repeated for the four different input-/output-polarization combinations.

- **Polarization-rotation geometry:** Under UHV conditions, where precise rotation of the sample may be difficult, polarization-rotation investigations are often employed. Here, an optical plane-of-incidence along a high symmetry azimuth is chosen, the input-polarization angle rotated, and the resulting SHG-signal of fixed output-polarization (typically s- and p-polarization) is measured. To extract the maximum amount of information, the SHG measurement is repeated for several different output-polarizations and planes-of-incidence.

### 2.5.1 Sample rotation

A schematic of the sample-rotation experimental configuration is shown in figure F2.5.1. The input-polarization of the fundamental-frequency optical-field is designated by small letters, while the output-polarization of the SH-field by capital letters. The normal convention of defining s- and p-polarization in relation to the optical plane of incidence is followed. $\theta$ is the external angle-of-incidence, and $\varphi$ is the azimuthal angle of the sample. When the SHG-signal from the surface is measured for the Ss, Sp, Ps and Pp input-/output-polarization combinations, while rotating the sample, in the presence of an applied magnetic-field, these plots can reveal information about the crystallography and magnetization of the thin film samples[7].

For the four different polarization combinations of the sample rotation experiment, the general form of the crystallographic and magnetically-induced SH electric fields with polarization, $G$, excited by an input field of polarization, $h$, may be expressed in terms of a truncated Fourier sum[8]:

$$E_{Gh}(2\omega; \varphi, M_L) \propto [E_0 + \sum_{n=1}^{3} (E_{nc} \cos n\varphi + E_{ns} \sin n\varphi)]E_h^2(\omega) \tag{E2.5.1}$$

$E_{Gh}(2\omega; \varphi, M_L)$ refers to the total SH-field, the superposition of both crystallographic and magnetization-induced contributions. $E_0$ is an isotropic term, and $E_{nc}$ and $E_{ns}$ are the amplitudes of the $\cos n\varphi$ and $\sin n\varphi$ components, respectively.
The different tensor elements and Fresnel factors contributing to $E_{nc}$ and $E_{ns}$ or the four common $S$, $Sp$, $Ps$ and $Pp$ input-/output-polarization combinations are given in Tables T2.5.1–T2.5.4. Because these tables are large and complicated, they are collected together, in the appendices.

Using E2.5.1 and Tables T2.5.1–T2.5.4 it is possible to simulate the SHG-signal observed from the magnetized vicinal surface measured in each of the four different input-/output-polarization combinations. These simulations prove a useful tool in choosing which polarization geometries are likely to provide the largest observable MSHG contributions in real experiments. Figures F2.5.2 and F2.5.3 illustrate a collection of simulated SHG sample-rotation plots, where it has been assumed that $|?o^{m}M^{o}| = 0.1|?o^{c}|[2]$, and that the phase-difference between $?o^{m}M^{o}$ and $?o^{c}$ is either 0 or $\pi/2$ radians. From these simple simulations it is clear that:
1) The MSHG contribution results in significant changes in the symmetry and amplitude of the SHG plot.

2) The MSHG contribution induces the greatest changes in the simulated SsMy SHG plots, modifying the amplitude of the SHG signal by ~50%

3) There exists a significant difference between the changes caused by Mx-MSHG and My-MSHG contributions in the simulated Ss SHG plots. The Mx-MSHG contribution induces an asymmetry in the amplitude of the four lobes in the SHG polar-plot, while the My-MSHG contributions modify the amplitude of all four lobes evenly.

4) Neither Ss or Ps SHG polar-plots are particularly sensitive to the phase difference between $\gamma^M_o M^o$ and $\gamma^C_o$.

![Simulated SsMx SHG plot (assuming $\pi/2$ phase diff.)](image1)

![Simulated SsMx SHG plot (assuming 0 rad. phase diff.)](image2)

![Simulated SsMx SHG plot](image3)

![Simulated SsMx SHG plot](image4)

**Figure F2.5.2:** Simulated Ss MSHG plots of an ultra-thin ferromagnetic film for Mx (in-plane, perpendicular to step direction) and My (in-plane, parallel to step direction) magnetizations. In all cases, it is assumed that $|\gamma^M_o M^o| = 0.1 |\gamma^C_o|$. 

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Figure F2.5.3: Simulated Ps MSHG plots of an ultra-thin ferromagnetic film for Mx (in-plane, perpendicular to step direction) and My (in-plane, parallel to step direction) magnetizations. In all cases, it is assumed that \(|\gamma^M_o M^o| = 0.1|\gamma^C_o|\).

2.5.2 Polarization rotation

A schematic of the four common combinations of the sample-orientation and output-polarization used in polarization-rotation investigations of surface SHG are illustrated in Figure F2.5.4. In this geometry, the crystallographic and magnetization-induced SH fields are very similar to those of the sample rotation geometry, but are distributed across fewer Fourier components. For an input-polarization of the fundamental-frequency optical-field at an angle \(\varphi\) to the plane-of-incidence (\(\varphi = 0^\circ \Rightarrow p\)-polarization), the G-polarized SH-field for a \(jz\) optical plane-of-incidence is given by:

\[
E_{Gj}(2\omega, \varphi, M_L) \propto (E_\theta + E_2c \cos 2\varphi + E_2s \sin 2\varphi)E^2_\theta(\omega)
\]

E2.5.2
Again, $E_0$ is an isotropic term, while $E_{2c}$ and $E_{2s}$ are the amplitudes of the $\cos 2\varphi$ and $\sin 2\varphi$ components, respectively. Depending on the plane-of-incidence and output-polarization combination of a given measurement, $E_0$, $E_{2c}$, and $E_{2s}$ will be composed of different crystallographic contributions and magnetization-induced contributions.

**Figure F2.5.4: Schematic of polarization-rotation SHG experimental geometry**
Since the SH-field in polarization-rotation measurements contains fewer Fourier components than the SH-field measured using the sample-rotation geometry, identification of individual tensor components with this approach is more difficult. The different tensor elements contributing to the field-components of the four common combinations of the sample-orientation and output-polarization are given in Tables T2.5.5–T2.5.8, in the appendices. Using E2.5.2 and these tables, it is possible to simulate the SHG-signal observed from each of the four azimuth/output-polarization combinations, from a magnetized vicinal surface. Figures F2.5.5 and F2.5.6 illustrate a collection of such simulated SHG sample-rotation plots, where it has again been assumed that $|\gamma^m_o M^o| = 0.1 |\gamma^e_o| [2]$, and that the phase-difference between $\gamma^m_o M^o$ and $\gamma^e_o$ is either 0 or $\pi/2$ radians. Examining these simulations reveals that:

1) The MSHG contribution results in significant changes in the symmetry and amplitude of the polarization rotation SHG plots.

2) Both Mx-MSHG and My-MSHG contributions to the Sx SHG polar-plots are of the same magnitude, making this geometry ideal for probing in-plane surface magnetization.

3) The effect of the Mx-MSHG contribution in the Px plot is to induce a $\pi$-shift, while leaving the amplitude of the SHG signal unchanged.

4) Practically no difference exists between simulated polarization-rotation SHG polar-plots simulated using a phase-difference of 0 or $\pi/2$ radians.

Additional polarization rotation experiments at normal-incidence can be used to identify $z$-independent components[9]. In this limiting case, the value of the Fresnel factors reduce to $F_s = f_s = 0$ and $F_c = f_c = 1$. This geometry is particularly attractive for MSHG investigations because it preferentially increases the ratio of the magnetization contribution to crystallographic contribution in the overall SHG-signal: in the ON-geometry there are 8 accessible elements of $\gamma^m_o M^o$ and 10 accessible elements of $\gamma^e_o$, while in the Nl-geometry there are 3 accessible elements of $\gamma^m_o M^o$ and 3 accessible elements of $\gamma^e_o$. 

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Figure F2.5.5: Simulated $S_x M_{SHG}$ plots of an ultra-thin ferromagnetic film for $M_x$ (in-plane, perpendicular to step direction) and $M_y$ (in-plane, parallel to step direction) magnetizations. In all cases, it is assumed that $|\gamma^M_o M^0| = 0.1 |\gamma^C_o|$. 
Figure F2.5.6: Simulated $P_x$ SHG plots of an ultra-thin ferromagnetic film for $M_x$ (in-plane, perpendicular to step direction) and $M_y$ (in-plane, parallel to step direction) magnetizations. In all cases, it is assumed that $|\mathbf{M}_0| = 0$.

2.6 MSHG contrast

The MSHG contrast[10], $\eta(\theta, \varphi, H)$, is defined as:

\[
\eta(\theta, \varphi, H) = \frac{\overline{I}(2\omega; \theta, \varphi, M(+H)) - \overline{I}(2\omega; \theta, \varphi, M(-H))}{\overline{I}(2\omega; \theta, \varphi, M(+H)) + \overline{I}(2\omega; \theta, \varphi, M(-H))}
\]  

If the conditions, $|E^C(2\omega; \theta, \varphi)|^2 >> |E^M(2\omega; \theta, \varphi, M(+H))|^2$ and $M(-\bar{H}) = -M(+\bar{H})$, are satisfied, then the following simplification can be made:
\[ \eta(\theta, \phi, H) = 2 \frac{E^M(2\omega; \theta, \phi, M(+H))}{E^C(2\alpha; \theta, \phi)} \cos \delta(2\alpha; \theta, \phi) \]  

E2.6.2

Where \( \delta(2\omega; \theta, \phi) \) is the phase-difference between \( E^C(2\omega; \theta, \phi) \) and \( E^M(2\omega; \theta, \phi, M(+H)) \). The value of \( \eta \) is simple to calculate from experimental data, making it a quick-and-easy indicator of the magnitude of MSHG from a surface. Experimentally, it benefits from an internal normalization, automatically compensating for any drift in the optical power during a measurement, thereby making it experimentally robust. Using E2.5.2 and the results of a Fourier analysis summarized in T2.5.1-T2.5.8, and E2.6.2 it is possible to determine simple analytical expressions for \( \eta(\phi, H) \) for SxMx and PxMx SHG polar-plots:

\[
\text{SxMx: } \eta(2\omega; \theta, \phi, H) = a(2\omega; \theta, H) \csc 2\phi + b(2\omega; \theta, H) \cot 2\phi \]  

E2.6.3

\[
\text{PxMx: } \eta(2\omega; \theta, \phi, H) = c(2\omega; \theta, H) \sin 2\phi + d(2\omega; \theta, H) \tan 2\phi \]  

E2.6.4

Comparing these analytical expressions for \( \eta(\phi, H) \) with those obtained by applying E2.6.1 to the Simulated SHG plots in Figures F2.5.5 and F2.5.6 reveals that both E2.6.3 and E2.6.4 are indeed excellent approximations, apart from the regions where \( E^C(2\omega; \theta, \phi) \) approaches zero. The reason for the failure of E2.6.3 in this region is that \( E^C(2\omega; \theta, \phi) = E^M(2\omega; \theta, \phi, M(+H)) \), breaking one of the assumptions that lead to E2.6.2.

It is clear that the MSHG contrast of the simulated SxMx SHG plots attain sharp maxima and minima where values of \( \phi \) lead to \( E^C(2\omega; \theta, \phi) \) approaching zero. These cusps prove a disadvantage in using \( \eta \) as a quantitative gauge of MSHG signal – fitting algorithms cannot accommodate the rapid changes in \( \eta(\phi, H) \), especially when real data and its accompanying noise is analysed. However, for measurements made at a fixed \( \phi \), the large contrasts available near these cusps can also be experimentally advantageous. With careful tuning of \( \phi \), either through sample-rotation or polarization-
rotation, it is possible to achieve values of $\eta$ approaching unity, for any given surface magnetization. When SHG measurements are performed at such a tuned, or optimized, value of $\varphi_0$, they contain proportionately large MSHG contribution and thereby benefit from an excellent SNR. The ability to achieve such good SNR in the MSHG signal is later employed to make high-quality measurements of the Curie-points of the ultra-thin films. However, care must be taken in the interpretation of measurements made at such tuned values of $\varphi_0$, since the condition $|E^C(2\omega, \theta, \varphi)|^2 >> |E^M(2\omega, \theta, \varphi, M(+H))|^2$ may no longer be valid and simple expressions such as E2.6.2, E2.6.3, and E2.6.4 may not be applied.

Figure F2.6.1: Simulated SxMx and PxMx SHG plots from F2.5.5 and F2.5.6 and their MSHG contrasts calculated using E2.6.1 and E2.6.3.
A further advantage in tuning \( \phi \) through the cusps of the MSHG contrast of the SxMx SHG plot is the possibility of making a measurement of \( \delta(2\omega;\theta,\phi) \), the phase difference between \( E^C(2\omega;\theta,\phi) \) and \( E^M(2\omega;\theta,\phi,M(+H)) \). As \( \phi \) is tuned through the cusp in the SxMx SHG plot, there must be a value of \( \phi \) where
\[
|E^C(2\omega;\theta,\phi)| = |E^M(2\omega;\theta,\phi,M(+H))|
\]
exactly. Using a simple differential argument, it is possible to show that there exists either a maximum or minima in the MSHG contrast, when this is the case. Conversely, if a maxima of minima is observed for a particular value \( \phi_c \), then
\[
|E^C(2\omega;\theta,\phi_c)| = |E^M(2\omega;\theta,\phi_c,M(+H))|
\]
It is easily shown that when this condition is satisfied, \( \eta(\theta,\phi_c,H) \) reduces to:

\[
\eta(\theta,\phi_c,H) = \cos \delta(\theta,\phi_c,H) \tag{E2.6.5}
\]
Or, alternatively:

\[
\delta(\theta,\phi_c,H) = \cos^{-1} \eta(\theta,\phi_c,H) \tag{E2.6.6}
\]
Thereby allowing a direct measurement of \( \delta(\theta,\phi_c,H) \), the phase-difference between \( E^C(2\omega;\theta,\phi) \) and \( E^M(2\omega;\theta,\phi,M(+H)) \). The principle disadvantages of this approach are:

1) The inability to measure \( \delta(\theta,\phi,H) \) in this way, for the whole range of \( \phi \).
2) The inability to extract \( \delta(H,\phi) \) from the Px, Sy, and Py SHG polar-plots.
3) The practical difficulty in fine-tuning \( \phi \) to the true maxima of the cusp.

Despite these disadvantages, E2.6.6 provides a useful approximation of \( \delta(H,\phi) \) without the need to perform specific phase-sensitive measurements.

Where the conditions
\[
|E^C(2\omega;\theta,\phi)|^2 >> |E^M(2\omega;\theta,\phi,M(+H))|^2
\]
and
\[
M(-\vec{H}) = -M(+\vec{H})
\]
are valid, E2.6.2 holds true, and when it is measured for a fixed \( \phi_o \), from a magnetized surface, \( \eta \) can be expressed as the product of the magnetization

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magnitude and a real number, \( \Theta(2\omega; \theta, \varphi_o) \), determined by the ratio of
\[
\left| E''(2\omega; \theta, \varphi_o, M(+H)) \right| \text{ and } \left| E'(2\omega; \theta, \varphi_o) \right| , \text{ and } \delta(2\omega; \theta, \varphi_o):
\]

\[
\eta(2\omega; \theta, \varphi_o, H) = \left\{ \frac{2 \left| E''(2\omega; \theta, \varphi_o) \right| \cos \delta(2\omega; \theta, \varphi_o)}{\left| E'(2\omega; \theta, \varphi_o) \right|} \right\} |M(+H)| \tag{E2.6.7}
\]

\[
\eta(2\omega; \theta, \varphi_o, H) = \Theta(2\omega; \theta, \varphi_o) |M(+H)| \tag{E2.6.8}
\]

The temperature dependence of \(|M(+H)|\) can be inferred from the temperature dependence of \(\eta\):

\[
\eta(2\omega; \theta, \varphi_o, H, T) = \Theta(2\omega; \theta, \varphi_o, T)|M(+H, T)| \tag{E2.6.9}
\]

\[
\frac{\partial \eta(2\omega; \theta, \varphi_o, H, T)}{\partial T} = \frac{\partial \Theta(2\omega; \theta, \varphi_o, T)}{\partial T} |M(+H, T)| + \Theta(2\omega; \theta, \varphi_o, T) \frac{\partial |M(+H, T)|}{\partial T} \tag{E2.6.10}
\]

In the region of the ferromagnetic-paramagnetic transition (close to the Curie point, \(T_c\)) any thermally induced change in the optical constants is dwarfed by the rapid changes in the magnetization, \(\Theta \frac{\partial M}{\partial T} \gg M \frac{\partial \Theta}{\partial T}\):

\[
\frac{\partial \eta(2\omega; \theta, \varphi_o, H, T)}{\partial T} = \Theta(2\omega; \theta, \varphi_o, T) \frac{\partial |M(+H, T)|}{\partial T} \tag{E2.6.11}
\]

\[
\eta(2\omega; \theta, \varphi_o, H, T) \propto |M(+H, T)| \quad \text{(close to } T_c) \tag{E2.6.12}
\]

Away from the Curie point, or over large ranges, it is reasonable to assume that allowances for temperature variations in the optical constants must to be made. Surprisingly, however, this is not the case. The first-order partial-differential analysis carried-out in the appendices A1 shows that:
\[
\frac{d\eta(2\omega; \theta, \varphi_0, H, T)}{dT} = \frac{2\chi''(2\omega; \theta, \varphi_0, T)}{\chi'(2\omega; \theta, \varphi_0, T)} dM(H, T)
\]

E2.6.13

This implies \( \theta \frac{dM}{dT} \gg M \frac{d\theta}{dT} \) \( \forall T \). Consequently, E2.6.12 is a generally valid statement (to a first-order approximation). There exists a direct proportionality between \( \eta(\varphi_0, H, T) \) and \( |M (+H, T)| \) for a wide range of temperatures:

\[
\eta(2\omega; \theta, \varphi_0, H, T) \propto |M (+H, T)| \quad \forall T
\]

E2.6.14

Figure F2.6.2: (A) Simulation of MSHG contrast \( \eta \) as a function of temperature, for the given relative magnetization, for various ratios of \( E_M \) and \( E_C \); (B) The simulations of \( \eta \) from (A), normalized such that \( \eta(T=0)=1 \).

The simulations illustrated in F2.6.2 clearly illustrate the excellent agreement between the temperature dependence of \( \eta(T) \) and \( M(H, T) \), provided \( |E_M / E_C| \leq 0.5 \). In these figures, the magnetization is assumed to exhibit simple hyperbolic temperature dependence. If \( |E_M / E_C| > 0.5 \), then the condition \( E^C(2\omega; \theta, \varphi) \gg |E^M(2\omega; \theta, \varphi, M(+H))|^2 \) is no longer valid, and the relationship \( \eta(2\omega; \theta, \varphi_0, H, T) \propto |M(+H, T)| \) (E2.6.14) breaks-down. In particular, it should be noted that an artefactual peak in \( \eta(T) \) is introduced whenever \( |E_M / E_C| > 1 \). Such a peak in
the $\eta(T)$ plot could easily be misconstrued as a real structure in the surface magnetization, so care must be taken to ensure that the condition $|E_m/E_c| \leq 0.5$ is obeyed at all times, whenever a one-to-one agreement between $\eta(T)$ and $M(H,T)$ is assumed.

2.7 Extracting $E^M$ and $E^C$ from MSHG data

Under certain conditions, described below, the values of both $E^M(2\omega; M(+H))$ and $E^C(2\omega)$ can be deduced from the $\bar{I}(2\omega; \theta, \phi, M(+H))$ and $\bar{I}(2\omega; \theta, \phi, M(-H))$ data. These determinations can be made either by fitting the SHG data to the Fourier components in T2.5.1-T2.5.8, or through algebraic manipulation of the raw SHG data. Both approaches have their advantages, and their limitations. Fitting the data provides a quantitative measure of the real and imaginary parts of $E^C(2\omega; \varphi)$ and $E^M(2\omega; \varphi, M(+H))$, but is potentially susceptible to generating artefactual structures, and non-unique solutions. On the other hand, when the algebraic extraction is performed, the relative-phase information regarding $E^C(2\omega; \varphi)$ and $E^M(2\omega; \varphi, M(+H))$ is lost. The methodology adopted in this thesis was to first determine solutions to $E^C(2\omega; \varphi)$ and $E^M(2\omega; \varphi, M(+H))$ using fitting algorithms, and then crosscheck these solutions with those deduced using a direct algebraic extraction.

