COHERENT X-RAY DIFFRACTION OF LASER-INDUCED MAGNETIZATION DYNAMICS AND NONLINEAR X-RAY EFFECTS

A DISSERTATION
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Abstract

Modern magnetism research has largely been driven by the rapid growth of magnetic data storage technologies over the last several decades. As device length scales become ever smaller, and operational time scales become ever faster, it becomes more important than ever to understand magnetic processes on their fundamental scales. For this, we need access to femtosecond dynamics on atomic length scales.

Coherent x-ray diffraction is an attractive tool for studying a wide range of condensed matter systems due to the many unique advantages of x-rays - small wavelengths, large penetration depths, and chemical and elemental specificity. Soft x-rays are particularly important for the study of magnetism, as many of the important magnetic elements have strong resonances in this regime. The polarization dependent dichroic absorption near these resonances, an effect known as x-ray circular magnetic dichroism, is the mechanism for magnetic contrast in many x-ray techniques.

This dissertation discusses two sets of coherent x-ray experiments. The first part focuses on the development of time-resolved optical pump x-ray probe experiments both at a synchrotron and an x-ray free electron laser (XFEL) source. Using this technique, I studied the femto- to picosecond relaxation dynamics in the labyrinth-like magnetic domains of a Co/Pd multilayer thin film following excitation by a femtosecond optical pulse. From the normalized correlation function, I isolated the elastic and fluctuating portions of the scattering intensity during the relaxation process.

The emergence of XFELs such as the Linac Coherent Light Source has dramatically altered the types of experiments that are now possible, including the systematic exploration of nonlinear x-ray-matter interactions. Nonlinear spectroscopy in the optical regime has contributed immensely to our understanding of microscopic
interactions and dynamical processes. The hope is to extend these spectroscopic techniques to the x-ray regime, to take advantage of the smaller wavelength, elemental and chemical specificity, and momentum resolution. One of the most promising nonlinear x-ray techniques is stimulated resonant inelastic x-ray scattering (RIXS), analogous to stimulated Raman scattering in the optical regime. The critical question is whether the threshold for stimulated RIXS will be low enough, below the sample damage threshold, for it to be a viable technique for systems of interest.

In the second half of this dissertation, I demonstrate strong indications of stimulated RIXS in a high intensity single shot coherent diffraction experiment at LCLS. By utilizing the strong resonant enhancements of the scattering cross-section, significant nonlinear changes in the diffraction as a function of x-ray pulse intensity were detected. These observations are consistent with calculated intensities for a stimulated inelastic scattering process. Further intensity dependent spectroscopy experiments are planned for LCLS to confirm the threshold for stimulated scattering. The development of nonlinear x-ray spectroscopic techniques will certainly revolutionize existing fields as well as spawn entirely new fields of research.
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Chapter 1

Introduction

Since the discovery of x-rays by Röntgen in 1895, x-rays have made significant contributions to our fundamental understanding of structure and matter. X-rays have many unique properties, including their large penetration depth due to their small absorption probability, which enables the probing of relatively think samples, their small wavelengths, which provides atomic length scale spatial information, and their elemental specificity due to the characteristic inner-shell binding energies, which enables the element-specific probing of nanostructures.

The role of x-rays in magnetism is a much more recent development, in large part because magnetic scattering is about a factor of $10^{-4}$ weaker than charge scattering [1]. The first observation of magnetic x-ray scattering were only achieved in 1972, with great effort by de Bergevin and Brunel [2]. A significant breakthrough came in 1985 when Blume developed the theoretical basis of resonant magnetic scattering, where the magnetic scattering cross section is enhanced by orders of magnitude by tuning to an absorption edge [3]. The effect was experimentally verified using tuneable synchrotron radiation [4], showing x-rays as an attractive alternative to neutron scattering for the study of magnetism on an atomic level. The prediction and subsequent demonstration of the x-ray magnetic linear dichroism (XMLD) and x-ray magnetic circular dichroism (XMCD) effects during the same time period further propelled the emergence of synchrotron based magnetic x-ray techniques [5, 6, 7].
Magnetism research has been closely linked with technological developments over the last several decades, in particular with the field of magnetic storage. Understanding the dynamical response of magnetic materials to external excitations has become one of the forefront problems in modern magnetism research. For a long time, the conventional way to control and manipulate magnetization was to apply a magnetic field, as is done in computer hard drives. More recently, other techniques to manipulate the magnetization have been employed, such as spin polarized currents or femtosecond optical excitations. From a scientific perspective, the desire is to understand the fundamental magnetic processes such as demagnetization, spin-orbit coupling, and the exchange interaction. From a technological perspective, the eventual goal is of course to control the magnetization on ever smaller and faster time scales for next generation magnetic storage devices.