2.7.1 Fitting Determination

For the case of the polarization-rotation experiments (by far, the most widely utilized geometry in this research) the SHG signal was shown to be of the form:

$$\bar{I}(2\omega; \theta, \phi, M(H)) = |E_0 + E_{2e} \cos 2\varphi + E_{2s} \sin 2\varphi|^2$$  \hspace{1cm} E2.7.1

Using Excel, or Origin computer packages, the magnitude and phase of $E_0$, $E_{2e}$, and $E_{2s}$ is varied until the best least-squares-fit of the data is achieved. Since only relative-
phase can be determined from a single intensity measurement, the phase of one of these terms is always arbitrarily set to zero. To determine the different crystallographic and magnetization induced electric-field contributions to the SHG signal, the fitting procedure is applied to the signal measured for both positive and negative magnetization.

\[
\tilde{I}(2\omega; \theta, \varphi, M(\pm H)) = \left| E_0^+ + E_{2c}^+ \cos 2\varphi + E_{2s}^+ \sin 2\varphi \right|^2 \quad E2.7.2
\]

\[
\tilde{I}(2\omega; \theta, \varphi, M(-H)) = \left| E_0^- + E_{2c}^- \cos 2\varphi + E_{2s}^- \sin 2\varphi \right|^2 \quad E2.7.3
\]

The different Fourier components of the crystallographic and magnetization-induced electric-field contributions are determined from the sums and differences of these six complex terms:

\[
E_0^C = \frac{1}{2} (E_0^+ + E_0^-), \quad E_{2c}^C = \frac{1}{2} (E_{2c}^+ + E_{2c}^-), \quad E_{2s}^C = \frac{1}{2} (E_{2s}^+ + E_{2s}^-) \quad E2.7.4
\]

\[
E_0^M = \frac{1}{2} (E_0^+ - E_0^-), \quad E_{2c}^M = \frac{1}{2} (E_{2c}^+ - E_{2c}^-), \quad E_{2s}^M = \frac{1}{2} (E_{2s}^+ - E_{2s}^-) \quad E2.7.5
\]

Once the Fourier components of the fields have been determined, in this way, it is trivial to reconstruct \( E^C(2\omega; \varphi) \) and \( E^M(2\omega \varphi, M(\pm H)) \):

\[
E^C(2\omega; \varphi) = E_0^C + E_{2c}^C \cos 2\varphi + E_{2s}^C \sin 2\varphi \quad E2.7.6
\]

\[
E^M(2\omega; \varphi, M(\pm H)) = E_0^M + E_{2c}^M \cos 2\varphi + E_{2s}^M \sin 2\varphi \quad E2.7.7
\]

The phase measurements deduced from the SxMx SHG plots, using E2.6.6, can be compared to the “fitted” phase predicted by E2.7.6 and E2.7.7, for \( \varphi_0 \). When performed at normal-incidence, using either the \( \perp \)- or \( \parallel \)-alignments, \( E^C(2\omega; \varphi) \) is composed solely of even or odd functions of \( \varphi \), respectively. Similarly, when measured with \( \perp \)- or \( \parallel \)-alignments, \( E^M(2\omega; \varphi, M(\pm H)) \) contains only even or odd functions of \( \varphi \), exclusively.
The presence of any statistically significant *forbidden* Fourier components indicates either poor alignment, or a failure of the phenomenological model.

### 2.7.2 Algebraic determination

If the conditions, \[ |E^C(2\omega; \theta, \phi)|^2 >> |E^M(2\omega; \theta, \phi, M(\pm H))|^2 \] and \[ M(-H) = -M(H) \]
are satisfied, then both \[ |E^C(2\omega; \theta, \phi)\] and \[ |E^M(2\omega; \theta, \phi, M(\pm H))| \cos \delta(2\omega; \theta, \phi)\] can be deduced from the \[ I(2\omega; \theta, \phi, M(H)) \] and \[ I(2\omega; \theta, \phi, M(-H)) \] data, directly:

\[
|E^C(2\omega; \theta, \phi) = \sqrt{\frac{I(2\omega; \theta, \phi, M(H)) + I(2\omega; \theta, \phi, M(-H))}{2}}
\]

\[
|E^M(2\omega; \theta, \phi, M(H))| \cos \delta(2\omega; \theta, \phi) = \frac{I(2\omega; \theta, \phi, M(H)) - I(2\omega; \theta, \phi, M(-H))}{\sqrt{8[I(2\omega; \theta, \phi, M(H)) + I(2\omega; \theta, \phi, M(-H)))]}}
\]

Applied to the SHG data, the deduced values of \[ |E^C(2\omega; \theta, \phi)\] and \[ |E^M(2\omega; \theta, \phi, M(H))| \cos \delta(2\omega; \theta, \phi)\] exhibit non-physical cusps and discontinuities, caused by the moduli. By convolving the values of \[ |E^C(2\omega; \theta, \phi)\] and \[ |E^M(2\omega; \theta, \phi, M(H))| \cos \delta(2\omega; \theta, \phi)\] with a square wave (bound by +1 and -1) of the correct frequency, the line-shape (but not the phase) of \[ E^C(2\omega; \theta, \phi)\] and \[ E^M(2\omega; \theta, \phi, M(H))\] can be recovered.

### 2.7.3 Temperature dependence of \( E^M \) and \( E^C \)

When \[ I(2\omega; \theta, \phi, M(H)) \] is measured in a fixed optical geometry (that is for fixed values of \( \phi_0 \) and \( \theta_0 \)) the temperature dependence of \[ |E^C(2\omega; \theta_0, \phi_0, T)| \] may be linearized into a function of temperature, \( \Theta^C(T) \), and a function of \( \phi_0 \) and \( \theta_0 \),
\( G^C(2\omega; \theta, \phi) \), while the temperature dependence of \( E^M(2\omega; \theta, \phi, M(+H,T), T) \) may be linearized into a function of temperature, \( \Theta^M(T) \), a function of \( \phi \) and \( \theta \), \( G^M(2\omega; \theta, \phi) \), and \( |M(+H,T)| \):

\[
E^C(2\omega; \theta, \phi, T) = G^C(2\omega; \theta, \phi) \Theta^C(T) \quad \text{E2.7.10}
\]

\[
E^M(2\omega; \theta, \phi, M(+H,T)) = G^M(2\omega; \theta, \phi) \Theta^M(T) |M(+H,T)| \quad \text{E2.7.11}
\]

Close to the Curie point, \( \Theta^M \frac{\partial M}{\partial T} \gg M \frac{\partial \Theta^M}{\partial T} \), and there exists a simple proportionality between \( |M(+H,T)| \) and \( |E^C(2\omega; \theta, \phi, T)| \) (close to Curie point):

\[
|E^M(2\omega; \theta, \phi, M(+H,T))| \propto |M(+H,T)| \quad \text{E2.7.12}
\]

However, unlike the \( \eta(\phi, H,T) \), \( E^M(2\omega; T; M(+H,T)) \) exhibits an additional temperature dependencies, \( \Theta^M(T) \). Therefore, unlike the contrast, there is no basis for proportionality between \( M^C(+H,T) \) and \( E^M(2\omega; T; M(+H,T)) \) over an extended temperature range. Instead of being a disadvantage, the enhanced temperature sensitivity of \( |E^C(2\omega; \theta, \phi, T)| \) and \( |E^M(2\omega; \theta, \phi, M(+H,T), T)| \) may, in fact, be useful. If a sudden change in \( E^C(2\omega; T) \) were observed, as the surface passes through its Curie point (as determined from the MSHG contrast), it would be a strong indication of magnetostriction at the crystal surface[11-13].

When studying the temperature dependence of \( E^M(2\omega; M(+H)) \) and \( E^C(2\omega) \), it is natural to choose a tuned value of \( \phi \) that maximizes the magnetization-induced electric field contribution to the SHG signal. In some instances, this value of \( \phi \) may lead to the condition \( |E^C(2\omega)|^2 \gg |E^M(2\omega; M(+H))|^2 \) becoming invalid, and the expressions E2.7.10 and E2.7.11 may then fail to accurately represent the temperature-dependence.
of the two fields. In this instance, the following expressions for \( |E^C(2\omega;\varphi,\varphi)|_{\text{max}} \) and 
\( |E^M(2\omega;\varphi,\varphi,M(+H))|_{\text{min}} \), derived in the appendices, may be used:

\[
E^C(2\omega;\varphi)_{\text{max}} = \sqrt{\frac{1}{2}(\Sigma + \sqrt{\Sigma^2 - \Delta^2})} \tag{2.7.13}
\]

\[
E^M(2\omega;\varphi,\varphi,M(+H))_{\text{min}} = \sqrt{\frac{1}{2}(\Sigma - \sqrt{\Sigma^2 - \Delta^2})} \tag{2.7.14}
\]

Where:

\[
\Sigma(\theta,\varphi,M(+H)) = \frac{1}{2}(\bar{T}(2\omega;\varphi,M(+H)) + \bar{T}(2\omega;\varphi,M(-H)))
\]

\[
\Delta(\theta,\varphi,M(+H)) = \frac{1}{2}(\bar{T}(2\omega;\varphi,M(+H)) - \bar{T}(2\omega;\varphi,M(-H)))
\]

For most cases, these complicated expressions are not necessary; even when analysing data where \( \eta = 0.7 \) (see section 2.6), the values of \( E^M(2\omega;M(+H)) \) and \( E^C(2\omega) \), determined with E2.7.8 and E2.7.9, differ very little from those determined with E2.7.13 and E2.7.14. However, these expressions become necessary when \( \eta \geq 0.7 \).

2.8 MSHG-derived hysteresis loops

For a fixed temperature and \( \varphi_0 \), the SHG signal from a magnetized surface is proportional to \( |E^C(2\omega) + E^M(2\omega;M(H))|^2 \). When this modulus is expanded-out, it is clear that \( \bar{T}(2\omega;M(H)) \) contains terms proportional to both \( |E^M(2\omega;M(H))|^2 \) and \( |E^C(2\omega;M(H))|^2 \):

\[
\bar{T}(2\omega;M(H)) = |E^C(2\omega)|^2 + |E^M(2\omega;M(H))|^2 + 2|E^C(2\omega)||E^M(2\omega;M(H))|\cos \delta \tag{2.8.1}
\]

This demonstrates that hysteresis loops of the MSHG signal are not directly equivalent to magnetic-hysteresis-loops of the surface. Recently, Valev et al [14] demonstrated that,
if care is not taken in interpretation of such experimental results, the asymmetries in the MSHG hysteresis loops may be mistakenly construed as novel magnetic behaviour. However, as suggested by Veenstra[15], the coherent addition an external SHG signal to that of the magnetized surface can be used ensure that 
\[ |E^C(2\omega)|^2 \gg |E^M(2\omega; M(H))|^2, \]
forcing a one-to-one equivalence between the MSHG hysteresis loop and the hysteresis loop of the surface magnetization. While this approach is elegant in its simplicity, the associated reduction in SNR caused by the additional \(|E^C(2\omega)|\) contribution is obviously undesirable. Higher SNR in the MSHG signal may be achieved by making measurements at \(\varphi_0\) and \(\theta_0\) such that 
\[ |E^C(2\omega; \theta_0, \varphi_0)| = |E^M(2\omega; \theta_0, \varphi_0, M(H))|, \]
but such MSHG hysteresis loops would be significantly skewed by the quadratic term in E2.8.1. This distortion is clearly evident in the simulated plots illustrated in F2.8.1, where \(E^C(2\omega; \theta_0, \varphi_0) = 2E^M(2\omega; \theta_0, \varphi_0, M(H))\).

The distortion manifests as:

1) An artefactual "exchange bias"-like displacement of the curve hysteresis-loop.
2) An asymmetry between the positive and negative saturation magnetizations.

**Figure F2.8.1:** Simulated hysteresis loop of a ferromagnetic surface magnetization and the MSHG hysteresis loop of that surface, assuming \(E^C = 2E^M M(H)\)
In order to deduce surface magnetization, $M(H)$, from the MSHG hysteresis loop, $\bar{T}(2\omega; M(H))$, a new expression relating $M(H)$ to $\bar{T}(2\omega; M(H))$, was derived (see appendices A.2):

$$M(H) = \sqrt{\bar{T}(2\omega; M(H)) - \Gamma(2\omega; \delta)} - \sqrt{\bar{T}(2\omega; M(H)) - \Gamma(2\omega; \delta)} > E2.8.2$$

Where:

$$\Gamma(2\omega; \delta) = \left| E^C(2\omega) \right|^2 \left( 1 - \cos^2 \delta \right)$$

Here $\sqrt{\bar{T}(2\omega; M(H)) - \Gamma(2\omega; \delta)}$ is the average value of $\sqrt{\bar{T}(2\omega; M(H)) - \Gamma(2\omega; \delta)}$ summed over the full MSHG hysteresis loop. As it depends on $\delta(2\omega; \theta, \varphi)$, the value of $\Gamma(2\omega; \delta)$ cannot, in general, be determined from $\bar{T}(2\omega; M(H))$. However, this issue can be side-stepped; $\Gamma$ can be treated as a fitting parameter, chosen to maximize the symmetry of the MSHG hysteresis loop. All ferromagnetic hysteresis loops can be broken down into four quadrants ($A$, $B$, $C$, and $D$, as illustrated in figures F2.8.1 and F2.8.2) and thermo-mechanical arguments, originally put forward by Stoner[16] in 1948, require that the area of quadrant $A$ must equal that of quadrant $C$, and similarly, the area of quadrant $B$ must equal that of quadrant $D$. However, MSHG hysteresis loops, $\bar{T}(2\omega; M(H))$, are skewed and the symmetry relations are not upheld. The hysteresis loop of the surface magnetization, $M(H)$, can be recovered from the skewed MSHG hysteresis loop, by applying E2.8.2, and varying the value of $\Gamma(2\omega; \delta)$ using a least-squares fitting algorithm, until the areas of quadrants $A$ and $C$, and quadrants $B$ and $D$, are equal, as required by thermo-mechanical arguments[16].

The effect of this procedure is illustrated in figure F2.8.2, where the hysteresis loop of the surface magnetization of the Au-capped 0.75ML Fe ultra-thin film grown on the vicinal W(110) surface at 80K is extracted from $\bar{T}(2\omega; M(H))$. In the uncorrected MSHG loop there are clear asymmetries in the loop-shape and a coercivity-bias. After applying E2.8.2, and manually setting $\Gamma$ equal to 0, 40Hz, 50Hz, and 60Hz, it is seen that the asymmetry of the quadrants (Relative AC asymmetry = [Area of A - Area of C]/[ Area of A + Area of C], Relative BD asymmetry = [Area of B - Area of D]/[ Area of B + Area of D]) exhibits a maximum near 50Hz. This value of $\Gamma = 50$Hz also produces a proper balancing of the coercivity fields, with values of 30mT and -30mT.
**Figure F2.8.2:** Hysteresis loop of the Au-capped 0.75ML Fe patch grown on vicinal W(110) surface at 80K deduced using E2.8.2 for indicated values of $\Gamma$.

<table>
<thead>
<tr>
<th>Area of A</th>
<th>Area of B</th>
<th>Area of C</th>
<th>Area of D</th>
<th>Relative AC asymmetry</th>
<th>Relative BD asymmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.57</td>
<td>5.71</td>
<td>20.95</td>
<td>8.82</td>
<td>0.19</td>
<td>-0.21</td>
</tr>
<tr>
<td>28.27</td>
<td>7.02</td>
<td>27.19</td>
<td>7.89</td>
<td>0.02</td>
<td>-0.06</td>
</tr>
<tr>
<td>27.90</td>
<td>7.27</td>
<td>28.46</td>
<td>7.60</td>
<td>-0.01</td>
<td>-0.02</td>
</tr>
<tr>
<td>27.32</td>
<td>7.66</td>
<td>30.86</td>
<td>7.00</td>
<td>-0.06</td>
<td>0.04</td>
</tr>
</tbody>
</table>
When the phase difference between $E^c(2\omega)$ and $E^m(2\omega; M(H))$ is very small, it is possible to approximate $\Gamma = 0$, and Eq. 2.8.2 reduces to the trivial result:

$$M(H) \propto \sqrt{I(2\omega; M(H))} = \sqrt{I(2\omega; M(H))}$$

(Eq. 2.8.3)

Often, even applying this simplified expression to the SHG signal produces hysteresis-loops with far better symmetry than original MSHG-hysteresis-loops.

### 2.9 Separating step-site and terrace-site contributions

Separating the terrace-site and step-site contributions to the total SHG signal from the magnetized surface is difficult. Three distinct approaches are explored:

1) A direct analysis of the SHG and MSHG tensor elements.

2) An analysis of the MSHG contrast as a function of temperature.

3) An analysis of the MSHG signal as a function of applied-field.

Despite the considerable effort expended in developing the rigorous tensor formalism for the phenomenological model, it is found that comparatively simple MSHG contrast temperature dependence analysis and magnetic-hysteresis-loop analysis work best.

#### 2.9.1 Tensor element analysis

Provided the Fresnel factors of the surface are sufficiently well-known, the fitting procedure described in Section 2.7.1 may be used to deduce some individual elements of $\gamma^m M^o$ and $\gamma^c$. These deduced tensor elements are themselves composed of the coherent superposition of elements of either $\gamma^c$, $\gamma^s$, or $\gamma^m M^s$ and $\gamma^m M^t$. In very limited cases, it is possible to deduce individual elements of $\gamma^c$, $\gamma^s$, $\gamma^m M^s$ and $\gamma^m M^t$, from the SHG signal. These 'deducible' elements, and their dependence on the observable tensor elements, are given in Table T2.9.1.
Table T2.9.1: Deducible MSHG tensor elements of the 1m step-sites of a magnetic vicinal surface.

<table>
<thead>
<tr>
<th>$M_y$</th>
<th>$f^S M_y = f M_y + \alpha(a M_y - c M_y - x M_y)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$u^S M_y = u M_y + \alpha(c M_y + 2 x M_y)$</td>
</tr>
<tr>
<td></td>
<td>$o^S M_y = o M_y + \alpha(r M_y)$</td>
</tr>
<tr>
<td></td>
<td>$s^S M_y = s M_y + \alpha(a M_y - 2 x M_y)$</td>
</tr>
<tr>
<td></td>
<td>$t^S M_y = t M_y + \alpha(b M_y)$</td>
</tr>
<tr>
<td>$M_x$</td>
<td>$p^S M_x = p M_x + \alpha(i M_x - m M_x)$</td>
</tr>
<tr>
<td></td>
<td>$d^S M_x = d M_x - y M_x$</td>
</tr>
<tr>
<td>$M_z$</td>
<td>$q^S M_z = q M_z + \alpha(j M_z - n M_z)$</td>
</tr>
<tr>
<td></td>
<td>$l^S M_z = l M_z$</td>
</tr>
<tr>
<td></td>
<td>$e^S M_z = e M_z - z M_z$</td>
</tr>
</tbody>
</table>

Unfortunately, often a meaningful deconvolution cannot be performed, because the Fresnel factors are not adequately known. If this is the case, it is only possible to deduce a single magnetization-induced tensor element that depends solely on the surface magnetization in the region of the step-sites: $l M_z \equiv l^S M_z = \chi_{x y z} M_z^S$. The MSHG signal from this tensor element can be measured using the custom geometry illustrated in figure F2.9.1. In this geometry, the sample is orientated in the x-azimuth configuration; the input optical-field is fixed at $\hat{s}$-polarized; and the output polarizer is fixed with a slight offset ($\beta$) from $\hat{s}$-polarized. The SHG signal measured in this geometry is proportional to $(\beta \chi_{x y} + \chi_{x y z} M_z^S)^2$, with a MSHG contribution arising from only from the surface magnetization in the region of the step-sites. Of course, a significant MSHG signal will only be observed with this geometry, if the easy-axis of magnetization of the sample is out-of-plane. For certain coverages, it is known that the Fe vicinal W(110) interface exhibits such an easy-axis[17].
2.9.2 MSHG contrast analysis

Because the co-ordination, surface stress, and dimensionality of the ferromagnetic atoms at the edge of the ultra-thin film is different to those at the centre of the stripe[3], it is possible that the surface magnetization may vary across the face of the ultra-thin films and nanostripes. This means that the surface magnetization in the region of the mm2 terrace-sites, \( M^T(+H,T) \), may be different to the surface magnetization in the region of the Im step-sites, \( M^S(+H,T) \). In this case, the contributions of \( M^T(+H,T) \) and \( M^S(+H,T) \) to the MSHG contrast of the surface must be accounted for separately:

\[
\eta(\theta, \phi, H) = \frac{2 |E^M(2\omega; \theta, \phi, M(+H))|}{|E^E(2\omega; \theta, \phi)|} \cos \delta(2\omega; \theta, \phi) \tag{E2.6.2}
\]