Figure 1.1: Spatial and temporal scales in magnetic devices and processes, modified from [8].
Representative magnetic devices and processes are shown in Figure 1.1. The spatial length scales extend all the way from micron sized domains to nano-sized bits. The time scale ranges from the typical read-write processes in the nanosecond range to the most fundamental interactions in magnetism which occur on the femtosecond time scale. In the optical regime, ultrafast lasers pulses on the order of femtoseconds provide excellent temporal resolution, but are limited in spatial resolution by their wavelengths. X-rays at third generation synchrotrons are the opposite, with spatial resolution on the atomic length scale, but a limited temporal resolution on the order of 10s of picoseconds. A new generation of X-ray Free Electron Laser (XFEL) facilities, including the Linac Coherent Lightsource (LCLS) [9], combine the advantages of lasers and x-rays, and has opened the door to studying dynamics on atomic length scales and femtosecond time scales. In combination with third generation synchrotron sources, XFELs thus enable the exploration of a wide range of dynamical processes with nanoscale resolution, including the topics covered in this thesis - laser-induced magnetization dynamics and intensity dependent nonlinear x-ray effects.

In this thesis, I will begin with a review of fundamental concepts in magnetism in Chapter 2. Building upon this foundation, I will then discuss magnetization dynamics, in particular the emerging field of "femtomagnetism". In chapter 3, I will introduce basic x-ray concepts, and show why x-rays are one of the preferred tools for studying magnetism. Results of our time-resolved coherent scattering experiments on magnetization relaxation at the Stanford Synchrotron Radiation Lightsource (SSRL) will be presented in chapter 4. The time-resolved coherent scattering experiments will be extended to the femtosecond time scale with our results at the Linac Coherent Lightsource (LCLS) in chapter 5. As we shall see, the unprecedented brightness and time scales accessible with LCLS enables the exploration of non-linear processes at x-ray wavelengths. The first experimental indications of stimulated inelastic x-ray scattering in a solid will be discussed in chapter 6. Finally, I will provide a brief summary and future outlook in the last chapter.

Now, let us begin!
Chapter 2

Magnetization Dynamics

Magnetism has been used for practical applications throughout history, from the compasses of ancient times to the hard-drives of the computer era. The intimate link between scientific research and technological applications in this field has been strengthened by the explosive growth of information storage and communication technologies over the last 50 years. The magnetization of excited states define the operation processes and time scales in magnetic devices. In current devices, magnetization reversal of the logical bits occurs through precessional switching, in which an applied magnetic field pulse causes the magnetization vector to precess about the field until the switching threshold is reached [8, 10]. Using the high magnetic fields associated with electron bunches from the Stanford Linear Accelerator, it was demonstrated that deterministic precessional switching breaks down for magnetic field pulses shorter than 2.3 ps [11]. However, the desire to explore the ultimate limits of magnetization dynamics have continued to spur an intense search for other methods to manipulate and to control magnetization on ever faster time scales and smaller length scales. This has led to the emerging field of "femtomagnetism" - magnetization dynamics on the sub-picosecond time scale. In this chapter, we will begin by introducing some basic concepts in magnetism. Building on this basis, we will then discuss some of the earliest experiments in the field of femtomagnetism - experiments on ultrafast demagnetization.
2.1 Basic Concepts in Magnetism

In this section, we will describe the fundamental relationship between magnetism and angular momentum, and the relevant magnetic energies in our samples. Further details may be found in many excellent texts on magnetism [8, 12, 13].

The fundamental object in magnetism is the magnetic moment. In the classical picture, for a current \( I \) around a loop of area \( dS \), the magnetic moment \( \mu \) is given by:

\[
\mu = I \int dS
\]  

(2.1)

Because the charged particles in the current loop are essentially orbiting masses, this suggests that the magnetic moment is related to angular momentum. For atoms, the magnetic moment \( \mu \) associated with an orbiting electron is given by:

\[
\mu = \gamma L
\]  

(2.2)

The proportionality constant \( \gamma \) is known as the gyromagnetic ratio and is given by:

\[
\gamma = \frac{qg\mu_0}{2m_e}
\]  