Where

\[
\begin{align*}
E^M(2\omega; \theta, \phi, M(H)) &= E^M_T(2\omega; \theta, \phi, M^T(H)) + E^M_S(2\omega; \theta, \phi, M^S(H)) \\
E^E(2\omega; \theta, \phi) &= E^E_T(2\omega; \theta, \phi) + E^E_S(2\omega; \theta, \phi)
\end{align*}
\]

\[
\eta(\theta, \phi, H) = \frac{|E^M_T(2\omega; \theta, \phi, M(H)) + E^M_S(2\omega; \theta, \phi, M(H))|}{|E^E_T(2\omega; \theta, \phi) + E^E_S(2\omega; \theta, \phi)|} \cos \delta(\theta, \phi) \tag{E2.9.1}
\]

\[
\eta(\theta, \phi, H) = \frac{|E^E_T(2\omega; \theta, \phi) + E^E_S(2\omega; \theta, \phi)|}{|E^M_T(2\omega; \theta, \phi, M(H)) + E^M_S(2\omega; \theta, \phi, M(H))|} \cos \delta(\theta, \phi) \tag{E2.9.2}
\]
\[ \eta(\theta, \phi, H) = \frac{E_s^c(2\omega; \theta, \phi) M^* (H) + E_s^m(2\omega; \theta, \phi) M^* (H)}{E_s^c(2\omega; \theta, \phi) + E_s^m(2\omega; \theta, \phi)} \cos \delta(\theta, \phi) \]  

(2.9.3)

Where

\[ \Theta^t(2\omega; \theta, \phi) = \frac{E_s^m(2\omega; \theta, \phi) \cos \delta(\theta, \phi)}{E_s^c(2\omega; \theta, \phi) + E_s^m(2\omega; \theta, \phi)} \]  

(2.9.4)

\[ \Theta^s(2\omega; \theta, \phi) = \frac{E_s^m(2\omega; \theta, \phi)}{E_s^m(2\omega; \theta, \phi)} \]

(2.9.5)

The temperature dependence of \[ |M^o(\theta, \phi, H_T)| \] can be inferred from the temperature dependence of \( \eta \):

\[ \eta(\theta, \phi, H_T) = \Theta^t(2\omega; \theta, \phi) M^* (H_T) + \Theta^s(2\omega; \theta, \phi) M^* (H_T) \]

(2.9.6)

By analogy with (2.6.1.4), it is possible to establish that:

\[ \eta(\theta, \phi, H_T) \propto |M^o(2\omega; \theta, \phi, H_T)| \]

(2.9.10)

It was previously shown (F2.5.8) that an excellent agreement between the temperature dependence of \( \eta(T) \) and \( M(H, T) \) exists, provided \( |E_s^m / E_s^c| \leq 0.5 \). The simulations of the temperature dependence of \( |M^o(\theta, \phi, H, T)| \), illustrated in Figure F2.9.2, should, therefore, reflect the experimentally observed temperature dependence of \( \eta(T) \).
(provided the surface magnetization in the region of the terrace-sites, \( M^T (+H,T) \), differs from that of the surface magnetization in the region of the step-sites, \( M^S (+H,T) \)). It is clear from the figures in F2.9.2 that if \( M^T (+H,T) \neq M^S (+H,T) \), then either a kink, or a peak is observed in the temperature dependence of \( |M^O(\theta,\varphi,H,T)| \). The kink or peak in the temperature dependence of \( |M^O(\theta,\varphi,H,T)| \) occurs at the Curie point of the region of surface magnetization with the lowest Curie point. The mean-field theory of ferromagnetism leads us to conclude that the Curie point of \( M^S (+H,T) \) will be less than that of \( M^T (+H,T) \), because of the step-sites have fewer nearest neighbour atoms than the terrace-sites; \( k_bT_C = 2NJJ(J + 1) \), where \( T_C \) is the Curie point of the atoms with \( N \) nearest-neighbouring. Therefore, the kink or peak in the temperature dependence of \( |M^O(\theta,\varphi,H,T)| \) may be ascribed to the Curie point of the surface magnetization in the region of the step-sites, \( M^S (+H,T) \), while the temperature at which \( |M^O(\theta,\varphi,H,T)| \) goes to zero is the Curie point of the surface magnetization in the region of the terrace-sites, \( M^T (+H,T) \). A kink in \( |M^O(\theta,\varphi,H,T)| \) is observed when the phase of \( \Theta^2(2\omega;\theta,\varphi) \) is positive, and a peak is observed when the phase of \( \Theta^2(2\omega;\theta,\varphi) \) is negative.

Although the presence of such peaks or kinks in the experimental observations of the temperature dependence of \( \eta(+H,T) \) would seem to indicate that \( M^T (+H,T) \neq M^S (+H,T) \) a priori, great care must be taken in interpreting the data. To avoid confusing the 'true' peaks in F2.9.2 with the artefactual peak illustrated in F2.6.2, it is critically important that the temperature dependence of \( \eta(T) \) be probed using an experimental geometry that ensures \( |E_M / E_c| \leq 0.5 \). Additionally, the presence of a strong temperature dependence in \( E_C(2\omega;\theta,\varphi,T) \) invalidate the assumption that a simple proportionality exists between the temperature dependence of \( \eta(+H,T) \) and \( |M^O(\theta,\varphi,H,T)| \). Strong temperature dependences in \( E_C(2\omega;\theta,\varphi,T) \) could arise from thermally induced strain in the interface, or magnetostriction effects[11-13]. Such
effects would introduce structure into the temperature dependence of $\eta(+H,T)$ that is not reflected in the underlying temperature dependence of the surface magnetization.

![Graphs showing temperature dependence of $M^\circ(+H,T)$ and $M^S(+H,T)$](image)

Figure F2.9.2: Simulated temperature dependence of $M^\circ(\theta,\varphi,H,T)$, given $M^T(+H,T)$ and $M^S(+H,T)$, for different values of $\Theta^\circ(2\omega;\theta,\varphi)$. For simplicity, it is assumed that $M^T(+H,T)$ and $M^S(+H,T)$ have simple hyperbolic temperature dependences. Note that a kink is observed when the phase of $\Theta^\circ(2\omega;\theta,\varphi)$ is positive, and a peak is observed when the phase of $\Theta^\circ(2\omega;\theta,\varphi)$ is negative.

### 2.9.3 MSHG-derived hysteresis loop analysis

It was shown in Section 2.8 that the hysteresis loop of the surface magnetization could be extracted from the MSHG hysteresis loop using the following expression:
If the surface magnetization in the region of the mm2 terrace-sites, \( M^T(H) \), differs from that of the surface magnetization in the region of the lm step-sites, \( M^S(H) \), then the hysteresis loops of the surface magnetization may be deduced from MSHG data using the following expression:

\[
M^O(2\omega; \theta, \phi, H) \approx \sqrt{\frac{1}{2}} \left[ \sqrt{M^T(2\omega; \theta, \phi, H)} - \sqrt{M^S(2\omega; \theta, \phi, H)} \right] - \Gamma - \sqrt{\frac{1}{2}} \left[ \sqrt{M^T(2\omega; \theta, \phi, H)} + \sqrt{M^S(2\omega; \theta, \phi, H)} \right] - \Gamma >
\]

Where:

\[
\Gamma = \left| E^C(2\omega) \right|^2 \left( I - \cos^2 \delta \right)
\]

The hysteresis of \( M^O(2\omega; \theta, \phi, H) \) depends on \( M^T(H) \), \( M^S(H) \), and the complex optical constant \( \Theta^0(2\omega; \theta, \phi) \). Therefore, the hysteresis of the observed surface magnetization, \( M^O(2\omega; \theta, \phi, H) \), is a function of the \( 2\omega \), \( \theta \) or \( \phi \) used in SHG experimental configuration:

- If the surface magnetization in the region of the terrace-sites differs from that of the surface magnetization in the region of the step-sites, then \( M^O(2\omega_1; \theta_1, \phi_1, H) \neq M^O(2\omega_2; \theta_2, \phi_2, H) \).

- If the surface magnetization in the region of the terrace-sites is the same as that of the surface magnetization in the region of the step-sites, then \( M^O(2\omega_1; \theta_1, \phi_1, H) = M^O(2\omega_2; \theta_2, \phi_2, H) \).

Assuming that the surface magnetization in the region of the terrace-sites does in fact differ from that of the surface magnetization in the region of the step-sites, MSHG-derived hysteresis loops are simulated in F2.9.3. When it is assumed that the hysteresis
of both $M^T(H)$ and $M^S(H)$ are hard ferromagnetic, then the observed surface magnetization is also hard, with a coercivity intermediate between that of $M^T(H)$ and $M^S(H)$. It is found that the coercivity of $M^O(2\omega; \theta, \varphi, H)$ depends on the magnitude and phase of $\Theta^O(2\omega; \theta, \varphi)$, which, in turn, depends on the experimental geometry through $2\omega$, $\theta$ or $\varphi$. Therefore, if $M^T(+H,T) \neq M^S(+H,T)$, a single-wavelength NI MSHG experiment (fixed $2\omega$ and $\theta=0$), $M^O(2\omega; \theta, \varphi, H)$ will exhibit a $\varphi$-dependent coercivity. The observation of such a $\varphi$-dependent coercivity in the MSHG-derived hysteresis loops of surface magnetization from ferromagnetic nanostripes would be a strong indication that $M^T(+H,T) \neq M^S(+H,T)$.

When it is assumed that the hysteresis of $M^T(H)$ is hard ferromagnetic and $M^S(H)$ is very soft ferromagnetic, or super-paramagnetic, then the observed surface magnetization is a moderately soft ferromagnet. In this situation, the coercivity of $M^O(2\omega; \theta, \varphi, H)$ still depends on the magnitude and phase of $\Theta^O(2\omega; \theta, \varphi)$, but much less sensitively than when $M^S(H)$ was a hard ferromagnet. Given the SNR of MSHG experiments, it is doubtful that such small changes in the $\varphi$-dependent coercivity of the surface magnetization could be observed.
F2.9.3: Simulated MSHG-derived hysteresis loops of the observed surface magnetization, $M^O(\theta, \phi, H)$, given that $M^T(H) \neq M^S(H)$, for different phases and magnitudes of $\Theta^4(2\omega, \theta, \phi)$.

5. Lüpke, G., D.J. Bottomley, and H.M. van Driel, Second- and third-harmonic generation from cubic centrosymmetric crystals with vicinal faces.

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3 Experimental details

3.0 Overview

The detailed preparation and characterization of the W(110) crystals, ultra-thin films of Fe, and capping-layers of Ag and Au are discussed. The LEED images and AES scans demonstrating the cleanliness and order of the ultra-thin films are shown. Details regarding the construction and calibration of the UHV compatible electromagnet used in the MSHG investigations are given. Technical details regarding the specifications of both the ellipsometer and RAS systems are also described. The different experimental geometries employed for both \textit{in situ} SHG measurements and \textit{ex situ} MSHG measurements are illustrated. The various combinations of sample azimuth, polarization alignment, and electromagnet orientation are also shown.
3.1 Sample preparation

Sub-monolayer ultra-thin films are highly susceptible to contamination. They must be prepared as quickly as possible and in the best possible vacuum, to minimise preparation-contamination. Once they have been prepared, all in situ investigation must also be carried-out quickly, before residual-gas adsorption modifies their properties[1-3]. Protecting the ultra-thin films with a capping-layer of noble metal can minimize the effects of gas adsorption. Provided the capping layer is sufficiently thick and stable, it is even possible to remove the capped ultra-thin films from the UHV environment.

3.1.1 The clean W(110) surface

A tungsten single-crystal with 99.9995% bulk purity was purchased from SPL-Netherlands, to act as the substrate for ultra-thin film deposition. This crystal was shaped like a shallow cylinder 8mm in diameter, 1mm in height, with two 300μm diameter channels spark-eroded through the body, perpendicular to the surface-normal, serving as mounting anchors for the UHV sample-holder. The surface of the crystal was specified orientated and polished 1.4° ±0.1° towards <100>, from the <110> direction. This particular off-cut was chosen, because the resulting vicinal surface is known to have regularly spaced single height atomic steps running in the <001> direction, separated by well-ordered terraces, approximately 10nm in width[4].

Carbon is the principle contaminant of this vicinal W(110) single-crystal[5]. In the UHV environment, this carbon segregates from the bulk to the surface, meaning that even crystals of high bulk-purity will have significant surface contamination. It was therefore unsurprisingly that both AES and LEED detected massive carbon-contamination at the surface of the as-received vicinal W(110) crystal. AES measurements showed a very pronounced carbon-peak at 272eV, while LEED images revealed a clear (15x3) carbon-induced reconstruction of the W(110) surface[5]. This carbon was removed by following the cycling procedure detailed in Grunze et al. [6]. Each cycle consists of heating the crystal to 1500K in 2x10⁻⁸ mB of O₂ for 15 minutes,
followed by several UHV flashes to 2200K. After a great many of these cleaning cycles, AES measurements revealed no carbon-peak at 271eV and the LEED images showed only the oblique (1x1) reconstruction of clean W(110).

![AES amplitude (arb.) vs Energy (eV)](image)

Figure F3.1.1: (A) AES scan of clean and C contaminated vicinal W(110) surface; (B) 145eV LEED image of the clean vicinal W(110) surface; (C) Detail from 160eV LEED image from clean vicinal W(110) surface illustrating spot-broadening.

A more detailed examination of the (1x1) LEED images from the vicinal W(110) sample revealed spot-broadening at certain energies. Such spot-broadening or spot-splitting in LEED pattern is consistent with the presence of well-ordered steps at the surface[7]. The direction of the observed spot-broadening and its magnitude relative to the inter-spot distances is consistent with the presence of well-ordered steps in the <001> direction, separated by approximately 10nm terraces. Without any SPM systems in the laboratory, this observation of spot-broadening was a reassuring verification of vicinality at the single-crystal surface. The synchronous rotation of the broadening, as the sample azimuth was rotated through 90° is strong evidence that the observed broadening was not simply an artefact of electron-optic focusing.
LEED images of the group’s supposedly planar single crystal revealed extensive spot-splitting and spot-broadening over much of sample surface. The LEED analysis indicated that the planar W(110) crystal is, in fact, covered with a high density of well-defined steps running in the \(<1\bar{1}0>\) direction. The width of terraces separating the surface steps on the ‘planar’ W(110) crystal varied across the face of the sample, but was typically just 2nm. When Fe is deposited and annealed on the vicinal W(110) surface (with surface-steps running in the \(<1\bar{1}0>\) direction) step-flow growth is not observed and poorly aligned Fe nanostripes are formed[8]. Since ferromagnetism would be suppressed in any Fe sub-monolayer ultra-thin grown on the ‘planar’ W(110) sample[8], no significant MSHG investigations were carried-out from Fe nanostructures grown on the ‘planar’ W(110) surface.

![Figure F3.1.2: 150eV LEED image of the clean ‘planar’ W(110) surface. The pronounced spot-splitting indicating that the surface is not planar (110), but vicinal (110), with steps running in the \(<1\bar{1}0>\) direction.](image)

3.1.2 The Fe/W(110) interface

A commercial e-beam evaporator was used to evaporate Fe from a 99.99% pure, 1mm diameter source-wire. A quartz crystal oscillator was found to be too insensitive to measure the fluxes used to deposit the ultra-thin Fe films. Instead, the Fe deposition-rate was deduced by comparing the rate of change of the 47eV Fe AES peak-height, as a function of deposition-time, for constant evaporation conditions, with the detailed
analysis of Przybylski et al [9]. The best compromise between flux and stability was achieved with a deposition-rate of 0.25MLmin⁻¹. With a deposition pressure of 2.0x10⁻¹⁰mB, this rate resulted in a preparation-contamination of less than 2%.

Figure F3.1.3: (A) AES calibration of Fe deposition; (B) AES profiling of Fe patches

Within the limits of detection, AES profiles of the surface indicated a constant evaporation flux, across the 8mm diameter surface of the crystal. To prepare the ultra-thin Fe films, the Fe was deposited onto the W(110) surface at room temperature, and then annealed to 800K for 3 minutes[4]. LEED images of sub-monomer as-deposited films have high backgrounds and poorly defined spots, indicating poor surface-order. LEED images of the annealed films show low backgrounds, with sharp, high-contrast (1x1) spots, indicating good pseudomorphic ordering of the annealed Fe films. The observed LEED patterns are in good agreement with previously published images[10]. After annealing the sub-monomer films, a slight reduction in the 47eV Fe AES peak is observed. However, since further annealing at the same temperature does not result in any additional peak-height reduction, this is taken as an indication of re-ordering in the Fe atoms, not desorption.
To increase the speed and accuracy with which *ex-situ* measurements could be made, ultra-thin films of a variety of different thickness were deposited onto different areas of the same W(110) single-crystal surface. This *patchwork* deposition was carried out using a masking technique. For early work, where Ag was used as the capping-material, sixteen discrete patches of Fe were used deposited on the same single-crystal surface. For later, more substantial work, where Au was used as the capping-material, the numbers of discrete Fe patches was reduced to four. This reduction was motivated by the observation of a macroscopic roughness at the centre of the crystal surface. The gradual emergence of this roughness during the cleaning cycles, and the absence of any unusual chemical signature in AES scans of this area, suggested that it was simply a thermally induced roughening of the surface. As a precautionary step, all subsequent optical measurements from the vicinal W(110) surface were made from the roughness-free annulus of the outer 3mm of the crystal. This precaution reduced substantially the surface area available for observation, and consequently the number of Fe patches that could be deposited.

### 3.1.3 Ag capping of Fe/W(110) interface

A standard Knudsen-cell was used to deposit Ag from a 99.99% pure source. To prevent disassociation of Pyrolitic Boro-Nitrate (PBN) components in this cell, the
deposition-temperature needed to be kept relatively low. A deposition-temperature of 1100°C was found to give a deposition-rate of 0.25 ML/min, with a background of just 5.0x10^{-10} mB. This deposition-rate was determined by comparing the rate of change of the 69eV Ag AES peak-height, as a function of deposition-time, with the detailed analysis of Bauer et al. [11].

![Graph](image.png)

**Figure F3.1.5:** AES calibration of Ag deposition using K-cell at 1100°C

These deposition conditions resulted in a preparation-contamination of less than 5%. To form the capping-layer, 20ML of Ag were deposited, at room temperature. It was hoped a film of this thickness would prove a significant barrier to contamination of the Fe films, while not significantly attenuating the SHG signal from the underlying ultra-thin Fe films. Unfortunately, this was not the case; after just a few days of *ex-situ* analysis, a golden miasma or patina became visible on the surface of the crystal. This patina was most apparent at the centre of the crystal, where the macroscopic surface roughness was most pronounced. RA spectra from the centre of the crystal, made before and after the development of the patina, showed significant differences in line-shape. Subsequent *in-situ* AES analysis of the sample revealed massive S contamination of the capping-layer, but this is expected - Ag is a known getter of S. SHG measurements, from the Ag-capped Fe patches on the vicinal W(110) surface, failed to detect any MSHG signal, from any of the patches. Ag-capped Fe films grown on vicinal W(110) are known to be ferromagnetic[9], so some evidence of MSHG should have been observed. The absence
of this signal was taken as tentative evidence that the S had diffused through the Ag capping-layer, contaminated the ultra-thin Fe film, and removed the surface magnetism.

### 3.1.4 Au capping of Fe/W(110) interface

Instead of using a thicker Ag capping-layer to protect the ultra-thin Fe films, attempts were made to deposit Au films to form capping-layers. Au is known to act as a stable capping layer of the ultra-thin Fe film grown on vicinal W(110)[12].

![Graph showing AES calibration of Au deposition using MBE cell at 1600K](image)

**Figure F3.1.6:** AES calibration of Au deposition using MBE cell at 1600K

While the standard K-cell was able to deposit Ag, it could not achieve the temperatures necessary to deposit Au. Alternative methods of depositing Au were examined, including a homemade e-beam evaporator and deposition from a hot tungsten filament, but all failed to provide the combination of high flux and stability necessary to deposit a successful capping-layer. Several months later, a high-temperature effusion cell became available in the laboratory. With this cell, Au was successfully deposited from a 99.99% pure source. The height of the 69eV Au Auger peak was recorded, as a function of room temperature deposition-time, and compared to the detailed analysis of Bauer et al.[11], to determine the rate of deposition. A deposition-rate of 1ML/min was achieved, with a deposition-pressure of $4.0 \times 10^{-10}$ mB at an evaporation-temperature 1600K. These deposition-conditions ensure a preparation-contamination of less than 1%. AES profiles of the sample surface indicated that the Au evaporation flux was constant across the
crystal face, within the tolerance of the detector. 30ML of Au were deposited to form the capping-layer.

3.2 Description of electromagnet

In order to investigate their magnetization-hysteresis, it must be possible to control the sign and magnitude of the magnetic-field applied to the ultra-thin films. This control is most easily achieved when an electromagnet is used to provide the applied-field, and so, one was built. Since it was originally hoped that significant MSHG investigations of ultra-thin Fe films on the W(110) surface would be made in-situ, this electromagnet was made from UHV compatible components only.

Figure F3.2.1: Schematic of UHV compatible electromagnet. The air-gap was adjustable between 20mm and 40mm, with maximum field strengths of 200mT and 100mT, respectively.

The armature was machined from Permalloy, a soft-ferromagnetic alloy with high permeability, and low remanence. The high permeability of Permalloy allows the magnet to be energized with low Joule heating of the windings, while the low remanence minimizes interference with LEED and AES systems. The armature was modular, allowing additional slices of Permalloy to be inserted into the base section, to increase the length of the air gap.
In determining the number of windings necessary to produce useful fields, the expression for the gap-field produced by an electromagnet of constant cross-sectional area, small air-gap \((g)\), many windings \((N)\), moderate currents \((I)\), and a high permeability \((\mu_r)\), was used; \(B_g = \mu_r \frac{NI}{g}\). To produce fields of about 100mT in an air-gap several centimetres wide, this expression predicts the need for approximately 1000 turns, given the limits of the available power supply. In practice, 3000 turns (250m) of Kapton-coated 1mm diameter OFHC Cu wire was used to wind the magnet. 1000 turns were placed on each pole piece, with the remaining 1000 turns on the base section. In practice, the fields generated by the electromagnet were in good agreement with the prediction of the above expression. Fields of approximately 200mT were achieved using an air-gap of 20mm, and 100mT using an air-gap of for a 40mm. Linearity of the gap-field with respect to current is observed up to 150mT and 80mT, for the 20mm and 40mm air-gaps, respectively. Field uniformity across the face of the 8mm diameter crystal is excellent, varying by just 3% with the 20mm air-gap.

![Figure F3.2.2](image)

**Figure F3.2.2:** (A) Field strength of electromagnet as a function of applied current, for different air-gaps; (B) Spatial variation of field-strength within air-gap.

### 3.3 Variable Angle Spectroscopic Ellipsometry

Variable Angle Spectroscopic Ellipsometry (VASE) measurements were made using a commercial rotating-analyser system produced by the French company SOPRA. This
ellipsometer has a useful spectroscopic range of 1.4eV to 5.0eV, and can make measurements with an external angle-of-incidence between 6° and 90°. The calibration of the system was regularly checked, by examining test-wafers of known composition and structure. Recently, Mr. Chris Smith installed twin UVFS lenses on the input- and output-arms of the ellipsometer, giving it “micro-spot” capability. This feature proved useful in probing the Au-capped Fe patches on the vicinal W(110) surface. Using the micro-spot lenses, the FWHM of the beam at the sample is less than 300μm, allowing an individual patch to be probed, without adjacent patches making contributions.

3.4 Reflectance Anisotropy Spectroscopy

During this research, a parallel project within the group was the construction of a novel Infra-Red Reflectance Anisotropy Spectroscopy (IR-RAS) system. Instead of a Photo-Elastic Modulator (PEM), this system employs mechanical components to rotate the polarization of the probe beam, allowing high-sensitivity IR detectors, too slow to follow the high frequency modulation of the PEM, to be used.

Unfortunately, this IR-RAS system was not finished in time to analyse the ultra-thin Fe films grown on the vicinal W(110) surface. Instead, all RA spectra were measured using an Aspnes-type system, borrowed from the Dublin Institute of Technology. Dr. Karsten Fleischer improved upon this RAS system by adding active computer control of the
PMT voltage, replacing existing optical elements with high-quality components, and improving PEM control. These enhancements significantly improved both the SNR and spectroscopic range of the RAS system. The principle behind RA measurements is straightforward. Using a PEM oscillating at $10^5$Hz, the difference between the intensity of light polarized in the $x$-direction, and that polarized in the $y$-direction is measured using a detector synchronized with the modulator’s frequency. At the same time, the average intensity of the reflected light is measured, providing real-time, point-by-point normalization of the intensity difference. The ratio of the intensity difference and the average intensity is proportional to the imaginary part of the optical anisotropy $(\varepsilon_x - \varepsilon_y) [10]$

$$\frac{I_x - I_y}{I_x + I_y} = \frac{\Delta R}{R} = \frac{2\pi d}{\lambda} \text{Im}\left(\frac{\varepsilon_x - \varepsilon_y}{\varepsilon_B - 1}\right)$$

E3.4.1

With a spectroscopic knowledge of $\varepsilon_B$ (the bulk dielectric function) and an approximate value of $d$ (the thickness of the anisotropic layer), the measurement of $\frac{\Delta R}{R}$ leads to a determination of the optical anisotropy of the surface, $\text{Im}(\varepsilon_x - \varepsilon_y)$. In principle, both $\varepsilon_B$ and $d$ can be determined from VASE measurements, however it is often difficult to simultaneously determine unique values of $\varepsilon_B$ and $d$.

3.5 In situ SHG geometries

For both in-situ and ex-situ SHG investigations, a MIRA 900-F fs-laser was used as the fundamental-frequency light source. Pumped with a solid-state VERDI V-10 laser, the MIRA generates 150fs pulses of laser-light reaching peak-powers of approximately $10^5$W. The central output-wavelength of the MIRA is continuously tuneable between 710nm and 980nm (1.25eV to 1.75eV) with a FWHM of about 12nm caused by the time-bandwidth product of ultra-short pulses.
In the UHV chamber, fine-control of sample rotation was not possible, so in-situ investigations could only be performed using polarization-rotation geometries. SHG measurements were carried-out using both off-normal (ON) and normal-incidence (NI) adaptations of the polarization-rotation geometry. In both ON- and NI-geometries, an achromatic IR half-wave plate, mounted on a computer-controlled motorized rotation-stage, was used to rotate the polarization of the fundamental-frequency light. After beam-expansion with a Galilean telescope, the fundamental beam was directed and focussed at the sample to a 40\(\mu\)m FWHM-diameter using multi-stack dielectric mirrors, after it had passed through an OG550 filter to remove any SH-frequency photons. After reflection from the sample, the beam was collimated using a UVFS lens and then directed to a dichroic mirror that transmitted the fundamental-frequency component of the beam into a beam-dump, while reflecting the SH-frequency component into a Glan-air polarizer. The orientation of this polarizer determined the output-polarization alignment of the experiment; \(\hat{s}\) or \(\hat{p}\) in the case of the ON-geometry; \(\perp\) or \(\parallel\) for the NI-geometry. After polarization-selection, the SH-frequency beam passed through a BG39 filter to remove any remaining fundamental-frequency photons, before entering a small monochromator, to be detected using a side-on photon-counting grade PMT. A computer-controlled photon-counter was used to discriminate and count the current-
pulses from the PMT. The fs-laser controller provided an output channel indicating the intensity of the fundamental-beam, allowing real-time normalization of the PMT SHG signal against the input-intensity.

![Figure F3.5.2: Schematic of in-situ SHG NI-polarization-rotation geometry](image)

To use the ON-geometry, and access the high SHG signal from the terrace-site of the surface, it is important that the azimuthal alignment of the sample is correct. If not, then the polar-plots of the surface will not have the correct symmetry, and the SHG data cannot be interpreted correctly. The azimuthal alignment of the sample was carried-out by monitoring the orientation of the LEED pattern while rotating the sample. The only critical alignment for the NI-geometry is that of the output-polarizer with respect to the atomic-steps on the vicinal surface, and this can be checked in the SHG signal, without referring to the LEED. The UHV chamber was configured so that SHG measurements could be made using the NI-geometry, while the sample surface faced towards the evaporation sources in the chamber. It was hoped that SHG measurements could be made during the deposition and annealing of the ultra-thin Fe films, and the subsequent deposition of the capping-layer. Unfortunately, it was discovered that the SHG signal was so low that it was lost in the background-light emitted by the evaporators during deposition. This background-light level was so high that calculations indicated that lock-in techniques would be incapable of extracting the surface SHG signal.
3.6 \textit{Ex situ} MSHG geometries

Outside the UHV chamber, SHG investigations were made using both sample-rotation and polarization-rotation geometries. Because it was not possible to rotate the optical cryostat while it was attached to the LN$_2$ transfer arm, all \textit{ex-situ} sample-rotation experiments were carried-out at room temperature. Because it is large and heavy, it was also not possible to rotate the electromagnet synchronously with the sample, during these experiments. Instead, the SHG signal from the sample was measured, after it had been magnetized with a single pulse from the electromagnet; then SHG signal was measured again, after the sample had been magnetized with a pulse from the electromagnet of opposite polarity. If the sample exhibits a significant remanence, then the two SHG plots will differ slightly in line-shape.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Figure_F3.5.3.png}
\caption{Schematic of \textit{ex-situ} MSHG sample-rotation geometry}
\end{figure}

The room temperature \textit{ex-situ} polarization-rotation geometries used to investigate the MSHG signal are practically identical to those of the \textit{in-situ} geometries. For these measurements, the SHG signal for positive and negative polarities of the applied-field were both measured, at each individual point of the angular scan.
Figure F3.5.4: Schematic of ex-situ MSHG ON-polarization-rotation geometry used for room temperature investigations

Low-temperature ex-situ SHG measurements were made using an optical cryostat. The high-vacuum environment in the cryostat protects the capped ultra-thin films from oxidation, and the laser-ablation of dust onto the sample surface. To reduce the intensity of the laser-spot at the input window, and so minimize artefactual SHG, the sample was pushed into the cryostat as far as possible. In this configuration, it was not possible to perform ON-polarization-rotation SHG investigations; only NI-polarization-rotation measurements could be made.
Figure F3.5.5: Schematic of ex-situ MSHG Ni-polarization-rotation geometry for low-temperature investigations. This geometry was used for to measure both the temperature dependence of the MSHG contrast, and the MSHG-derived hysteresis loops of the surface magnetization.


Experimental results: Linear optics

4.0 Overview

The RA spectrum of the clean and oxidized vicinal W(110) surface are reported for the first time, and compared to existing RA spectra of the planar surface. A significant step-site electronic surface-state is identified on the clean vicinal surface. It is shown that the optical anisotropy of the nanostripes gives rise to only small, broad structures in the RA spectra of the ultra-thin Fe films. It is also shown that the RA spectra of the Ag- and Au-capped Fe ultra-thin films are dominated by anisotropy signals from the capping-layers, largely obscuring the contribution made by the nanostripes. The effect on the RA spectra of cooling the samples is examined. It is demonstrated that the VASE lacks the sensitivity necessary to detect the presence of the ultra-thin films of Fe.
4.1 RAS of clean vicinal W(110)

Existing RA spectra of the clean planar W(110) surface have measured a broad positive anisotropy centred at 3.0eV and a broad negative anisotropy at 3.9eV, that are both quenched on oxidation[1]. Calculations in the same reference indicate that these optical anisotropies arise from electronic surface-states. RA spectra of the clean vicinal W(110) surface measured in this study (with the Aspnes-type geometry described in Section 3.4) also show a broad positive anisotropy at low energies and a broad negative anisotropy at higher energies, but these are now centred at 3.1eV and 4.6eV, respectively. Since the only physical difference between these two surfaces is the presence of regular monatomic-height steps on the vicinal surface, it must be these step-sites that must give-rise to the differences in the spectra. Step-site contributions to the spectra of both Cu(111)[2] and Au (110)[3] have also been observed in this spectral range.

![Image: Room temperature (RT) RA spectra of clean planar W(110)[1] and clean vicinal W(110)]

F4.1.1: Room temperature (RT) RA spectra of clean planar W(110)[1] and clean vicinal W(110)

The adsorption of O$_2$ on the vicinal W(110) surface quenches the RA spectra to almost zero, in direct analogy to the behaviour of the planar surface. This indicates that oxidation removes the electronic surface-states associated with both the step- and terrace-sites.
4.2 RAS of ultra-thin Fe films and nanostripes

The RA spectra of the nanostripes formed by the annealing of sub-monolayer ultra-thin films of Fe on the vicinal W(110) surface are given in figure F4.2.1A. Since these nanostripes are all of monatomic-height, the different film thicknesses (0ML to 1ML of Fe, in 0.2ML increments) correspond to stripes with average widths of 0nm, 1.8nm, 3.6nm, 5.4nm, 6.4nm, and 9.0nm, respectively. The principle feature of this series of RA spectra is the rapid dampening of the broad positive anisotropy, followed by a much slower dampening of the negative anisotropy. In contrast to the quenching observed on oxidation, there is evidence of a new broad surface optical anisotropy centred at 4.1eV, introduced by the Fe nanostripes. This optical feature also persists at low integer Fe monolayer coverages, exhibiting a slight dampening as the Fe increases. With no comparable RA spectra from films grown on the planar W(110) surface available in the literature to serve as a comparison, it cannot be determined whether this new optical anisotropy arises from step- or terrace-sites in the Fe film.

F4.2.1: (A) Room temperature (RT) RA spectra of sub-monolayer ultra-thin films of Fe grown on W(110); (B) RT RA spectra of integer monolayer ultra-thin films grown on W(110)

Comparing the different RA spectra illustrated in figure F4.2.1, it is clear that the greatest changes in the optical anisotropy occur during the deposition of the first monolayer. After this first monolayer, the deposition of additional Fe changes the RAS spectra only very slightly - a small but monotonic reduction in the amplitude of the negative anisotropy at 4.1eV is observed.
4.3 RAS of Ag-capped ultra-thin Fe films and nanostripes

In increments of 0.25ML, Fe patches of between 0.25ML and 3.0 ML in thickness were deposited on the face of the vicinal W(110) sample. This patchwork sample was annealed to form well-ordered Fe nanostripes from the sub-monolayer ultra-thin films, capped with 18 ML of Ag, and removed from the UHV chamber. To maximize disorder in the capping layer, the Ag was deposited at room temperature. Ag is a known getter of S, so it was expected that the Ag-air interface would rapidly contaminated in the laboratory atmosphere, further reducing the surface anisotropy of the capping-layer. The RA spectra from this Ag-capped sample should, therefore, probe only the buried Ag-Fe-vicinal W(110) interface, with very little signal coming from the disordered and contaminated Ag-capping layer.

F4.3.1: Room temperature RA spectra of Ag-capped ultra-thin Fe films grown on vicinal W(110). The horizontal line passing through the spectra of each Fe film represents the 'zero'-line of the spectra. To aid clarity of presentation, the 3.0ML to 0.75ML spectra are each offset by 5 RAS units, while those of the 0.5ML and 0.25ML spectra are offset by 10 and 20 RAS units, respectively.
The RAS spectra of the Ag-capped Fe ultra-thin films and nanostripes grown on vicinal W(110) are shown in F4.3.1. These spectra are clearly different to those of the uncapped Fe films. Compared to the uncapped spectra in F4.2.1, the most pronounced feature of the Ag-capped RA spectra in F4.3.1 is the order-of-magnitude greater anisotropy observed for the uncapped 0.25ML Fe film. The RA spectrum of the Ag-capped 0.25ML Fe exhibits two large positive anisotropies, the first a broad structure at 2.0eV, the second a sharper structure centred at 3.45eV. The comparatively sharp 3.45eV peak is also evident in the RA spectrum of the Ag-capped 0.5ML Fe ultra-thin film (corresponding to 20 atom-wide Fe nanostripes) on vicinal W(110), but its amplitude is significantly reduced, while the broad 2.0eV peak has all but disappeared. As the thickness of the ultra-thin Fe film increases, the 3.5eV peak continues to diminish and is effectively absent from the spectra of Fe films thicker than 1ML. The significant difference between the 3.5eV peak-height in the RA spectra of the Ag-capped 0.25ML patch and higher coverages indicates that the optical anisotropy of the Ag-W(110) interface at this energy is significantly greater than that of the Ag-Fe(110) and Fe-W(110) interfaces. Although no existing RA spectra of the Ag-W(110) interface are available, a number of RAS investigations of the clean Ag(110) surface have been published [3-5] (these studies use a different sign convention, but are easily adapted). The RA spectra of the Ag(110) surface depends on preparation conditions— for the planar Ag(110) surface, the RA spectrum consists of a single narrow, positive peak at 3.9 eV, while for the vicinal surface (with steps running in the \(<110>\) direction) a derivative line-shape at the same energy is observed. These features are attributed to intra-band transitions and optical absorption by a surface plasmon. The 3.5eV peak observed in the RA spectrum of the Ag-capped 0.25ML Fe ultra-thin film (corresponding to 10 atom-wide Fe nanostripes) is comparable in magnitude and line-shape to that of this 3.9eV Ag(110) peak. Since the majority of the RAS signal from the Ag-capped 0.25ML Fe film originates at the Ag-W(110) interface, it is plausible that this spectral feature arises from similar optical effects.

For the Ag-capped Fe ultra-thin films between 0.5ML Fe and 2.0ML in thickness, the 2.0eV peak is absent from the RA spectra, but develops again for thicker films. It is a well-defined spectral feature in the 2.75ML and 3.0ML Fe films. At coverages above
2ML, Fe deposited onto the vicinal W(110) surface forms into islands aligned with the steps, on top of a pseudomorphic Fe(110) monolayer. Since its peak-height develops at the coverages at which these islands form, it is likely that the 2.0eV peak is associated with the optical anisotropy at the interface between these Fe islands and the Ag capping layer.

4.4 RAS of Au-capped ultra-thin Fe films and nanostripes

Three different Au-capped Fe W(110) samples were prepared; the first sample was composed of Fe nanostripes with average widths of 0nm, 2.25nm, 4.5nm, and 6.75nm (corresponding to 0ML, 0.25ML, 0.5ML, 0.75ML annealed ultra-thin Fe films) arranged in four patches, grown on the vicinal W(110) surface, and capped with 30ML of Au; the second sample was composed of 0ML, 1.0ML, 2.0ML, and 3.0ML ultra-thin Fe films, arranged in four patches, grown on the same vicinal W(110) surface, and capped with the same quantity of Au; the third sample was composed of a 1ML ultra-thin Fe film on the planar W(110) surface, capped with 30ML of Au.

Compared to the Ag-capped ultra-thin Fe films shown in F4.3.1, the RA spectra of these Au-capped Fe ultra-thin films, shown in F4.4.1 are relatively complicated. These spectra share the same essential features; a broad negative anisotropy at about 2.0eV; a sharp positive anisotropy at 3.7eV; with additional negative anisotropy structure between a broad negative anisotropy between 3.8eV and 5.0eV; with additional structure between 4eV and 5eV, and 2.5eV and 3.0eV. Since these features are observed from both planar and vicinal surfaces, it is clear that they cannot be attributed to the presence of the well-ordered steps found only on the vicinal W(110) surface. Many of the spectral features observed in the RA spectra of the Au-capped ultra-thin Fe films have already been observed in existing RA investigations of the Au(110) surface. The RA spectra of a polished Au(110) surface in ambient air has sharp positive peaks at 3.7eV, 2.8eV, and 2.5eV, while the RA spectra of UHV clean Au(110)-(1x2) has broad negative peaks around 2.0eV and 4.5eV[6].
Although the gross lineshape of the RA spectra of Au-capped Fe films seem to be dominated by the anisotropy of the Au capping-layer, some differences between the spectra of the different Fe films are observed. While the RA spectra of the Au-capped 0ML and 0.25ML Fe ultra-thin films are very similar, there is a pronounced difference between the spectra of the 0ML and 0.5ML Fe films. This difference between the spectra of the Au-capped 0ML and 0.5ML Fe films is the same as that observed between the spectra of the 0ML and 3ML Fe ultra-thin films, indicating that the Fe-induced changes in the RA spectra have effectively finished after just 0.5ML. The obvious difference between these 0ML and 0.5ML Fe films is the contact area between
the Au-capping layer and the vicinal W(110) surface. The observations of different spectra for high- and low-sub-monolayer coverage may then be explained in terms of different weighting of the contributions from the Au-vicinal W(110) and Fe-Au interfaces. Since the RAS of the Au(110) surface is known to depend sensitively on surface morphology, it is unsurprising that the optical anisotropy of the Au-W(110) interface should be significantly different to that of the Au-Fe(110) interface, and that different weighting of these two anisotropies should result in appreciably different spectra.

F4.4.2: Differences between RA spectra of the Au-capped 0ML and 0.5ML Fe ultra-thin films (F4.4.1A), and 0ML and 3ML ultra-thin films (F4.4.1A), both grown on vicinal W(110).