(2.3)

where \( q \) is the charge of the particle, \( g \) the g-factor which has an approximate value of 2, \( \mu_0 \) the permeability of free space, and \( m_e \) the mass of the electron. The sign of \( \gamma \) depends on the charge of the particle, and is negative for electrons. In other words, the magnetic moment for an electron is antiparallel to its angular momentum. For atomic magnetic moments, a convenient unit is the Bohr magneton:

\[
\mu_B = \frac{e\hbar}{2m_e} = 9.274 \times 10^{-24} \text{Am}^2
\]  

(2.4)

The relationship between magnetic moments and angular momentum is a central concept in magnetism. Because a magnetic solid typically contains a large number of individual magnetic moments, it is easier to consider the magnetization \( M(r) \), or the magnetic moment per unit volume. The magnetization can be separated into two
components:

\[ M(r) = M_s m(r) \] (2.5)

where \( M_s \) is the constant saturation magnetization, while \( m(r) \) is the direction of magnetization, which may change with time, but has constant magnitude of 1.

The equation of motion for the spin is the well known Landau-Lifshitz equation:

\[ \frac{d}{dt} M = -\gamma M \times H + \alpha \left( M \times \frac{d}{dt} M \right) \] (2.6)

The first term is related to the precession of spins around a magnetic field \( H \), while the second term is a phenomenological damping term that describes how the magnetization eventually aligns with the effective field direction, with \( \alpha \) being the damping constant. In general, we need to take into account both internal and external fields. Four of the most relevant energy terms are discussed below: Zeeman, exchange, anisotropy and stray field [13].

The first energy term is the Zeeman term, arising from the splitting of degenerate energy levels in the presence of an applied magnetic field, which accounts for the effects of external magnetic excitations:

\[ E_H = -\mu_0 M_s \int_{\text{sample}} H_{\text{ex}} \cdot m \, dV \] (2.7)

The second term is the exchange energy, or the spin-spin interaction energy term that describes the tendency of ferromagnetic spins to align parallel with neighboring spins:

\[ E_{ex} = A \int_{\text{sample}} (\nabla m)^2 \, dV \] (2.8)

where the exchange constant \( A \) is a material constant. In ferromagnetic transition metals such as Fe and Co, the exchange field leads to an energy separation between
the spin-up and spin-down density of states (DOS), an effect known as exchange splitting [8]. This imbalance of spin creates a net magnetic moment in the system.

The third term is the anisotropy energy. There are a variety of anisotropy energies that may be present in a magnetic system, but the two dominant ones that we will consider are magnetocrystalline and shape anisotropy. The origins of the magnetocrystalline anisotropy is spin-orbit coupling, which links the spin and orbital moments. This leads to an easy axis (energetically favourable) and a hard axis (energetically unfavourable) for the magnetization in crystals. For the case of uniaxial anisotropy, where the energy depends on the angle between the magnetization and a single axis, the anisotropy has the form:

\[ E_{Ku} = \int_{\text{sample}} K_1 \sin^2 \theta + K_2 \sin^4 \theta dV \]  

(2.9)

where \( K_1 \) and \( K_2 \) are anisotropy constants and \( \theta \) is the angle between the magnetization and the easy axis.

The second type of anisotropy is associated with the shape of the sample. For example, in the thin film samples of our experiments, the shape anisotropy favours keeping the magnetization in the plane of the film, and is given by:

\[ E_{Ks} = \frac{1}{2} \mu_0 M^2 \cos^2 \theta \]  

(2.10)

The last energy term is the stray field energy due to the interaction of the magnetization with the magnetic field of the sample. Starting from Maxwell’s equation:

\[ \nabla \cdot B = \mu_0 \nabla \cdot (H + M) = 0 \]  

(2.11)

We obtain for the stray field \( H_d \):

\[ \nabla \cdot H_d = -\nabla \cdot M \]  

(2.12)
The stray field energy is then:

$$E_d = -\frac{\mu_0}{2} \int_{\text{sample}} \mathbf{H}_d \cdot \mathbf{M} dV$$  \hspace{1cm} (2.13)

The stray field energy needs to be calculated over the entire sample for every point in the sample, and is a major reason why micromagnetic simulations take so long, as we shall see in the following section.

The equilibrium magnetization configuration in a system is determined by energy minimization of the different competing energies. For example, in a ferromagnet, magnetic domains can form as a result of competition between the anisotropy energy, which is minimized when the magnetization lies along the easy axis, and the stray field energy, which is minimized when flux closures are formed. In the same way, the width of the domain wall is a balance between the exchange and the anisotropy energies.

As an illustration, the effects of altering the exchange and the anisotropy are demonstrated in Figure 2.1 using the Object Oriented MicroMagnetic Framework (OOMMF) developed by the Information Technology Laboratory at the National Institute of Standards and Technology (ITL/NIST) \[14\]. Figure 2.1(a) shows the component of the magnetization perpendicular to the sample plane for a 20 nm Co/Pd multilayer structure with the following parameters: saturation magnetization $M_s = 700 \times 10^3$ A/m, exchange stiffness $A = 1 \times 10^{-11}$ J/m, uniaxial perpendicular anisotropy $K_1 = 4 \times 10^5$ J/m$^3$, and damping $\alpha = 0.04$.

Co/Pd multilayer films with perpendicular anisotropy are a model system for many of our experiments. They have been extensively studied as a candidate system for perpendicular magnetic recording media and have strong scattering cross sections, making them ideal for scattering and imaging experiments \[15, 16\]. Because of the strong uniaxial perpendicular anisotropy, the magnetization in the sample points either into or out of the sample plane, as represented by red for +1 and blue for -1. An additional advantage for these systems is that the perpendicular magnetization provides maximum magnetic contrast through the X-ray Magnetic Circular Dichroism
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Figure 2.1: Micromagnetics simulations of equilibrium domain configurations in a magnetic thin film for different parameters. Magnetization perpendicular to sample surface is shown. (a) Initial domain configuration. (b) Effects of increasing exchange. (c) Effects of increasing perpendicular anisotropy. In all cases, the field of view is 2 μm by 2 μm.

When the exchange stiffness $A$ is increased by 50\% to $A = 1.5 \times 10^{-11}$ J/m while all other material parameters are held constant, the correlation between neighbouring spins is significantly increased, leading to much larger domains, as shown in Figure 2.1(b). When the uniaxial perpendicular anisotropy $K_1$ is increased by 20\% to $6 \times 10^4$ J/m$^3$ while all other material parameters are held constant, the stronger out-of-plane stray field is compensated by smaller domains, as shown in Figure 2.1(c). The correlation between perpendicular anisotropy and the magnetic domain size is one of the keys in reducing the magnetic bit size in magnetic storage devices, and is an active area of research.
2.2 Ultrafast Demagnetization

Some of the earliest experiments in the field of ultrafast demagnetization explored the loss of magnetic order when a magnetic system is hit with a femtosecond optical excitation. In 1991, Vaterlaus et al measured using time- and spin-resolved photoemission experiments on Gd, obtaining a demagnetization time of $100 \pm 80$ ps [17]. This was consistent with view at the time that the dynamic response is largely governed by the spin-lattice relaxation time, which was calculated to be 48 ps [18]. With this view, the femtosecond optical excitation is absorbed by electrons close to the Fermi level, resulting in a hot electron gas that equilibrates via electron-electron scattering within 10s of fs. The electronic excitations decay via electron-phonon scattering over 100s of fs. Finally, the lattice and the spin system reach an equilibrium after the spin-lattice relaxation time of approximately 100 ps.

In 1996, using a time-resolved magneto-optical Kerr effect (MOKE) setup, Beaurepaire et al made a surprising discovery - the demagnetization in Ni thin films occurs within a picosecond after a femtosecond pulsed-laser excitation, as shown in the left of Figure 2.2 [19].

![Figure 2.2: Left: Time-resolved MOKE measurement of the magnetization in a Ni thin film following a femtosecond optical excitation [19]. Right: Time-resolved XMCD measurement of the magnetization in a Ni thin film following a femtosecond optical excitation [20].](image)
This sub-ps demagnetization was soon confirmed by several other groups, and marked the beginning of the field of "femtomagnetism" - the manipulation of magnetization on femtosecond time scales [21, 22, 23]. Beaurepaire et al introduced a phenomenological three-temperature model to describe the interaction between three reservoirs of energy: the electrons, the spins, and the lattice as shown in Figure 2.3 below [19].

![Figure 2.3: Energy and angular momentum in the system are stored in three interconnected reservoirs - the electrons, the spins, and the lattice [24].](image)

The initial optical excitation pumps energy into the electron system, resulting in hot electrons that rapidly thermalize to a temperature $T_{el}$. Electron-phonon interactions equilibrate the electron system with the lattice at temperature $T_{lat}$. Interactions between the spin system and the electrons, as well as between the spin system and the lattice, cause a heating of the spin system to a temperature $T_{sp}$. By assigning heat capacities to the three reservoirs ($c_{el}$, $c_{lat}$, and $c_{sp}$), and fitting coupling constants for the exchange between the reservoirs, the experimental demagnetization curves can be reproduced. However, such a phenomenological model gives no insight to the microscopic mechanisms behind the ultrafast demagnetization process, which has remained a hotly debated topic [25, 26, 27, 28].
One short-coming of the three-temperature model is that it does not take into account the transfer of angular momentum, essential for understanding magnetization dynamics. The key is to understand the time constants for both energy and angular momentum exchange between the different reservoirs. Both the electron-spin ($\tau_{el-sp}$) and electron-lattice ($\tau_{el-lat}$) interactions are fairly fast, but the spin-lattice interaction was thought to be much slower. A common belief is that there must be an ultrafast channel of spin angular momentum dissipation in order to explain ultrafast demagnetization.