RAS investigations of the Au-capped Fe ultra-thin films were also made at cryogenic temperatures. These measurements were motivated by the observation of significant temperature dependence in the crystallographic SHG signal from some of the Fe films. These low-temperature RAS measurements were made from samples mounted in an optical cryostat, where perfect crystallographic alignment and orientation was difficult.
On cooling, the features of the RA spectra sharpened-up, and consequently increased slightly in amplitude. The sharp peak around 3.5eV is blue-shifted by 0.07eV, an effect that is in accordance with the order-of-magnitude changes predicted by ab initio calculations of electron-phonon interaction[7]. The shoulder structure at 2.8eV resolves itself into a well-defined peak (as present in the RAS of the polished Au(110) surface in ambient air). The pronounced changes observed in the SHG signal were not reproduced in the RA signal. While the samples were mounted in the cryostat, low-temperature MOKE-RAS investigations were carried-out. Given the limits placed on the geometry by the design and dimensions of the cryostat and electromagnet, only an in-plane magnetic-field could be applied. No significant MOKE-RAS signal was detected from any of the ultra-thin Fe films, for this magnetization geometry.

4.5 VASE of Au-capped ultra-thin Fe films and nanostripes

Ellipsometry measurements were performed on the Au-capped 0ML, 1ML, 2ML and 3ML Fe films grown on the vicinal W(110) surface. When the values of tan\(\Psi\) and cos\(\Delta\) from the four Au-capped ultra-thin Fe films are measured and compared, they are found to be practically identical. Those differences that do exist are within the error associated with translating the sample to access the different patches of Fe deposited onto the vicinal W(110) surface.
Having demonstrated that the ellipsometer cannot detect the presence of the ultra-thin Fe films, the tan\(\Psi\) and cos\(\Delta\) data were used to deduce the thickness of the Au-capping layer. This determination was made using a two-layer model; a Au thin-film of unknown thickness, on top of a semi-infinite substrate of W(110). The library files in the ellipsometer database provided the dielectric function of the Au-capping layer and W(110) substrate. The thickness-value of the Au capping-layer determined in this way was 14nm, in good agreement with the AES determination of 12nm (30ML x 4Å).


Experimental results: \textit{in situ} SHG

5.0 Overview

The SHG-signal from the clean vicinal W(110) surface is investigated, and found to depend sensitively on residual gas contamination. Oxidation of the vicinal W(110) surface is found to induce massive changes in the observed SHG-signal from the surface. The SHG-signal from the ultra-thin Fe films grown on the vicinal W(110) surface are shown to be small, and not strongly dependent on film-thickness, or film-order. It is demonstrated that residual gas contamination of the ultra-thin Fe films quickly modifies the observed SHG-signal, even at $5 \times 10^{-11}$ mB. These changes in SHG-signal are large enough to obscure the observation of any MSHG contribution to the SHG-signal from the ultra-thin Fe films. The motivations for capping the ultra-thin Fe films for stable ex-situ investigations are discussed.
5.1 Clean vicinal W(110)

Both Off-Normal (ON) and Normal-Incidence (NI) polarization-rotation investigations were carried-out on the clean vicinal W(110) surface. The SHG-signals observed from the clean vicinal W(110) surface were very low, in some cases comparable to the 20Hz dark-count of the PMT. Even though the base-pressure of the UHV chamber was approximately of $4 \times 10^{-11}$ mB, the SHG-signal from the clean vicinal W(110) surface was found to be very sensitive to contamination from residual-gas. In figure F5.1.1 are shown the ON-Py plots measured from the freshly-cleaned vicinal W(110) surface, and the same surface after 60 minutes of room temperature exposure to the UHV residual-gas (with a base pressure of $4 \times 10^{-11}$ mB, 60 minutes of UHV exposure is equivalent to just a few percent of a monolayer of H$_2$). Evidently, even these tiny quantities of adsorbed gas induce substantial changes in the non-linear polarizability of the W(110) surface. This demonstrates the high sensitivity of SHG to surface adsorbents.

![Graph showing ON-Py SHG plots of the clean vicinal W(110) surface and residual-gas contaminated vicinal W(110) surface.](image)

*Figure F5.1.1: ON-Py SHG plots of the clean vicinal W(110) surface and residual-gas contaminated vicinal W(110) surface. (\(\varphi = 0^\circ \Rightarrow \vec{E}(\omega) \text{ in } y - z \text{ plane;}\)

\[\varphi = 90^\circ \Rightarrow \vec{E}(\omega) \parallel \hat{x}.\]*)

To examine the effect of residual-gas contamination at the step-sites of the vicinal surface, polarization-rotation SHG investigations were also carried-out using the NI-geometry (in this geometry a large proportion of the SHG-signal originates at the step-sites, see Section 2.3 and Section 2.4).
The SHG-signal observed in this geometry was so small that long integration-times were necessary to make meaningful measurements. Because they took so long (typically 20 minutes; 10s integration at 90 points), it was difficult to finish these measurements before the plots were skewed by residual-gas contamination. This skewing is clearly evident in the NI-∥ plot, illustrated in figure F5.1.2.

**Figure 5.1.2:** NI-∥ SHG plots of the clean vicinal W(110) surface. Skewing from residual-gas adsorption during measurement is evident. ( ϕ = 0° ⇒ E(ω)|| x; ϕ = 90° ⇒ E(ω)|| y).

The magnitude of individual elements of the $\mathcal{P}^\omega_\omega$ tensor may be investigated, by fixing the input- and output-polarizations used in the NI-geometry. Using the results of Table T2.5.6, it is possible to show that a NI-⊥ SHG polar measurement results in an intensity of $I(2\omega) \propto |B|^2 I^\omega(\omega)$ and $I(2\omega) \propto |A|^2 I^\omega(\omega)$, for $ϕ = 0°$ and $ϕ = 90°$, respectively. In this way, it was possible to monitor the magnitudes of $\chi^{C}_{xxx} = A$ and $\chi^{C}_{xyy} = B$ as a function of exposure to the UHV residual-gas. The exposure (in monolayers of H$_2$) was calculated from the 4x10$^{-11}$mB base-pressure by assuming that the residual gas consisted solely of H$_2$ with a unity sticking-coefficient on the W(110) surface. A kink is observed in the magnitudes of both $\chi^{C}_{xxx}$ and $\chi^{C}_{xyy}$, for 0.1ML of H$_2$ contamination. The
fact that both elements show a kink at the same exposure indicates a common underlying origin behind the effect. Unfortunately, the nature of this effect could not be determined.

![Graph](image)

**Figure 5.1.3:** Magnitude of some $\gamma^C_\theta$ elements as function of residual-gas adsorption at $4 \times 10^{11}$ mB, measured using the NL-\perp SHG geometry for $\phi = 0^\circ$ and $\phi = 90^\circ$. (A unity sticking coefficient is assumed: 25 min~0.1 ML of contamination).

### 5.2 Oxidation of vicinal W(110)

RA investigations have shown that RT oxidation quenches the optical anisotropies of both the vicinal and planar W(110) surfaces. NL-polarization-rotation SHG investigations were carried-out to determine if a similar quenching of the non-linear optical response also occurs. In fact, instead of observing a quenching of the response, a massive increase in the SHG-signal was observed. Figure F5.2.1, illustrates the NL-\perp SHG plots measured from the clean and RT oxidized vicinal W(110) surface. The oxidation of the sample was achieved by exposing the sample to $3 \times 10^7$ mB of O$_2$ at room temperature for 10 minutes (~150L). Despite this heavy dosing, it is known that the W(110) surface becomes saturated with O$_2$ after the adsorption of 0.75ML, at RT[1]. Therefore, the increase in the SHG-signal by a factor of 200 is due to the addition of just 0.75ML of extra material, demonstrating the remarkable surface sensitivity of SHG.
An inverse relationship is known to exist between the magnitude of SHG measured from a surface, and the work-function of that surface[2]. Because metal oxide surfaces are generally less polarizable then clean metal surfaces, the oxidized W(110) surface should produce less SHG-signal than the clean W(110) surface. This is clearly not the case, so factors other than simple work-function shifts must be responsible for the changes in the SHG-signal. To gather further information on this interesting behaviour, the magnitude of the tensor elements, $\chi^C_{xxx} = A$, $\chi^C_{yyy} = B$, and $\chi^C_{pxy} = F$, were monitored as a function of O$_2$ exposure, using the same fixed polarization geometry used to investigate the role of residual gas contamination. The measurements made for room temperature exposure to O$_2$ with backpressures of $3\times10^{-8}$ mB and $3\times10^{-9}$ mB are illustrated in figure F5.2.2. As the surface oxidation progresses, the magnitudes of these tensors elements undergo significant variation, exhibiting multiple peaks and kinks.
Figure 5.2.2: Magnitude of $\chi^C$ elements as function of oxidation, measured using the NI-\perp SHG geometry for $\phi = 0^\circ$ and $\phi = 90^\circ$ and the NI-\parallel SHG geometry for $\phi = 45^\circ$.

It is evident that the magnitudes of $\chi_{xxx}^C$, $\chi_{xyy}^C$ and $\chi_{xvy}^C$ depend on both the quantity of O$_2$ adsorbed at the surface and the backpressure at which the oxidation takes place. This is a strong indication that surface-dynamics play an important role in the oxidization of the vicinal W(110) surface, a supposition supported by existing investigations demonstrating the sensitive dependence of the O$_2$ sticking-coefficient on the magnitude and direction of off-cut for the vicinal W(110) surface. The origin of this effect is attributed to the diffusion of the gas molecules adsorbed at the step-sites onto the terrace-sites of the surface. In an effort to observe this step-to-terrace diffusion with SHG, the magnitude of $\chi_{xxx}^C$ was monitored as the surface was exposed to 30s pulses O$_2$ at 3x$10^{-8}$mB, separated by 20 minutes relaxation periods. Having flashed the TSP immediately before preparing the clean vicinal W(110) surface, the pressure recovered to 2x$10^{-10}$mB, 90s after the O$_2$ pulse had ended, and then slowly continued to fall further. Despite their short duration, changes in $\chi_{xxx}^C$ were observed for up to 7 minutes after the end of the O$_2$ pulses, as illustrated in figure F5.2.3. Since no new O$_2$ is being adsorbed on the surface during this time, the changes in $\chi_{xxx}^C$ must be due to the diffusion of the O$_2$ across the surface, finding its minimum energy configuration.
Both ON- and NI-polarization-rotation investigations were carried-out on sub-monolayer and integer-monolayer ultra-thin Fe films grown on the vicinal W(110) surface. Even when the high-count ON-Py geometry is used, the SHG-signal from these ultra-thin films is very small. With SHG-signals of this size, the detection of any MSHG contribution would be very challenging. In figure F5.3.1, the ON-Py plots of as-deposited sub-monolayer ultra-thin Fe films, and the nanostripes they form after suitable annealing, are shown.

Although LEED images indicate a clear improvement in surface-order on annealing, only modest changes in the ON-Py SHG-plots of the ultra-thin films occurs. This is surprising, SHG is usually a sensitive probe of surface morphology, and it was expected the formation of the nanostripes from the disordered ultra-thin films would result in a very pronounced change in the observed SHG-signal. Another surprising feature of the SHG-plots is the poor correlation between width of the Fe nanostripes, and the amplitude and line-shape of the SHG-signal. The ON-Py plots of the as-deposited 0.25ML, 0.5ML and 0.75ML ultra-thin Fe films grown on the vicinal W(110) surface are almost indistinguishable. Even the ON-Py plots of ultra-thin Fe films with integer-
monolayer thickness, shown in figure F5.3.2, show no significant variations in amplitude or line-shape.

Figure F5.3.1: (A) Room temperature (RT) ON-Py SHG plot of disordered as-deposited sub-monolayer ultra-thin Fe films on vicinal W(110); (B) RT ON-Py SHG plot of annealed sub-monolayer ultra-thin Fe films on vicinal W(110); (C) RT Difference plot of as-deposited and annealed sub-monolayer ultra-thin Fe films on vicinal W(110).
Figure F5.3.2: Room temperature ON-Py SHG plots of annealed integer monolayer ultra-thin Fe films on vicinal W(110)

NI-polarization-rotation investigations proved equally insensitive to both the thickness of the ultra-thin Fe films, and the formation of the nanostripes from the sub-monolayer ultra-thin film. Because the Fe evaporation source emitted too much light during deposition, it was not possible to continuously monitor the magnitudes of $\chi_{xxx}^C$, $\chi_{xyy}^C$ and $\chi_{xyz}^C$ as a function of Fe coverage, in the NI-geometry. In contrast to its comparative insensitivity to the thickness and morphology of the ultra-thin Fe films, the SHG-signal exhibits pronounced sensitivity to residual-gas contamination of the films. Although it is observed in both ON- and NI-geometries, the effect of this contamination is more pronounced in measurements made using the ON-geometry. As shown in figure F5.3.3, this is especially true for the ON-Sy plots, where residual-gas adsorption during the measurement skews the plots significantly.
The small SHG-signal observed from the ultra-thin Fe films, and the sensitivity of that signal to residual-gas contamination has critical implications for any proposed in-situ MSHG investigations of the Fe nanostripes. Because the SHG-signal is so low, long integration-times would be necessary to achieve the necessary SNR to isolate the small MSHG contribution to the SHG-signal. However, if these long integration-times were used, the resulting SHG-plots would be skewed by residual gas contamination, potentially obscuring any shifts caused by the MSHG contribution. With the higher intensities provided by an OPO and regenerative amplifier, these MSHG measurements could be made quickly enough to avoid this problem, but to make useful MSHG measurements with the MIRA fs-laser available in the lab, a different approach must be taken. As described in section 3.1, patchwork samples composed of ultra-thin Fe film of different thickness were prepared on the surface of the vicinal W(110) crystal, and capped with either Ag or Au. With the protection afforded by these capping-layers, long integration-times could be used to improve the SNR of the SHG signal, without any concerns over contamination. It was also hoped that the lattice mismatch between the ultra-thin Fe films and the capping-layer might strain the Fe nanostripes, increasing the surface anisotropy, and thereby further enhancing the SHG signal. Instead of depositing thin capping-layers and investigating the SHG-signal from the Fe nanostripes *in-situ*, it was decided to immediately prepare samples with capping-layers thick enough to allow

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Figure F5.3.3: Room temperature ON-Sy SHG plots of freshly prepared and residual-gas contaminated 1ML ultra-thin Fe films
the sample to be removed from the UHV chamber, for *ex-situ* investigations. In addition to being easier to perform, these *ex-situ* investigations are important in determining if the Fe nanostripes can survive the transition from the UHV environment to ambient conditions. Any future technological application of ferromagnetic nanostripes will exploit the properties they exhibit in the ambient environment, not the UHV chamber.

Experimental results: 

ex situ SHG

6.0 Overview

It is shown that the presence of the Au capping-layer massively enhances the observed SHG-signal from the ultra-thin Fe films and nanostripes. An EFISH-like effect is observed in the Au capping-layer, but its deleterious effects are minimized by adopting the normal-incidence SHG geometries. Small MSHG contributions to the SHG-signal are observed at room temperature, and large MSHG contributions are observed at 80K. MSHG contributions are measured from the Au-capped 10 atom-wide Fe nanostripe (0.25ML Fe ultra-thin film), demonstrating the sensitivity of MSHG as probe of surface magnetization. MSHG hysteresis loops are measured from the ultra-thin films and nanostripes, and the hysteresis of the film’s surface magnetization deduced using the expression developed in section 2.8. The hysteresis loops of certain ultra-thin films exhibit behaviour consistent with the presence of a surface magnetization gradient across face the film. The temperature dependence of the MSHG contrast from some of the ultra-thin films and nanostripe samples are similarly consistent with the premise that a spatial variation of the surface magnetization exists.
6.1 SHG: Ag-capped ultra-thin Fe films and nanostripes

Capping of the Fe ultra-thin films was first carried-out using Ag, principally because it was the only noble metal that could be deposited by the evaporators available in the lab, at the time. Ag is known to enhance both the Curie-point and average magnetic-moment of the Fe atoms in the ultra-thin films[1]. Although it was thought that an 18ML capping-layer would provide weeks of protection, a golden patina was observed on the sample surface after just a few days ex-situ exposure. SHG-investigations of the Ag-capped sample were only made after the discovery of this contamination. These were carried-out using both the sample-rotation and polarization-rotation geometry, with MSHG investigations limited to the ON-polarization-rotation-geometry, at room temperature.

![Figure 6.1.1](image_url)

**Figure 6.1.1:** Room temperature sample-rotation sP SHG polar-plots from the Ag-capped ultra-thin Fe films grown on the vicinal W(110) surface using a 45° AOI.

The sP-plots from several Ag-capped Fe ultra-thin films grown on the vicinal W(110) sample are illustrated in figure F6.1.1. Relative to in-situ measurements, no substantial increase in the SHG-signal is observed, but the protection afforded by the capping allows longer integration times to be used, increasing the SNR in the plots. The SHG-signal of these Ag-capped Fe films appears to reduce as a monotonic function of Fe-coverage, over the full 0ML to 3ML range. Such consistent changes in the SHG-signal...
were not observed in the *in-situ* measurements, indicating that the Ag capping-layer improves the Fe coverage-distinction of the SHG-signal. Although the development of the golden patina suggests that contamination of the ultra-thin Fe films may have occurred, MSHG investigations of the Ag-capped Fe films on the vicinal W(110) substrate were still carried-out. Since no optical cryostat was available, these investigations were limited to Ag-capped ultra-thin Fe films thicker than 1ML, where it was expected that the Curie point would be greater than room temperature. These MSHG investigations were carried-out using several different combinations of output-polarization, sample-orientation, and applied-field orientation. No MSHG was observed in any of the SHG-plots, for any of the Ag-capped Fe films. The Ag-capped Fe films grown on vicinal W(110) are known to be ferromagnetic[1], so some evidence of MSHG should have been observed. The complete absence of MSHG signal from all of the plots was taken as evidence that the Ag capping-layer had failed and contamination of the ultra-thin Fe films had occurred.

\[\text{Figure 6.1.2: Room temperature sample-rotation SHG polar-plots from the Au-capped 1ML ultra-thin Fe film using a 45°AOI}\]

### 6.2 SHG: Au-capped ultra-thin Fe films and nanostripes

Instead of preparing another patchwork sample with a far thicker Ag capping-layer, a Au capping-layer was deposited using a newly arrived high-temperature effusion cell.
Such Au capping-layers are known to be very robust. At first, it appeared that this Au-capping layer was an unmitigated success – the SHG signal observed from the Au-capped ultra-thin Fe films was twenty-times greater than that observed from uncapped films. Admittedly, strange asymmetries and spikes were observed in the SHG-plots, but these were initially attributed to poor optical-alignment, and inadequate light-proofing of the PMT housing. However after several days of improving the alignment and stability of the arrangement, these odd structures persisted. It was then discovered that a sample translation of $100\mu m$ with respect to the laser spot induced a sharp change in the SHG-signal, followed by a gradual recovery to its original value. This effect is illustrated in Figure 6.2.2. The strange peaks and asymmetries in the SHG-plots can be attributed to this effect, since slight translations of the sample are inevitably associated with the mechanical rotation of the sample.