Angular momentum transfer was explicitly addressed by Koopmans et al in his microscopic three-temperature model (M3TM) [26]. Before the excitation, the angular momentum in the system is carried mainly by the spins of the electrons, which are aligned in the magnetization direction. The femtosecond optical excitation is absorbed by electrons close to the Fermi level, resulting in a nonequilibrium distribution that then thermalizes via electron-electron and electron-phonon scattering. Spin-flip scattering can then alter the magnetization of the system. In the M3TM, Koopmans proposed enhanced spin-flip scattering probabilities at local hotspots in the band, similar to a Elliott-Yafet type of scattering, as the mechanism for the ultrafast dissipation of angular momentum to the lattice.

Using XMCD with femtosecond x-ray pulses, Stamm et al was able to disentangle the spin and orbital contributions to the angular momentum in a ferromagnetic Ni thin film following excitation by a femtosecond optical pulse [20]. Their results ruled out a significant transfer of angular momentum between the orbital and spin moment, suggesting the existence of a novel channel for angular momentum dissipation into the lattice as being responsible for ultrafast demagnetization. These results are in agreement with Koopmans' M3TM.

In direct contrast, in a recent paper, Battiato et al suggested that the superdiffusive transport of excited spin-polarized electrons following laser excitation may play a significant role in the transfer of angular momentum [28]. With their model, they were able to explain the experimentally observed demagnetization without the need for a channel of angular momentum dissipation between the spin and the lattice. Clearly, there remains a great deal of debate about the mechanisms behind ultrafast
The major challenge in elucidating the origins of ultrafast demagnetization has been the difficulty of describing the laser excited electronic system. Other than phenomenological models such as Koopmans’ M3TM, no ab initio theory exists. At the same time, further progress has been impeded by a lack of experimental access to the microscopic details behind the transfer of angular momentum on femtosecond time scales. The emergence of x-ray free electron laser sources with intense, femtosecond x-ray pulses, time-resolved x-ray scattering may finally provide the key to understanding this fascinating phenomenon.
Chapter 3

X-ray Absorption and Scattering

In this chapter, we will cover the x-ray and diffraction concepts necessary to understand the experimental results presented later. We will begin with the two most basic x-ray processes - absorption and scattering. The polarization and phase dependence of charge and magnetic scattering will be explored through a semi-classical picture of scattering from a free electron. As we shall see, when extended to the case of scattering from an atom, the scattering can be described in terms of the complex atomic scattering factor, which has a simple relation to the optical constants. These optical constants can then be related to the concept of cross-sections, a easily measured experimental parameter in the x-ray regime. Further details on x-ray-matter interactions can be found in texts such as [1, 8, 29].

In the second half of this chapter, we will lay down the theory for our particular experimental technique - x-ray diffraction. Starting from the illustrative case of a double slit diffraction experiment, we will discuss the effects of the optical constants on the intensity and contrast in the diffraction pattern. We will then cover the typical experimental setup for our coherent diffraction measurements - transmission geometry, and explain the polarization dependence for the diffraction. Finally, we will briefly cover the reconstruction of a real space image from the farfield diffraction using a technique known as Fourier Transform Holography (FTH).
3.1 X-ray Absorption

An x-ray photon can interact with a sample in one of two ways - it can be absorbed, or it can be scattered. In the x-ray absorption process, energy from the incident field is absorbed, and the energy is transferred to an electron. If the resulting kinetic energy of the electron is high enough, it can escape into the continuum, leaving behind an ionized atom. Upon passage through the sample, the x-ray beam is attenuated exponentially, with the intensity given by Beer’s law:

\[
I(z) = I_0 e^{-\mu z}
\]

where \( I_0 \) is the incident intensity, and \( \mu \) is the absorption coefficient.

Figure 3.1: (a) Labeling of electron shells. (b) X-ray absorption: an incident photon of sufficient energy \( \hbar \omega \) is absorbed by the atom, ejecting a photoelectron with kinetic energy equal to the photon energy minus the binding energy. (c) Non-radiative Auger decay: an electron falls from an outer shell to fill the core hole. Energy is conserved with the ejection of a second electron of characteristic energy. The second electron does not need to be from the same shell as the first. (d) X-ray emission or fluorescence: an electron from the outer shell fills the core hole, accompanied by the emission of a photon of characteristic energy. Adapted from [1, 29].
When an x-ray photon expels an electron from an inner shell, the absorption process creates a core hole. The core hole can be filled in two ways - fluorescence or Auger decay. When the core hole is filled by an electron from the outer shell accompanied by the emission of a photon, the emitted radiation is known as fluorescence. When the core hole is filled by an electron from an outer shell, and the excess energy is transferred to another electron which is then emitted, the process is known as Auger decay. X-ray absorption, Auger decay, and fluorescence are shown in Figure 3.1. Auger decay and fluorescence are thus two competing mechanisms of core hole decay.

For low atomic number elements, Auger dominates over fluorescence, as can be seen in Figure 3.2 below. In our experiments, typically done at the Co L-edges, the Auger yield is approximately two orders of magnitude larger than the fluorescence yield.

Figure 3.2: Comparison of Auger and fluorescence yields as a function of atomic number Z [29].
3.2 X-ray Scattering

The second important class of x-ray-matter interaction is x-ray scattering. Although scattering is at its heart a quantum mechanical phenomenon, important insights can be gained through a classical treatment. In the classical picture, the electric field of the incident x-rays causes charges to oscillate. The accelerating charges then radiate scattered waves. When the wavelength of the incident radiation is long compared to the size of the scatterer, contributions from induced dipoles will dominate over higher order multipoles. Classically, the scattering is elastic - the scattered wave has the same wavelength as the incident wave. In the quantum mechanical description, the incident X-ray photon has momentum $\hbar \mathbf{k}$ and energy $\hbar \omega$. Energy may be transferred to the electron, resulting in inelastic scattering.

3.2.1 Scattering by a Free Electron

Let us start with the most elementary scattering scenario - scattering of an x-ray by a single electron. Consider the case where a linearly polarized incident wave, with its unit polarization vector $\mathbf{\hat{e}}_x$ along the $x$ axis and propagating along $z$. The incident electromagnetic wave has the form:

$$E_0(r, t) = \mathbf{\hat{e}}_x E_0 e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})}$$

(3.2)

This incident electromagnetic wave causes the electron to oscillate, creating an electric dipole aligned along the incident electric field. It can be shown that the electric field radiated by this dipole is [8]:

$$E_{e_{chg}}(t) = -\frac{e^2}{4\pi\varepsilon_0 m_e c^2} \frac{e^{i\mathbf{k}'r}}{r} \left[ \mathbf{k}_0' \times \mathbf{E}(t) \right] \times \mathbf{k}_0'$$

(3.3)

$$= -r \frac{e^{i\mathbf{k}'r}}{r} \left[ \mathbf{k}_0' \times \mathbf{E}(t) \right] \times \mathbf{k}_0'$$

(3.4)

where $\mathbf{k}'_0$ is the scattered wave vector, $m_e$ is the mass of the electron, and the classical
electron radius or the Thomson scattering length $r_e$ is defined as:

$$ r_e = \frac{e^2}{4\pi\epsilon_0 m_e c^2} = 2.82 \times 10^{-6} \text{ nm} \quad (3.5) $$

In the classical picture of charge scattering, the incident electric field sets up an oscillating electric dipole, which then re-radiates a scattered wave with the same polarization as the incident field, but with a phase shift of $\pi$.

Just as how the incident electric field can induce an electric dipole and re-radiate a charge scattered wave, the incident magnetic field can induce a magnetic dipole and an associated spin scattered wave. Using the same incident wave as in equation (3.2), the incident magnetic field is:

$$ B(r, t) = \frac{1}{c}(k_0 \times \epsilon) E_0 e^{-i(\omega t - k \cdot r)} \quad (3.6) $$

The spin $s(t)$ will precess in a cone around a constant magnetic field according to the torque equation:

$$ \frac{ds(t)}{dt} = -\frac{e}{m_e} s(t) \times B \quad (3.7) $$

Each time the incident magnetic field switches sign, the direction of precession around the cone changes according to equation (3.7). The perpendicular component of the spin thus represents an oscillating magnetic dipole. The electric field radiated by this magnetic dipole is [8]:

$$ E'_{mag}(t) = i \frac{e^2}{4\pi\epsilon_0 m_e c^2 m_e c^2} \frac{\hbar \omega}{r} e^{ik'r} [s \times (k_0 \times E(t))] \times k'_0 \quad (3.8) $$

$$ = i r_e \frac{\hbar \omega}{m_e c^2} \frac{e^{ik'r}}{r} [s \times (k_0 \times E(t))] \times k'_0 \quad (3.9) $$