![Figure 6.2.1: Illustration of the EFISH-like effect in the SHG-signal from the Au-capped ultra-thin Fe films](image)

Observations of analogous behaviour have been reported in SHG investigations of native oxide coated Si wafers[2]. Here, the origin of effect is well understood - the incident photons excite electrons from the surface region of the semi-conducting Si into the insulating layer of SiO$_2$, establishing a local $E$-field there that modifies the SHG signal through the EFISH-effect. It is not possible to establish an $E$-field from trapped-charges in a sample composed of three layers of metallic conductors, so a different
process is responsible for the effect in the case of the Au-capped ultra-thin Fe films on the vicinal W(110) surface. Both modest heating of the sample, and placing the sample in a High Vacuum (HV) environment, were found to significantly reduce the magnitude of the EFISH-like effect, indicating that the effect is likely due to the adsorption of atmospheric contaminants. The EFISH-like effect is most pronounced in Pp-plots and almost entirely absent in Ss-plots and SHG-signal measured using the NI-geometry, demonstrating that this contamination makes only significant out-of-plane contributions. The existence of this effect has a significant impact on the type of SHG investigations that can be carried-out on the Au-capped ultra-thin Fe films grown on the vicinal W(110) surface. The effect skews sample-rotation SHG measurements, causing distortions large enough to prevent unique fits of data from being made. Therefore, SHG investigations are effectively limited to the polarization-rotation geometry, where precession of the laser-spot at the sample can be made extremely small. These polarization-rotation geometry investigations proved very successful, reproducibly measuring high SHG-signals with good SNR, devoid of the aberrant spikes observed in the sample-rotation investigations. The SHG-signal from the Au-capped ultra-thin films are up to two orders-of-magnitude greater than those observed from the bare films and Ag-capped films. Using the ON- geometry, excellent patch-distinction was observed in each of the four common output-polarization/sample-orientation combinations. The significant difference in both the magnitude and line-shape of the SHG-plots from the Au-capped 0ML patch, and Au-capped Fe films, demonstrates that a significant proportion of the SHG-signal originates at the Fe interface. This contrasts strongly with the RA spectra observed from the Au-capped Fe films, where the anisotropies of the Au capping-layer dominated the optical response. The ratio of the SHG signal from the P- and S-polarizations alignments is approximately 5:1 for the Fe films, but just 1:1 for the 0ML patch. This indicates that the Au-capped Fe films have a much greater out-of-plane response, than the Au-capped 0ML patch. In the NI geometry, the Sx and Py alignments converge to the ||-alignment (the steps lie in the direction parallel to the output polarizer), while the Px and Sy alignments converge to the ⊥-alignment (the steps lie in the direction perpendicular to the output polarizer). Because the SHG signal in these plots is composed of only in-plane contributions, the large differences in SHG signal between the 0ML patch and Fe films are not observed. The different SHG-plots
measured during these ON- and NI-geometry investigations are given in the following section.

### 6.3 MSHG: Room temperature polar-plots

Extensive room temperature SHG investigations were carried-out on the Au-capped integer-monolayer patchwork sample, using both ON- and then NI-polarization-rotation geometries, in an effort to detect any MSHG contribution.

![Figure 6.3.1](image)

**Figure 6.3.1:** Room temperature Off-Normal (45° AOI) MSHG plots of Au-capped integer monolayer Fe films grown on vicinal W(100) using ±80mT applied field. **(A)** SxMx-geometry, **(B)** PxMx-geometry, **(C)** SyMz-geometry, and **(D)** PyMy-geometry.

Despite the high signal, and good SNR in the SHG-plots from these measurements, statistically significant MSHG contribution was observed from just three configurations.
Using these three geometries, MSHG contributions to the SHG-signal were detected from each of the Au-capped ultra-thin Fe films on the vicinal W(110) substrate.

![Graph A](image)

**Figure 6.3.2:** Room temperature Normal Incidence MSHG plots of Au-capped integer monolayer Fe films grown on vicinal W(100) using ±80mT applied field. (A) ||-Mx-geometry and (B) \perp-Mx- geometry.

The MSHG contributions are difficult to observe in the raw data, but they are present, demonstrated by the observation of a non-zero MSHG contrast. As shown in figure F6.3.3, unlike the 0ML patch, the Au-capped Fe films exhibit non-zero MSHG contrasts that depend on a definite way on the polarization angle $\varphi$. The lack of MSHG signal from the 0ML patch, indicates that both the ON and NI geometries are robust and free of artefactual MSHG contributions. The solid lines in the MSHG contrast plots are least-squares best-fits, generated from the relative differences of fits for the SHG-signal for “positive” and “negative” magnetizations, respectively. In these plots, the functional dependence of the MSHG contrasts on $\varphi$ compares well with the contrast models developed in section 2.6, indicating good agreement with the phenomenological model. The reproducible observation of MSHG from the sample demonstrates the successful magnetization of the Au-capped ultra-thin Fe films.
Figure 6.3.3: RT MSHG contrast plots of Au-capped integer monolayer Fe films grown on vicinal W(100) using ±80 mT applied field. (A) ON SxMx-geometry, (B) NI \|-Mx-geometry and (C) \|/Mx-geometry. For clarity, the contrast plot from each Fe film has been 0.25.

The functional dependence of $E^C(2\omega;\varphi)$ and $E^M(2\omega;\varphi)$ of on $\varphi$ were deduced using the techniques discussed in section 2.7.1 and 2.7.2. The values of $E^C(2\omega;\varphi)$ and $E^M(2\omega;\varphi)$ determined using the least-squares best-fits of the SHG-plots (section 2.8) agrees well the determination made using algebraic extraction from the raw data (section 2.7.2).
Table 6.3.1: Fourier components of SxMx plots of Au-capped ultra-thin 1ML Fe films along with standard deviation in values, as determined by least squares fit.

<table>
<thead>
<tr>
<th>Patch</th>
<th>$E^C(2\omega;\varphi)$</th>
<th>$E^M(2\omega;\varphi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sin2$\varphi$</td>
<td>DC</td>
</tr>
<tr>
<td>0ML Fe</td>
<td>42.0(2)</td>
<td>-0.02(8) - i0.00(8)</td>
</tr>
<tr>
<td>1ML Fe</td>
<td>46.5(2)</td>
<td>0.21(8) + i0.50(8)</td>
</tr>
<tr>
<td>2ML Fe</td>
<td>48.6(2)</td>
<td>0.13(8) - i0.17(8)</td>
</tr>
<tr>
<td>3ML Fe</td>
<td>37.2(2)</td>
<td>0.23(8) + i0.17(8)</td>
</tr>
</tbody>
</table>

Figure 6.3.4: $E^C(2\omega;\varphi)$ and $E^M(2\omega;\varphi)$ deduced from the (A) ON SxMx-, (B) N1 Mx- and (C) ±-Mic-plots in F6.3.1 and F6.3.2. In these plots, the open-circles designate values determined from the algebraic manipulation of the data, while the solid lines are the values determined from the fits of the SH-plots.
The functional dependences of both $E^C(2\omega;\varphi)$ and $E^M(2\omega;\varphi)$ on $\varphi$ are in good agreement with those predicted in the phenomenological model (see E2.5.2 and T2.5.5 and T2.5.6). For the SxMx- and ||-Mx-plots, $E^C(2\omega;\varphi)$ and $E^M(2\omega;\varphi)$ are shown to be of the form $a \sin \varphi$ and $b + c \cos 2\varphi$, respectively; for the \perp-Mx polar-plots, the opposite is true, $E^C(2\omega;\varphi)$ and $E^M(2\omega;\varphi)$ are shown to be of the form $b + c \cos 2\varphi$ and $a \sin \varphi$, respectively. In the SHG polar-plots measured using the SxMx, ||-Mx, and \perp-Mx geometries, it is clear that $E^M(2\omega;\varphi)$ is dominated by $\cos 2\varphi$, $DC$, and $\sin 2\varphi$ terms, respectively. The different trigonometric dependence of these magnetization-induced contributions accounts for the different MSHG contrast observed with the different experimental geometries.

From these room temperature observations, it is possible to deduce several properties of the Au-capped ultra-thin Fe films. It is clear that the Au capping-layer has successfully protected the ultra-thin films from oxidation – if this were not the case, then no MSHG signal would be expected. A significant proportion of the magnetic-domains in the Au-capped ultra-thin Fe films have Curie-points above room temperature. This is a significant enhancement beyond the Curie-point of the bare, or Ag-capped ultra-thin films[3]. The easy-axis of magnetization for the Au-capped integer-monolayer ultra-thin Fe films lies in the film-plane, across the steps, in the $<1\bar{1}0>$ direction as expected[4].

6.4 MSHG: Low temperature polar-plots

It was discovered that the UV Fused Silica (UVFS) optical-flat windows of the cryostat skewed the SHG-signal from the sample when measured using the ON-geometry, so low temperature MSHG investigations were limited to the NI-geometry.
Figure 6.4.1: 80K Normal Incidence MSHG plots of Au-capped integer monolayer Fe films grown on vicinal W(100) using ±80mT applied field. Left column: $||-M_x$-plots & right column: $\perp-M_x$-plots.
**Figure 6.4.2:** 80K Normal Incidence MSHG plots of Au-capped sub-monolayer Fe films grown on vicinal W(100) using ±80mT applied field. Left column: \( ||-M_x \) plots & right column: \( \perp -M_x \) plots.
With the odd exception of the 0.5ML Fe film, significant Mx-MSHG contributions to the 80K SHG-signal were observed from every ultra-thin Fe film grown on the vicinal W(110) surface. In contrast those observed at room temperature, these MSHG contributions are immediately obvious in the raw data of SHG plots, being one order-of-magnitude greater in size. The largest MSHG contributions are observed for the integer-monolayer ultra-thin Fe films, with the magnitude of $E^M(2\omega, \phi)$ being approximately 10% that of $E^C(2\omega, \phi)$, for the 2ML and 3ML ultra-thin Fe films. While they are still clearly observable in the raw data of the SHG-plots, the MSHG contributions for the 1ML, 0.75ML and 0.25ML ultra-thin Fe films and nanostripes are significantly smaller. For the 0.25ML and 0.75ML Fe films (equivalent to 10 atom-wide and 30 atom-wide nanostripes), the relative MSHG contribution to the SHG-signal in the $\|\cdot$-Mx-plots is the same. Given that the 0.75ML film contains at least three times the number of terrace-sites of the 0.25ML film, this is an encouraging indication that a substantial component of the MSHG contribution originates at the step-sites of the stripes. Even though they are significantly altered by the large MSHG contributions on magnetization reversal, the $\|\cdot$-Mx and $\perp\cdot$-Mx SHG-plots are still consistent with, and well fitted by, the phenomenological model. The dependence of $E^C(2\omega, \phi)$ and $E^M(2\omega, \phi)$ on $\phi$ deduced from these plots are in full agreement with those predicted in the phenomenological model (see Tables T2.5.5 & T2.5.6)

Given the large MSHG contributions in the other ultra-thin Fe films, it is curious that the 0.5ML Fe film (corresponding to 20 atom-wide Fe nanostripes) should have such a small MSHG contribution in both the NI $\|\cdot$-Mx and $\perp\cdot$-Mx plots. To exclude local contamination as the trivial explanation, SHG measurements were made at many different points across the 0.5ML Fe film, but all were found to have the same small MSHG contribution. It is difficult to imagine a scenario in which the whole 0.5ML Fe patch is corrupted, while the other patches remain intact, so it is likely that the small Mx-MSHG contribution in the 0.5ML Fe patch is a real effect. It is possible that this signifies that the easy-axis of magnetization for the 0.5ML Fe nanostripes is no longer across in the film-plane, across the steps, but lies in another direction. To investigate this possibility, SHG measurements were carried-out with the applied-field aligned in
the film-plane, along the step, in the $\hat{y}$-direction. It was not possible to perform full SHG measurements for an applied field in the $\hat{z}$-direction, because of the dimensions of the cryostat and electromagnet. Although a small $\text{My-MSHG}$ contribution to the 80K SHG-signal in the $\perp\text{-My}$ plot of the Au-capped 3ML ultra-thin Fe films was detected, no such contribution was observed in the Au-capped 0.5ML Fe film.

![Graph](image)

**Figure 6.4.3:** 80K Normal Incidence $\perp\text{-My}$ MSHG plot of Au-capped 3ML Fe films grown on vicinal $W(100)$ using ±80mT applied field.

This $\text{My-MSHG}$ contribution to the 3ML Fe film is far smaller than that of $\text{Mx-MSHG}$ contribution, being comparable that observed in the $\perp\text{-Mx}$ plot of the Au-capped 0.5ML Fe film. This comparison is made to demonstrate that the low $\text{Mx-MSHG}$ contribution in the 0.5ML Fe is consistent with that arising from an applied-field along a hard-axis of magnetization. It is possible, then, that the easy-axis of magnetization for the Au-capped 0.5ML ultra-thin Fe film lies in the $\hat{z}$-direction, where it cannot be probed by the current experimental configuration. Since it is only observed for the 3ML Fe film, it is likely that the $\text{My-MSHG}$ contribution to the SHG-signal originates at the Fe islands on top of a pseudomorphic Fe(110) monolayer. The line-shapes of the MSHG contrast and $E^M(2\alpha, \phi)$ from the $\perp\text{-My}$ plot of the Au-capped 3ML ultra-thin Fe film is different to that of the $\perp\text{-Mx}$ plots of the 3ML film. The observation of such a difference is consistent with the predictions of the phenomenological model.
Having demonstrated the presence of measurable MSHG contributions to the SHG-signal of Au-capped ultra-thin Fe films in section 6.4, the nature of the surface-magnetization making these contributions was investigated. MSHG-derived hysteresis loops were measured from the Au-capped ultra-thin films at 80K using the \( N1 \parallel Mx \) experimental geometry and two or more values of \( \phi \). Hysteresis-loops of the surface magnetism were deduced from these MSHG-derived loops were using the algorithm described in section 2.8. As discussed in section 2.9, if the surface magnetization varies across the face of the ultra-thin film or nanostripe, then the magnetization in the region of the terrace-sites, \( M^T(H) \), will differ from that of the step-sites, \( M^S(H) \). Under such circumstances, the hysteresis loops derived from the MSHG data will exhibit \( \phi \)-dependent coercivities.

The hysteresis loops of the Au-capped 2ML and 1ML ultra-thin Fe films are clearly ferromagnetic with coercivities of 30mT and 45mT, respectively. For these ultra-thin films, the measured coercivity is independent of \( \phi \), indicating that no substantial magnetization gradient exists across the film faces. In the case of the 1ML ultra-thin film, the magnetization-reversal occurs over a single 3mT increment of the applied-field, making it a textbook example of easy-axis magnetization in a hard ferromagnet. The coercivity of 45mT in the Au-capped 1ML ultra-thin film is one order-of-magnitude greater than MOKE determinations of the uncapped Fe films [5], thereby demonstrating the strong role played by capping materials in the properties of surface magnetism.

In contrast to the 1ML and 2ML ultra-thin films, the hysteresis loops of the Au-capped 3ML Fe film exhibits a pronounced dependence on \( \phi \). The coercivity of the 3ML loop is 20mT when measured using the \( N1 \parallel Mx \) MSHG geometry at \( \phi=3^\circ \) and 38mT when measured using the \( N1 \parallel Mx \) MSHG geometry at \( \phi=87^\circ \). This difference in coercivity is clearly visible in figure F6.5.1. This behaviour closely resembles the simulations illustrated in F2.9.3, where it is assumed that \( M^T(H) \neq M^S(H) \). Both of the 3ML
loops are ferromagnetic, though they are significantly softer than that observed from the Au-capped 1ML Fe ultra-thin film. The observation of a $\varphi$-dependent coercivity strongly indicates the presence of a spatial variation in surface magnetization across the 3ML ultra-thin Fe film. Because Fe on W(110) undergoes Stranski–Krastanov growth, the 3ML ultra-thin film consists of Fe islands on top of a single pseudomorphic Fe layer. Therefore, the existence of a spatial variation of the surface magnetization in the film seems plausible—it is to be expected that the surface magnetization in the 3D Fe islands is greater than that of the 2D pseudomorphic layer. In fact, there is evidence in the literature that, for certain Fe coverages, these islands are ferromagnetic, while the intra-island pseudomorphic layer is not.[6]

Despite the tiny quantities of magnetic material involved, it was possible to measure the 80K hysteresis loops of the Au-capped 30 atom-wide and 10 atom-wide Fe nanostripes. The hysteresis loop of the Au-capped 30 atom-wide Fe nanostripes exhibits a $\varphi$-dependent coercivity, though it is significantly smaller than that observed from the Au-capped 3ML Fe film, and more difficult to discern because of the poorer SNR of the MSHG signal. The coercivity of the 30 atom-wide nanostripe loop is 26mT when measured using the $N_1 \parallel M_x$ MSHG geometry at $\varphi=4^\circ$, and 36mT when measured using the $N_1 \parallel M_x$ MSHG geometry at $\varphi=86^\circ$. The 30 atom-wide nanostripe loops are ferromagnetic, though they are significantly softer than any of the loops from the Au-capped integer monolayer films. Also, there is no evidence of full-saturation in the loops, indicating that the 80mT applied field cannot completely flip all the domains in the stripes.
Figure 6.5.1: 80K Magnetic-hysteresis-loops of Au-capped integer monolayer ultrathin Fe film deduced from MSHG signal measured in the NI \(\parallel Mx\)-geometry using the indicated values of \(\phi\). Moving Point Averages (MPA) are included as a guide to the eye.
Unlike the 3ML Fe film, where similar ϕ-dependent behaviour was observed and attributed to the presence of Fe islands on a single pseudomorphic Fe layer, the 30 atom-wide Fe nanostripes are entirely pseudomorphic, meaning that the surface magnetization gradient must occur across the stripes themselves. Specifically, the observation of ϕ-dependent behaviour in the hysteresis loops of the pseudomorphic 30 atom-wide Fe nanostripes indicates that the surface magnetization at the centre of the nanostripes (mm2 terrace-sites), $M^T(H)$, differs substantially from the surface magnetization at the edge of the nanostripes (1m step-sites), $M^S(H)$. This gradient could be due the reduced co-ordination of the Fe atoms near the step-sites, the increased stress experienced by the Fe atoms at the edge of the nanostripe, the lower dimensionality of the quasi-1D string of Fe atoms along the edge of the nanostripe[6]. In fact, since there are two distinct edges to each nanostripe (a W-Fe edge and a Fe-Au) the surface magnetization gradient may be asymmetrical across the stripes (see section 2.9.3). From the MSHG derived hysteresis loops in F6.5.2, it is not possible to determine the coercivity of either $M^T(H)$ or $M^S(H)$, but it is possible to use them to place bounds on the possible values of the surface magnetization: the maximum coercivity of the surface magnetization of the Au-capped 30 atom-wide Fe nanostripes must be greater than or equal to 36mT, while the minimum coercivity must be less than or equal to 26mT.

In contrast to the other observed loops, those of the Au-capped 10 atom-wide Fe nanostripes do not exhibit any appreciable hysteresis, although the poor SNR in their measurements makes any definitive determination impossible. The observed loop is consistent with the behaviour of either a super-paramagnet, or a very soft ferromagnet. Hypothetically, a similar measurement made with better SNR might determine which scenarios is the case here – super-paramagnets exhibit no hysteresis at all, while even the softest ferromagnet exhibits some hysteresis. Unfortunately, this determination could not be made using the current experimental data.
Moving Point Averages (MPA) are included as a guide to the eye.

6.6 Temperature dependence of MSHG contrast

It was shown in section 6.5 that the surface magnetism of all the Au-capped Fe ultrathin films and some of the Au-capped Fe nanostripes is ferromagnetic. All ferromagnetic systems have a Curie point, above which they become paramagnetic and consequently are not expected to exhibit significant MSHG contributions to their SHG signal. As demonstrated in section 2.6, the temperature dependence of the surface magnetization is often proportional to the temperature dependence of the MSHG contrast. Therefore, by measuring the MSHG contrast as a function of temperature, it is
possible to deduce the temperature dependence of the surface magnetization. If a surface magnetization gradient exists across the film or nanostripe, then instead of exhibiting a fairly monotonic dependence on temperature, the MSHG contrast may exhibit characteristic peaks or kinks, as illustrated in F2.9.2. The MSHG contrast measurements illustrated in figures F6.6.1 and F6.6.2 were carried-out by cooling the Au-capped ultra-thin Fe films and nanostripes to 80K, allowing them to equilibrate at that temperature, and then gradually heating them to 320K, over a 40 minute period. The contrast was measured using the NI ||-Mx MSHG geometry with the indicated value of φ, and a ±80mT applied field that was flipped every 10s.

The temperature dependence of the MSHG contrast of the Au-capped 1ML Fe film exhibits simple ferromagnetic behaviour; as the film is cooled below its Curie point of 320K, the magnetization of the film increases linearly down to 210K, after which it begins to saturate. There is no indication in the monotonic plot of any of the peaks or kinks associated with the presence of a surface magnetization gradient across the film; an observation consistent with the lack of a φ-dependent coercivity in the MSHG-derived hysteresis loops of the film (see F6.5.1).

The temperature dependence of the MSHG contrast of the Au-capped 2ML Fe film is more complicated than that of the 1ML. Like the 1ML film, the 2ML film has a well-defined Curie point at about 320K, but there is also a definite kink in the temperature dependence at 255K after which the contrast increases linearly with decreasing temperature. A linear relationship between surface magnetization and temperature such as this is characteristic of super-paramagnetic behaviour, but the hysteresis loops of the 2ML film (see F6.5.1) clearly indicate that the film is ferromagnetic. Similarly, the kink cannot be taken to be the result of a surface magnetization gradient, because no φ-dependent coercivity was observed in the MSHG-derived hysteresis loops of the film was observed. It is possible that other effects such as magnetostriction or a temperature induced strain occur in the film, both of which would cause the simple proportionality of the temperature dependence of the surface magnetization to the temperature dependence of the MSHG contrast to break-down, could cause the kink (see section 6.7

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This illustrates that great care must be taken in the interpretation of the MSHG contrast plots.