In addition to a phase shift by $\pi/2$ due to the factor $i$ in the magnetic dipole moment, the spin scattered wave has a polarization rotated by $\pi/2$ relative to the incident wave. A comparison of equation (3.3) and (3.8) reveals that spin scattering is
weaker than charge scattering by a factor of $\frac{\hbar \omega}{m_e c^2}$. This is because only electrons with unpaired spin in open shells contribute to magnetic scattering, while all electrons contribute to charge scattering. This factor explains the initial experimental difficulties in observing non-resonant magnetic scattering [1].

### 3.2.2 Scattering from an atom

Scattering from a free electron can be extended to scattering from an atom with the superposition of scattered field contributions from an electron density $\rho(r)$. Consider a scatterer located at $r$ relative to the origin as shown in Figure 3.3. The incident wave will experience a phase change $k \cdot r$ before being scattered. The scattered wave will experience a phase change $-k' \cdot r$. Thus the resulting phase difference is $(k - k') \cdot r$. This is usually written as $Q \cdot r$, where $Q = k - k'$ is known as the scattering vector. As shown in Figure 3.3b, the magnitude of $Q$ is given by:

$$Q = \frac{4\pi}{\lambda} \sin \theta$$

(3.10)

![Figure 3.3](image-url): (a) Schematic showing scattering from a charge distribution $\rho(r)$. (b) Schematic showing the relationship between $Q, k, k'$ and the scattering angle $2\theta$. 

Summing together the contributions from all volume elements, we obtain the atomic form factor:

$$F^0(Q) = \int_{\text{sample}} \rho(r)e^{iQ \cdot r} dr$$  \hspace{1cm} (3.11)

For a charge distribution concentrated entirely at the origin (i.e., $Q = 0$), equation (3.11) reduces to $F^0(Q) = Z$, the total number of electrons in the atom. As $Q$ increases, the scattered amplitude decreases due to destructive interference, and $F^0(Q \to \infty) = 0$. Note that from equation (3.11), the scattering factor is in fact the Fourier transform of the electron density. This close relationship between scattering and the Fourier transform will come up again and again.

Atomic electrons have discrete energy levels, and hence we expect an energy dependence in the scattering. Furthermore, the response of the electron must have a phase lag with respect to the driving field [1]. Thus in general, the scattering can be expressed in terms of a complex atomic scattering factor $F(Q, \omega)$:

$$F(Q, \omega) = F^0(Q) + F'(\omega) - iF''(\omega)$$  \hspace{1cm} (3.12)

where again $F^0(Q)$ is the atomic form factor, and $F'(\omega)$ and $F''(\omega)$ are the dispersive and absorptive contributions to the scattering. For the case of forward scattering, where the momentum transfer $Q$ is small, the atomic scattering factor simplifies to:

$$F(\omega) = Z + F'(\omega) - iF''(\omega)$$  \hspace{1cm} (3.13)

$$= f_1(\omega) - i f_2(\omega)$$  \hspace{1cm} (3.14)

where $Z$ is the number of electrons in the atom, and $f_1(\omega)$ and $f_2(\omega)$ are known as the Henke-Gullikson factors, defined as:

$$f_1(\omega) = Z + F'(\omega)$$

$$f_2(\omega) = F''(\omega)$$  \hspace{1cm} (3.15)

$f_1$ and $f_2$ can be linked to the familiar dispersion and absorption optical constants.
\[ \delta(\omega) \text{ and } \beta(\omega) \text{ through:} \]

\[
\delta(\omega) = \frac{\lambda^2}{2\pi} r_c N f_1(\omega) \\
\beta(\omega) = \frac{\lambda^2}{2\pi} r_c N f_2(\omega)
\]  

(3.16)

where \( r_c \) is the classical electron radius, \( \lambda \) the x-ray wavelength, and \( N \) the atomic number density.
3.3 Cross-Sections

An important concept that links experimental results with theory is that of the cross-section. Conceptually, the cross-section is the effective area of interaction that removes energy from the incident wave. The absorption cross-section is given by the ratio between the number of absorption events $\Gamma_{\text{tot}}$, and the incident flux $\Phi_0$:

$$\sigma_{\text{abs}} = \frac{\Gamma_{\text{tot}}}{\Phi_0} \quad (3.17)$$

Experimentally, the absorption can be easily measured in the transmission geometry. The incident flux is usually measured with total electron yield from a gold mesh, and the transmitted flux behind the sample is recorded with a photodiode. The absorption cross-section is directly related to the imaginary part of the refractive index, $\beta$, through:

$$\sigma_{\text{abs}} = \frac{4\pi}{N\lambda} \beta \quad (3.18)$$

Using the experimentally measured absorption cross-section, the dispersion can be calculated through the Kramers-Kronig relation.