Figure 6.6.1: Temperature dependence of the MSHG contrast of Au-capped integer monolayer ultra-thin Fe films measured using the NI ||-Mx MSHG geometry with the indicated value of $\varphi$. 
The temperature dependence of the MSHG contrast of the Au-capped 3ML Fe film is more complicated, again, than that of the 2ML film. Like both the 1ML and 2ML Au-capped ultra-thin films, the 3ML film exhibits a well-defined Curie point at about 320K, but there is also significant additional structure in the temperature dependence of the contrast. There is a broad asymmetric peak at 255K (approximately the same temperature at which a kink is observed from the 2ML film), and also a small, but sharp, dip in the contrast at 145K. Such behaviour in the temperature dependence of the contrast is consistent with the premise that a surface magnetization gradient exists across the film (also indicated by the \( \varphi \)-dependent coercivity in the hysteresis loops of the 3ML film (see F6.5.1)). Since the 3ML ultra-thin film consists of Fe islands on top of a single pseudomorphic Fe layer (Fe on W(110) undergoes Stranski-Krastanov growth) the existence of a variation in the surface magnetization seems plausible[6].

![Graphs showing temperature dependence of MSHG contrast](image)

**Figure 6.6.2:** Temperature dependence of the MSHG contrast of Au-capped Fe nanostripes measured using the NI \( \parallel \)-Mx MSHG geometry with the indicated value of \( \varphi \).
Illustrated in figure F6.6.2, the temperature dependence of the MSHG contrast of the Au-capped 30 atom-wide Fe nanostripes (0.75ML Fe film) is significantly different to that measured from the integer monolayer ultra-thin films. The 30 atom-wide Fe nanostripes exhibit a Curie point of 270K, below which the contrast increases with decreasing temperature until 145K, and then begins to rapidly decrease with temperature. It is not possible for the surface magnetization of the nanostripes to decrease as they are cooled, because the exchange interaction driving the ferromagnetic ordering in the stripes is always in competition with the spin-disorder caused by the thermal energy of the system. Therefore, such behaviour in the temperature dependence of the contrast may indicate that a surface magnetization gradient exists across the film, a premise consistent with the observation of a $\phi$-dependent coercivity in the hysteresis loops of the film (see F6.5.2)). Unlike the 3ML Fe film, where similar $\phi$-dependent behaviour of the hysteresis loops, and peaks in the temperature dependence of the MSHG contrast was observed, the 30 atom-wide Fe nanostripes are entirely pseudomorphic, meaning that the surface magnetization gradient may occur across the width of the stripes themselves, and cannot be attributed to the presence of Fe islands on a single pseudomorphic layer. The observed temperature dependence of the MSHG contrast of the Au-capped 30 atom-wide Fe nanostripes is almost identical to one of the simulations of F2.9.2, where it was assumed that the surface magnetization in the region of the terrace-sites, $M^T(T)$, differs so greatly from that of the surface magnetization in the region of the step-sites, $M^S(T)$, that two discrete Curie points were required to fully describe the behaviour of the response. In these simulation, the peak in the temperature dependence of the contrast occurs at the Curie point of $M^S(T)$, while the temperature at which the contrast goes to zero is the Curie point of $M^T(T)$. If the premise $M^T(T) \neq M^S(T)$ is true for the Au-capped 30 atom-wide Fe nanostripes, then the Curie point of $M^S(T)$ is 145K and $M^T(T)$ is 270K.

The temperature dependence of the MSHG contrast of the Au-capped 10 atom-wide Fe nanostripes is more straightforward than that of the 30 atom-wide Fe stripes, exhibiting only a well-defined Curie point at 160K. The contrast increases sharply on further
cooling, until 120K where it begins to saturate, although the poor SNR and limited temperature range make it impossible to determine if full saturation has been reached at 80K. There is no indication in the plot of any of the peaks or kinks associated with a surface magnetization gradient across the film, an observation consistent with the lack of a \( \varphi \)-dependent coercivity in the MSHG-derived hysteresis loops of the film (see F6.5.1). The 160K Curie point of the Au-capped 10 atom-wide Fe nanostripes is very close to the proposed 145K Curie point of \( M^s(T) \) of the 30 atom-wide Fe stripes. Since the 10 atom-wide Fe stripes contain a significantly higher ratio of steps-sites to terrace-sites relative to the 30 atom-wide stripes, it is unsurprising that the Curie point of their surface magnetization should be close to that of the conjectured \( M^s(T) \) of the 30 atom-wide nanostripes.

### 6.7 Possible strain and magnetostriction effects

During temperature-scans of the MSHG contrast, pronounced temperature sensitivities of \( E^C(2\omega;\varphi,\theta,T) \) were observed for the Au-capped 10 atom-wide and 30 atom-wide Fe nanostripes, along with the 1ML ultra-thin Fe film, but not the Au-capped 2ML and 3ML ultra-thin Fe films, as illustrated in figure F6.7.1 (the values of \( E^C(2\omega;\varphi,\theta,T) \) in this figure were deduced from the same MSHG data used to determine the temperature dependence of the contrast in F6.6.1 and F6.6.2, using E2.7.8). It would appear that these pronounced changes in \( E^C(2\omega;\varphi,\theta,T) \) are due to a non-magnetic temperature-related strain induced in the Au-Fe interface, Fe-W interface, or in the Fe nanostripes themselves, and not magnetostriction effects in the stripes\[7-9\]. This deduction can be made by observing that the sudden changes in \( E^C(2\omega;\varphi,\theta,T) \) are observed from the Au-capped 10 atom-wide Fe nanostripes at a number of temperatures (270K, 250K, and 220K) above the Curie point (160K) of the stripes (see F6.6.2).
Figure 6.7.1: Magnitudes of $E^C(2\omega; \varphi)$ for 0.25ML, 0.75ML, and 1ML Fe films, as a function of temperature

The presence of such sharp changes in $E^C(2\omega; \varphi, \theta, T)$ as a function of temperature may lead to a break-down of the simple proportionality between the temperature dependence of the surface magnetization to the temperature dependence of the MSHG contrast, assumed in the interpretation of F6.6.1 and F6.6.2. For example, such changes in $E^C(2\omega; \varphi, \theta, T)$ might be responsible for the unexplained kink observed in the temperature dependence of the Au-capped 2ML ultra-thin Fe film contrast at 255K. This illustrates that great care must be taken in interpreting the temperature dependence of the MSHG contrast, whenever sharp changes in $E^C(2\omega; \varphi, \theta, T)$ are revealed by the application of E2.7.8 to the same data.


7

Discussion of results

7.1 Summary of results

RA spectra of the clean vicinal W(110) surface were measured and compared to existing RAS measurements of the clean planar W(110) surface. This comparison demonstrated that the step-sites of the vicinal W(110) surface make significant contributions to the optical anisotropy of the W(110) surface. RA spectra of Fe nanostructures and Fe ultra-thin films grown on the vicinal W(110) surface were measured, and revealed a significant dampening of the optical anisotropy during the deposition of the first Fe monolayer, after which the deposition of further Fe has little effect. Although annealing of the deposited Fe was observed to increase the sharpness of LEED patterns from the Fe/W(110) interface, it had little or no effect on the RA spectra. RA spectra of both Ag-capped and Au-capped Fe nanostructures and Fe ultra-thin films grown on the vicinal W(110) surface were also measured, and found to differ significantly from the spectra of the uncapped Fe films, thereby demonstrating the strong role played by capping material in determining the optical anisotropy of ultra-thin films and nanostructures.
SHG measurements from the clean vicinal W(110) surface, at photon energies of $h\omega=1.5$eV, revealed that the non-linear hyper-polarizability of the surface is very small and sensitive to contamination by residual gas in the UHV chamber. NI SHG measurements from the vicinal W(110) surface clearly illustrated a large increase (approximately a factor of 200) in the hyper-polarizability of the well-defined 1m step-sites as a function of room temperature oxidation. Such behaviour clearly illustrates the sensitivity of SHG in the study of surface adsorbates. NI SHG measurements of Fe nanostripes grown on the vicinal W(110) surface demonstrated that the 1m non-linear hyper-polarizability associated with the step-sites of the nanostripes is very small and sensitive to contamination by residual gas in the UHV chamber.

80K NI MSHG measurements of Au-capped Fe ultra-thin films and nanostripes grown on the vicinal W(110) surface exhibited significant MSHG contributions, for surface magnetization in the plane of the sample, across the steps of the vicinal surface. MSHG contributions were observed from Au-capped 10 atom-wide nanostripes, demonstrating the high sensitivity of non-linear optic as a probe of surface magnetism. Measuring the temperature dependence of the MSHG contrast from the Au-capped Fe ultra-thin films and nanostripes as a function of temperature allowed the temperature dependence of their surface magnetization to be determined and their Curie points to be established. The Curie points of the Au-capped 1ML, 2ML, and 3ML Fe ultra-thin films were all found to be about 320K, while the Curie points of the Au-capped 30 atom-wide and 10 atom-wide Fe nanostripes were found to be 270K and 160K, respectively. The temperature dependence of the MSHG contrast for the Au-capped 3ML Fe ultra-thin film and 30 atom-wide Fe nanostripes exhibited structure consistent with the premise of spatial variation in the surface magnetization across the face of the films. For the case of the Au-capped 3ML Fe ultra-thin film, it is assumed that this variation of the magnetization is due to the presence of the strongly magnetic 3D Fe islands aligned along the step-sites, on top of the weakly magnetic pseudomorphic Fe layer. However, given that Au-capped 30 atom-wide nanostripes are pseudomorphic and just one atom thick, a similar scenario cannot be put forward to explain the pronounced peak observed in the temperature dependence of the MSHG contrast from the stripes. Given that they are only one atom thick and tens of atoms wide, it does not seem reasonable that they
could contain discrete terrace-site and step-site magnetic domains, either. Instead, it is possible that surface strain, nearest neighbour effects, and dimensionality considerations, produce a gradual variation in the surface magnetization between the region of the terrace-sites and step-sites of the nanostripes. Measuring the MSHG signal of the Au-capped Fe nanostripes and ultra-thin films as a function of applied magnetic field allowed the hysteresis loops of their surface magnetization to be deduced. The shape of these hysteresis loops indicated that the Au-capped 3ML, 2ML, and 1ML Fe ultra-thin films, along with the Au-capped 30 atom-wide Fe nanostripes, are ferromagnetic. Because of poor SNR in the MSHG measurements, it could not be determined if the Au-capped 10 atom-wide Fe nanostripes are super-paramagnetic or very soft ferromagnetic. The observation of a $\phi$-dependent coercivity in the MSHG-derived hysteresis loops of the Au-capped 3ML Fe ultra-thin film and 30 atom-wide Fe nanostripes is again consistent with the premise that a spatial variation of the surface magnetization across these films and nanostripes exists. Again, for the case of the Au-capped 3ML Fe ultra-thin film, such an observation may be understood as arising from the presence of 3D Fe islands aligned along the step-sites, on top of a 2D pseudomorphic Fe layer, while it is possible that surface strain, nearest neighbour effects, and dimensionality considerations, produce a gradual variation in the surface magnetization in the region of the terrace-sites and step-sites of the nanostripes. The observation of significant temperature dependence in the crystallographic SHG signal from the Au-capped Fe nanostripes illustrates that care must be taken in attributing the temperature dependence in the MSHG signal to the temperature dependence of the surface magnetization of the nanostripes.
7.2 Conclusions

The structural properties of ultra-thin Fe films and nanostripes grown on vicinal W(110) were studied using both in situ and ex situ RAS and SHG. The magnetic properties of these films were studied using ex situ MSHG. Employing Au as a capping material allowed the transfer of the ultra-thin Fe films and nanostripes from the UHV environment, in which they were prepared, to the ambient laboratory atmosphere, without destroying their magnetic properties. MSHG contributions to the SHG signal of Au-capped 10 atom-wide Fe nanostripes were observed, demonstrating the extreme sensitivity of non-linear optic techniques to the study of surface magnetization. Measuring the temperature dependence of the MSHG signal allowed the Curie point of the surface magnetization of the Au-capped Fe nanostripes and ultra-thin films to be determined, while measuring the MSHG signal as a function of applied magnetic field allowed the hysteresis of the surface magnetization to be deduced. The Curie point of the 1ML Fe Au-capped film was found to be 320K, while the Curie point of the Au-capped 30 atom-wide and 10 atom-wide Fe nanostripes is 270K and 160K, respectively. The hysteresis loops of the Au-capped 3ML, 2ML, and 1ML Fe ultra-thin films, along with the Au-capped 30 atom-wide nanostripes are ferromagnetic, while the 10 atom-wide nanostripes may be either very soft ferromagnetic or super-paramagnetic. For the Au-capped 3ML Fe ultra-thin film and Au-capped 30 atom-wide nanostripes, the behaviour of the MSHG signal is consistent with premise that the surface magnetization varies spatially across the films and nanostripes. Specifically, for the case of the Au-capped 30 atom-wide nanostripes, the behaviour of the MSHG signal indicates that the surface magnetization in the region of the terrace-sites of the Fe nanostripes is not the same as the surface magnetization in the region of the step-sites of the nanostripes. Given that these nanostripes are only one atom thick and tens of atoms wide, it does not seem reasonable that that they could contain discrete terrace-site and step-site magnetic domains. Instead, it is likely that surface strain, nearest neighbour effects, and dimensionality considerations, cause the surface magnetization in the region of the mm2 terrace sites to differ slightly from the surface magnetization in the region of 1m step-sites.
7.3 Future work

1. The MSHG investigations of the Au-capped ultra-thin Fe films and nanostripes carried-out in this thesis would be benefit greatly from complimentary MOKE measurements. A MOKE investigation of the critical behaviour in the Au-capped ultra-thin Fe films, with the research group of Prof. David Venus was planned, but funding for the visit was not secured. A Wollaston-prism-type MOKE system is currently being developed in the Surface Optics laboratory to supplement future SHG investigations. Because they have been careful persevered, it may even be possible to use this MOKE system to retroactively examine the Au-capped ultra-thin Fe films investigated during this research.

2. MSHG contributions to the SHG-signal were observed from the Au-capped 10 atom-wide Fe nanostripes, suggesting that the technique of MSHG might be sensitive enough to detect the magnetization of Au-capped single-atom nanowires of Fe. This would allow the properties of this one-dimensional magnetic system to be optically probed.

3. The MSHG investigations of the Au-capped Fe nanostripes revealed significant differences between the magnetic behaviour of the 10 atom-wide, 20 atom-wide, and 30 atom-wide nanostripes, demonstrating that the magnetic properties of the nanostripes are sensitive to changes in width of the order of a few atoms. To better probe the dependence of the surface magnetization on nanostripe width, future MSHG investigations should be carried-out on samples consisting of Fe wedges, rather than discrete Fe patches. Since the spot-size of the laser can be easily focussed to 100μm diameter, it is reasonable to expect that this approach could be used to investigate differences in coverage of just 1% of a monolayer on an 8mm diameter crystal.

4. With the current experimental geometry, while making NI SHG measurements, it is only possible to apply a magnetic-field in the film-plane. The adoption of cruciform electromagnet into the geometry would allow the magnetic-field to be applied along each of the orthogonal axes of the nanostripes, providing more information about the magnetic properties of the surface.
5. Close to the Curie-point, the temperature dependence of a ferromagnetic surface magnetization is governed by a power-law; \( M(T) = (T_c - T)^\beta \) the exponent of which can depend on the dimensionality of the ferromagnetic system. These laws are only applicable for a small range of temperatures below the Curie-point \( (T_c > T > 0.9T_c) \) and so detailed temperature scans of the MSHG contrast in this region need to be carried-out as a priority. Such scans might reveal power-law behaviour consistent with quasi-one-dimensional magnetization in the nanostripes.
A.1 Temperature dependence of $\eta(T)$

For a fixed optical geometry, and in the limited case of $|\chi^M(T)M(T)|^2 \ll |\chi^C(T)|^2$, the MSHG contrast, $\eta$, at a temperature, $T$, is given by:

$$\eta(T) = \frac{2\chi^M(T)M(T)}{\chi^C(T)}$$

A1.1

The rate-of-change of $\eta$ with respect to $T$ can be determined by using the chain-rule for partial differentiation:

$$\frac{d\eta(T)}{dT} = \frac{\partial \eta}{\partial M} \frac{dM}{dT} + \frac{\partial \eta}{\partial \chi^M} \frac{d\chi^M}{dT} + \frac{\partial \eta}{\partial \chi^C} \frac{d\chi^C}{dT}$$

A1.2

$$\frac{d\eta(T)}{dT} = \frac{2\chi^M M}{\chi^C} \frac{dM}{dT} + \frac{2M \chi^M}{\chi^C} \frac{d\chi^M}{dT} + \frac{2 \chi^M M \chi^C}{(\chi^C)^2} \frac{d\chi^C}{dT}$$

A1.3
\[
\frac{d\chi^M(T)}{dT} = 2\chi^M \frac{dM}{dT} + \frac{2M(\frac{d\chi^M}{dT} - \frac{\chi^M}{\chi^C} \frac{d\chi^C}{dT})}{\chi^C}
\]

A1.4

In order to simplify this expression, it is necessary to establish a relationship between \(\frac{d\chi^M}{dT}\) and \(\frac{d\chi^C}{dT}\). This may be achieved by recognizing the magnetization-induced polarization-field tensor, \(\chi^M\), as a small perturbation of the overall polarization-field contribution \(\chi\):

\[
P(2\omega; M) = \chi^C E^\prime(\omega) + \chi^M M E^\prime(\omega)
\]

A1.5

\[
P(2\omega; \Delta M) = \chi E^\prime(\omega) + \left( \frac{\partial \chi(M)}{\partial M} \Delta M \right) E^\prime(\omega)
\]

A1.6

From these equations it follows that:

\[
\chi^M = \frac{\partial \chi}{\partial M}
\]

A1.7

\[
\chi^C = \chi - \frac{\partial \chi}{\partial M}
\]

A1.8

Provided that \(\chi\) can be linearized with respect to the magnetization, \(M\), and temperature, \(T\), it is possible to express \(\chi(M, T)\) as the product of exclusive functions of \(M\) and \(T\):

\[
\chi(M, T) = f(M)g(T)
\]

A1.9

In this notation, \(\chi^M(M, T)\) and \(\chi^C(M, T)\) can be expressed as:

\[
\chi^M(M, T) = f'(M)g(T)
\]

A1.10

\[
\chi^C(M, T) = (f(M) - f'(M))g(T)
\]

A1.11
And the derivatives of \( \chi^M(M,T) \) and \( \chi^C(T) \) with respect to temperature can be expressed as:

\[
\frac{d\chi^M}{dT} = f'(M)g'(T) \quad \text{A1.12}
\]

\[
\frac{d\chi^C}{dT} = (f'(M) - f(M))g'(T) \quad \text{A1.13}
\]

From which it immediately follows that:

\[
\frac{d\chi^M}{dT} = \frac{\chi^M}{\chi^C} \frac{d\chi^C}{dT} \quad \text{A1.14}
\]

Substituting this result into A1.4 gives:

\[
\frac{d\eta(T)}{dT} = \frac{2\chi^M}{\chi^C} \frac{dM(T)}{dT} \quad \text{A1.15}
\]

Or, alternatively:

\[
\frac{d\eta}{dT} \propto \frac{dM}{dT} \quad \text{A1.16}
\]

Therefore, a measurement of temperature dependence of \( \eta \) is equivalent to a measurement of the temperature dependence of \( M \).

**A.2 Extraction of hysteresis loops from \( \tilde{T}(2\omega; M(H)) \)**

\[
\tilde{T}(2\omega; M(H)) = |E^C(2\omega) + E^M(2\omega; M(H))|^2 \quad \text{A2.1}
\]

Expanding the squared modulus and arranging as a quadratic equation:
\[ |E^M(2\omega; M(H))|^2 + 2|E^C(2\omega)||E^M(2\omega; M(H))|\cos \delta + |E^C(2\omega)|^2 - \bar{I}(2\omega; M(H)) = 0 \]  

A2.2

Applying the \(-b\) formula, to solve the quadratic equation:

\[ |E^M(2\omega; M(H))|^2 = \pm \sqrt{\bar{I}(2\omega; M(H)) - |E^C(2\omega)|^2 (1 - \cos^2 \delta)} - |E^C(2\omega)| \cos \delta \]  

A2.3

For a fixed optical geometry, \( |E^M(2\omega; M(H))| = \Theta^M |M(H)| \):

\[ \Theta^M |M(H)| = \sqrt{\bar{I}(2\omega; M(H)) - |E^C(2\omega)|^2 (1 - \cos^2 \delta)} - |E^C(2\omega)| \cos \delta \]  

A2.4

Performing a path-integral around the full hysteresis-loop:

\[ \int \Theta^M |M(H)| dH = \int \left( \bar{I}(2\omega; M(H)) - |E^C(2\omega)|^2 (1 - \cos^2 \delta) - |E^C(2\omega)| \cos \delta \right) dH \]  

A2.5

Aside: Technically, \( M(H) \) is not a function of \( H \), since there does not exist a unique value of \( M(H) \) for every \( H \). In order to perform a meaningful path-integral of the modulus of \( M(H) \), it is necessary to break-down \( M(H) \) into two actual functions; \( M_1(H) \) and \( M_2(H) \):

\[ M(H) = \begin{cases} M_1(H) & \text{when } H \text{ is 'decreasing'} \\ M_2(H) & \text{when } H \text{ is 'increasing'} \end{cases} \]
The path integral of the modulus of the hysteresis-loop is then given by the sum of the definite integral of \(|M_1(H)|\) (between the 'positive' saturation field, +\(H^*\), and 'negative' saturation field, -\(H^*\)) and the definite integral of \(|M_2(H)|\) (between the 'negative' saturation field, -\(H^*\), and 'positive' saturation field, +\(H^*\)): 

\[
\Theta^M \int |M(H)| dH = \Theta^M \int_{-H^*}^{H^*} |M_1(H)| dH + \Theta^M \int_{H^*}^{-H^*} |M_2(H)| dH
\]

For a closed-loop, thermo-mechanical arguments ensure that \(M_2(H) = -M_1(-H)\): 

\[
\Theta^M \int |M(H)| dH = \Theta^M \int_{-H^*}^{H^*} |M_1(H)| dH + \Theta^M \int_{H^*}^{-H^*} -M_1(-H) dH
\]

Which is equivalent to: 

\[
\Theta^M \int |M(H)| dH = \Theta^M \int_{-H^*}^{H^*} |M_1(H)| dH - \Theta^M \int_{H^*}^{-H^*} M_1(H) dH
\]

Or simply: 

\[
\int |M(H)| dH = 0
\]

Applying the identity, \(\int |M(H)| dH = 0\), for a closed loop:

\[
\sqrt{\int (2\omega; M(H)) - |E^C(2\omega)|^2 (1 - cos^2 \delta) dH} - \int |E^C(2\omega)| cos \delta dH = 0 \quad \text{A2.6}
\]

This allows \(|E^C(2\omega)| cos \delta\) to be expressed as:
\[ |E^C(2\omega)| \cos \delta = \frac{\int \sqrt{I(2\omega; M(H))} - |E^C(2\omega)|^2 (1 - \cos^2 \delta) dH}{\int dH} \quad \text{A2.7} \]

Which, when substituted into A2.4, after making the following straightforward substitutions:

\[ \Gamma = |E^C(2\omega)|^2 (1 - \cos^2 \delta) \quad \text{A2.8} \]

\[ M(H) = \cos \delta |M(H)|, \text{ gives:} \quad \text{A2.9} \]

Gives the solution:

\[ M(H) \propto \sqrt{I(2\omega; M(H))} - \Gamma - \frac{\int \sqrt{I(2\omega; M(H))} - \Gamma dH}{\int dH} \quad \text{A2.10} \]

The ratio of integrals on the RHS of this expression is immediately recognizable as the average value of \( \sqrt{I(2\omega; M(H))} - \Gamma \) around the full loop:

\[ M(H) \propto \sqrt{I(2\omega; M(H))} - \Gamma - \left( \sqrt{I(2\omega; M(H))} - \Gamma \right) \quad \text{A2.11} \]

**A.3 Temperature dependence of \( E^C(2\omega, \theta, \varphi) \) and \( E^M(2\omega, \theta, \varphi, M(+H)) \)**

Using the following parametric functions of \( \tilde{I}(2\omega; \varphi, M(+H)) \) and \( \tilde{I}(2\omega; \varphi, M(-H)) \):

\[ \Sigma(\varphi, M(+H)) = \frac{1}{2} \left( \tilde{I}(2\omega; \varphi, M(+H)) + \tilde{I}(2\omega; \varphi, M(-H)) \right) \quad \text{A3.1} \]

\[ \Delta(\varphi, M(+H)) = \frac{1}{2} \left( \tilde{I}(2\omega; \varphi, M(+H)) - \tilde{I}(2\omega; \varphi, M(-H)) \right) \quad \text{A3.2} \]
It is possible to generate a pair of parallel expressions for \( |E^C(2\omega; \varphi)\) and \( |E^M(2\omega; \varphi, M(+ H))| \):

\[
\Sigma(2\omega; \varphi, M(+ H)) = 2|E^C(2\omega; \varphi)| |E^M(2\omega; \varphi, M(+ H))| \cos \delta(2\omega; \varphi) \quad \text{A3.3}
\]

\[
\Delta(2\omega; \varphi, M(+ H)) = |E^C(2\omega; \varphi)|^2 + |E^M(2\omega; \varphi, M(+ H))|^2 \quad \text{A3.4}
\]

These equations can be solved using the \(-b\) formula for quadratic equations:

\[
|E^C(2\omega; \varphi)| = \sqrt{\frac{1}{2} \left( \Sigma + \sqrt{\Sigma^2 - \left( \frac{\Delta}{\cos \delta(2\omega; \varphi)} \right)^2} \right)} \quad \text{A3.5}
\]

\[
|E^M(2\omega; \varphi, M(+ H))| = \sqrt{\frac{1}{2} \left( \Sigma - \sqrt{\Sigma^2 - \left( \frac{\Delta}{\cos \delta(2\omega; \varphi)} \right)^2} \right)} \quad \text{A3.6}
\]

Without knowing \( \cos \delta(2\omega; \varphi) \), the values of \( |E^C(2\omega; \varphi)| \) and \( |E^M(2\omega; \varphi, M(+ H))| \) cannot be determined uniquely. However, bounds can be placed on their maximum and minimum values:

\[
|E^C(2\omega; \varphi)|_{\text{max}} = \sqrt{\frac{1}{2} \left( \Sigma + \sqrt{\Sigma^2 - \Delta^2} \right)} \quad \text{A3.7}
\]

\[
|E^M(2\omega; \varphi, M(+ H))|_{\text{min}} = \sqrt{\frac{1}{2} \left( \Sigma - \sqrt{\Sigma^2 - \Delta^2} \right)} \quad \text{A3.8}
\]
Table T2.5.1: SH electric field components for the crystallographic and magnetic terms, using Ss sample rotation geometry

<table>
<thead>
<tr>
<th>Field</th>
<th>Crystal</th>
<th>$M_y$</th>
<th>$M_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_{1c}$</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{4}(2g+i+3k)M_x$</td>
</tr>
<tr>
<td>$E_{2c}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_{3c}$</td>
<td>0</td>
<td>0</td>
<td>$-\frac{1}{4}(2g+i-k)M_x$</td>
</tr>
<tr>
<td>$E_{1s}$</td>
<td>$-\frac{1}{4}(3A+B+2F)$</td>
<td>$-\frac{1}{4}(3a+b+2r)M_y$</td>
<td>0</td>
</tr>
<tr>
<td>$E_{2s}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_{3s}$</td>
<td>$\frac{1}{4}(A-B-2F)$</td>
<td>$\frac{1}{4}(a-b-2r)M_y$</td>
<td>0</td>
</tr>
</tbody>
</table>
Table T2.5.2: *SH electric field components for the crystallographic and magnetic terms, using Sp sample rotation geometry*

<table>
<thead>
<tr>
<th>Field</th>
<th>Crystal</th>
<th>$M_y$</th>
<th>$M_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>0</td>
<td>0</td>
<td>$-f_c f_s (d - p) M_z$</td>
</tr>
<tr>
<td>$E_{1c}$</td>
<td>0</td>
<td>0</td>
<td>${ -\frac{1}{4} f_c^2 (2g - 3i - k)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$+ f_s^2 (m) } M_x$</td>
</tr>
<tr>
<td>$E_{2c}$</td>
<td>0</td>
<td>0</td>
<td>$f_c f_s (d + p) M_x$</td>
</tr>
<tr>
<td>$E_{3c}$</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{4} f_c^2 (2g + i - k) M_x$</td>
</tr>
<tr>
<td>$E_{1s}$</td>
<td>$-\frac{1}{4} f_c^2 (A + 3B - 2F)$</td>
<td>${ -\frac{1}{4} f_c^2 (a + 3b - 2r)$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$- f_s^2 (C)$</td>
<td>$- f_s^2 (c) } M_y$</td>
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<tr>
<td>$E_{2s}$</td>
<td>$- f_c f_s (D - E)$</td>
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<tr>
<td>$E_{3s}$</td>
<td>$-\frac{1}{4} f_c^2 (A - B - 2F)$</td>
<td>$-\frac{1}{4} f_c^2 (a - b - 2r) M_y$</td>
<td>0</td>
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</tbody>
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### Table T2.5.3: \(SH\) electric field components for the crystallographic and magnetic terms, using \(Ps\) sample rotation geometry

<table>
<thead>
<tr>
<th>Field</th>
<th>Crystal</th>
<th>(M_y)</th>
<th>(M_x)</th>
<th>(M_z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_0)</td>
<td>(\frac{1}{2} F_y \varepsilon(G + H))</td>
<td>(\frac{1}{2} F_y \varepsilon(s + t)M_y)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(E_{1c})</td>
<td>(-\frac{1}{4} F_c (A + 3B - 2F))</td>
<td>(-\frac{1}{4} F_c (a + 3b - 2r)M_y)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(E_{2c})</td>
<td>(-\frac{1}{2} F_y \varepsilon(G - H))</td>
<td>(-\frac{1}{2} F_y \varepsilon(s - t)M_y)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(E_{3c})</td>
<td>(\frac{1}{4} F_c (A - B - 2F))</td>
<td>(\frac{1}{4} F_c (a - b - 2r)M_y)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(E_{1s})</td>
<td>0</td>
<td>0</td>
<td>(\frac{1}{4} F_c (2g - 3i - k)M_x)</td>
<td>(\frac{1}{4} F_c (2h - 3j - l)M_z)</td>
</tr>
<tr>
<td>(E_{2s})</td>
<td>0</td>
<td>0</td>
<td>(- F_c \varepsilon(y)M_x)</td>
<td>(- F_c \varepsilon(z)M_z)</td>
</tr>
<tr>
<td>(E_{3s})</td>
<td>0</td>
<td>0</td>
<td>(\frac{1}{4} F_c (2g + i - k)M_x)</td>
<td>(\frac{1}{4} F_c (2h + j - l)M_z)</td>
</tr>
</tbody>
</table>
### Table T2.5.4: SH electric field components for the crystallographic and magnetic terms, using Ss sample rotation geometry

<table>
<thead>
<tr>
<th>Field</th>
<th>Crystal</th>
<th>$M_y$</th>
<th>$M_x$</th>
<th>$M_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>$-F_c f_s f_s (D + E)$</td>
<td>{-F_c f_s f_s (f + o)}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>$+\frac{1}{2} F_s g f_c^2 (G + H)$</td>
<td>$+\frac{1}{2} F_c g f_c^2 (s + t)$</td>
<td>$+F_c g f_c^2 (u) M_y$</td>
<td>$-F_c f_s f_s (c)$</td>
</tr>
<tr>
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<td>$+F_c g f_c^2 (I)$</td>
<td>$+F_c g f_c^2 (u) M_y$</td>
<td>$-F_c f_s f_s (c)$</td>
<td>$+2F_c g f_s f_s (x) M_y$</td>
</tr>
<tr>
<td>$E_{1c}$</td>
<td>$-\frac{1}{4} F_c f_s^2 (3A + B + 2F)$</td>
<td>{-$\frac{1}{4} F_c f_s^2 (3a + b + 2r)$}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$-F_c f_s^2 (C)$</td>
<td>$-F_c f_s^2 (c)$</td>
<td>$+2F_c g f_s f_s (x) M_y$</td>
<td>$-F_c f_s f_s (x)$</td>
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<td>$+\frac{1}{2} F_c g f_c^2 (G - H)$</td>
<td>$+\frac{1}{2} F_c g f_c^2 (s - 0) M_y$</td>
<td>$+2F_c g f_s f_s (x) M_y$</td>
<td>$-F_c f_s f_s (c)$</td>
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<tr>
<td>$E_{2c}$</td>
<td>$-F_c f_s f_s (D - E)$</td>
<td>{-$F_c f_s f_s (f - o)$}</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>$+\frac{1}{2} F_c g f_c^2 (G - H)$</td>
<td>$+\frac{1}{2} F_c g f_c^2 (s - 0) M_y$</td>
<td>$+2F_c g f_s f_s (x) M_y$</td>
<td>$-F_c f_s f_s (x)$</td>
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<tr>
<td>$E_{3c}$</td>
<td>$\frac{1}{4} F_c f_c^2 (-A + B + 2F)$</td>
<td>$\frac{1}{4} F_c f_c^2 (-a + b + 2r) M_y$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_{1s}$</td>
<td>0</td>
<td>${-\frac{1}{4} F_c f_c^2 (2g + i + 3k)}$</td>
<td>${-\frac{1}{4} F_c f_c^2 (2h + j + 3l)}$</td>
<td>${-\frac{1}{4} F_c f_c^2 (2h + j + 3l)}$</td>
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<td></td>
<td>0</td>
<td>$-F_c f_s f_s (m)$</td>
<td>$-F_c f_s f_s (n)$</td>
<td>$+2F_c g f_s f_s (w) M_z$</td>
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<tr>
<td></td>
<td>0</td>
<td>$+2F_c g f_s f_s (w) M_z$</td>
<td>$+2F_c g f_s f_s (w) M_z$</td>
<td>$-F_c f_s f_s (x)$</td>
</tr>
<tr>
<td>$E_{2s}$</td>
<td>0</td>
<td>${-2F_c f_s f_s (d)}$</td>
<td>${-2F_c f_s f_s (e)}$</td>
<td>${-2F_c f_s f_s (e)}$</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$+F_c g f_c^2 (y) M_x$</td>
<td>$+F_c g f_c^2 (z) M_z$</td>
<td>$+F_c g f_c^2 (z) M_z$</td>
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<tr>
<td>$E_{3s}$</td>
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<td>$-\frac{1}{4} F_c f_c^2 (2g + i - k) M_x$</td>
<td>$-\frac{1}{4} F_c f_c^2 (2h + j - l) M_z$</td>
<td>$-\frac{1}{4} F_c f_c^2 (2h + j - l) M_z$</td>
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Table T2.5.5: SH electric field components for an Sx polarization rotation geometry (xz optical plane of incidence)

<table>
<thead>
<tr>
<th>Field</th>
<th>Crystal</th>
<th>$M_y$</th>
<th>$M_x$</th>
<th>$M_z$</th>
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<tbody>
<tr>
<td>$E_0$</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{2} {(k) + f_s^2(i)}$</td>
<td>$\frac{1}{2} {(j) + f_s^2(j)}$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$+ 2f_c f_s(p) + f_s^2(m) M_x$</td>
<td>$+ 2f_c f_s(q) + f_s^2(n) M_z$</td>
</tr>
<tr>
<td>$E_{2c}$</td>
<td>0</td>
<td>0</td>
<td>$-\frac{1}{2} {(k) - f_s^2(i)}$</td>
<td>$-\frac{1}{2} {(j) - f_s^2(j)}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$- 2f_c f_s(p) - f_s^2(m) M_x$</td>
<td>$- 2f_c f_s(q) - f_s^2(n) M_z$</td>
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<tr>
<td>$E_{2s}$</td>
<td>$f_c(F) + f_s(E)$</td>
<td>${f_c(r) + f_s(o)} M_y$</td>
<td>0</td>
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Table T2.5.6  *SH electric field components for an Sy polarization rotation geometry (yz optical plane of incidence)*

<table>
<thead>
<tr>
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<th>Crystal</th>
<th>$M_y$</th>
<th>$M_x$</th>
<th>$M_z$</th>
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<tbody>
<tr>
<td>$E_0$</td>
<td>$\frac{1}{2}(A + f_s^2(B) + f_s^2(C))$</td>
<td>$\frac{1}{2}(a) + f_s^2(b)$</td>
<td>$-f_c f_s(d) M_y$</td>
<td>$-f_c f_s(e) M_y$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$+ f_s^2(c) M_y$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{2c}$</td>
<td>$-\frac{1}{2}(A - f_c^2(B) - f_s^2(C))$</td>
<td>$-\frac{1}{2}(a) - f_c^2(b)$</td>
<td>$-f_c f_s(d) M_y$</td>
<td>$-f_c f_s(e) M_y$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$- f_c^2(c) M_y$</td>
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<tr>
<td>$E_{2s}$</td>
<td>$f_s(D)$</td>
<td>$f_s(f) M_y$</td>
<td>$-f_c(g) M_x$</td>
<td>$-f_c(h) M_z$</td>
</tr>
<tr>
<td>Field</td>
<td>Crystal</td>
<td>$M_y$</td>
<td>$M_x$</td>
<td>$M_z$</td>
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</tr>
<tr>
<td>$E_0$</td>
<td>Crystal A/</td>
<td>$\frac{1}{2} {F_x g f^2_x (G) + F_z g f^2_z (I)}$</td>
<td>$\frac{1}{2} {F_x g f^2_x (s) + F_z g f^2_z (u)}$</td>
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<tr>
<td></td>
<td></td>
<td>$- F_x f^2_x (A) - 2 F_x f_x f_z (D) - F_x f^2_x (a) - 2 F_x f_x f_z (f)}$</td>
<td></td>
<td></td>
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<tr>
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<td></td>
<td>$+ 2 F_x g f_x f_z (J) - F_x f^2_x (C) + 2 F_x g f_x f_z (x) - F_x f^2_x (c)}$</td>
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<tr>
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<td>$+ F_x e (H) - F_x (B)}$</td>
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<tr>
<td>$E_{2c}$</td>
<td></td>
<td>$- \frac{1}{2} {F_x g f^2_x (G) + F_z g f^2_z (I)}$</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$- F_x f^2_x (A) - 2 F_x f_x f_z (D) - F_x f^2_x (a) - 2 F_x f_x f_z (f)}$</td>
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<tr>
<td></td>
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<td>$+ 2 F_x g f_x f_z (J) - F_x f^2_x (C) + 2 F_x g f_x f_z (x) - F_x f^2_x (c)}$</td>
<td></td>
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<tr>
<td></td>
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<td>$- F_x e (H) + F_x (B)}$</td>
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<td>$E_{2s}$</td>
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<tr>
<td>Field</td>
<td>Crystal</td>
<td>$M_y$</td>
<td>$M_x$</td>
<td>$M_z$</td>
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</tr>
<tr>
<td>$E_0$</td>
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<td>$\frac{1}{2} { F_s \sigma_c^2 (H) + F_s \sigma_g^2 (J) }$</td>
<td>$\frac{1}{2} { F_s \sigma_c^2 (t) + F_s \sigma_g^2 (u) }$</td>
<td>$\frac{1}{2} { F_s (i) + f_c^2 F_e (k) }$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-2 f_c f_e f_s (E) + F_s \varepsilon (G)$</td>
<td>$-2 f_c f_e f_s (o) + F_s \varepsilon (s) } M_y$</td>
<td>$\frac{1}{2} { F_s (j) + f_c^2 F_e (l) }$</td>
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<tr>
<td>$E_{2c}$</td>
<td></td>
<td>$\frac{1}{2} { F_s \sigma_c^2 (H) + F_s \sigma_g^2 (J) }$</td>
<td>$\frac{1}{2} { F_s \sigma_c^2 (t) + F_s \sigma_g^2 (u) }$</td>
<td>$\frac{1}{2} { F_s (i) - f_c^2 F_e (k) }$</td>
</tr>
<tr>
<td></td>
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<td>$+2 f_c f_e f_s (E) + F_s \varepsilon (G)$</td>
<td>$+2 f_c f_e f_s (o) + F_s \varepsilon (s) } M_y$</td>
<td>$-\frac{1}{2} { F_s (j) - f_c^2 F_e (l) }$</td>
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<tr>
<td>$E_{2s}$</td>
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<td>$- F_c f_e (F) + F_s \sigma_f (J)$</td>
<td>$- F_c f_e (r) + F_s \sigma_f (x)$</td>
<td>${ f_s F_e (p) - f_c F_e (y) } M_z$</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>${ f_s F_e (q) - f_c F_e (z) } M_z$</td>
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