In a similar vein, the scattering cross-section is equivalent to the effective area for redirecting incident radiation, as given by the ratio between the average radiated flux and the average incident flux. The scattering cross-section for a free electron, also known as the Thomson cross-section, is [29]:

$$\sigma_e = \frac{8\pi}{3} r_e^2 = 6.65 \times 10^{-25}\text{cm}^2 \quad (3.19)$$

where $r_e$ is the classical electron radius as given in the previous section. Unlike absorption measurements, where the transmitted beam in the forward direction is measured, the scattered beam may be emitted into any direction in a $4\pi$ solid angle. In this case, the solid angle covered by the detector needs to be taken into account when measuring the scattered intensity.
The absorption and scattering cross-sections for Fe near the Fe L3 absorption edge are shown in Figure 3.4 [30]. As can be seen, the absorption cross-section is approximately three orders of magnitude larger than the scattering cross-section. The dominance of the absorption cross-section has important implications for x-ray diffraction in the transmission geometry, which is based on the interference of wave fields in the farfield. As we shall see in section 3.5, the contrast in our experimental diffraction is almost entirely due to absorption dichroism.
3.4 X-ray Magnetic Circular Dichroism

The polarization dependent absorption effect known as X-ray Magnetic Circular Dichroism (XMCD) is the basis for magnetic contrast in many x-ray imaging techniques. As we saw in section 3.2.1, polarization and scattering are intimately related.

3.4.1 Polarization Basis

The photon angular momentum, or the photon spin, is defined as the expectation value of the angular momentum operator along the propagation direction $z$, or $\langle L_z \rangle$. A general polarization state can be written as a linear combination of two orthogonal basis states in one of two forms - with two linearly polarized (vertical and horizontal) basis states or two circularly polarized (left and right) basis states.

Let us consider a wave propagating in $z$ with frequency $\omega$ and wavelength $\lambda = \frac{2\pi}{|k|}$. For linearly polarized light, the electric field vector oscillates along an axis in the $x - y$ plane. We can define two linearly polarized basis states for the position and time dependent electric field $E(r, t)$ to be:

$$\begin{align*}
E_x(z, t) &= \hat{e}_x E_0 e^{i(kz - \omega t) + i\phi_0} \\
E_y(z, t) &= \hat{e}_y E_0 e^{i(kz - \omega t) + i\phi_0}
\end{align*}$$

(3.20)

where $\phi_{0x}$ and $\phi_{0y}$ define the initial phase.

For circularly polarized light, the electric field rotates in space and time, along a circular helical path. The circularly polarized wave can thus be viewed as a superposition of two orthogonal linearly polarized waves with equal amplitude, but with a relative phase shift of $\pi/2$. The electric field is given by:

$$\begin{align*}
E_R(z, t) &= E_+(z, t) = -\frac{1}{\sqrt{2}} (\hat{e}_x + i\hat{e}_y) E_0 e^{i(kz - \omega t) + i\phi_0} \\
E_L(z, t) &= E_-(z, t) = \frac{1}{\sqrt{2}} (\hat{e}_x - i\hat{e}_y) E_0 e^{i(kz - \omega t) + i\phi_0}
\end{align*}$$

(3.21)

The two basis states for waves propagating along $z$ are shown in Figure 3.5, along with the projection of the electric field vector onto the $x - y$ plane.
Figure 3.5: In the linearly polarized basis, the two basis states are horizontal and vertical linearly polarized light. For a wave traveling in the $z$ direction, the electric field vector projected onto the $x-y$ plane oscillates along either the $x$-axis or the $y$-axis. In the circularly polarized basis, the two basis states are right and left circularly polarized light (RCP and LCP). For a wave traveling in the $z$ direction, the electric field vector projected onto the $x-y$ plane moves along a circle, either clockwise or counter-clockwise.

The most general form of polarization is elliptically polarized light. By breaking the wave down into its right ($E_+$) and left ($E_-$) circularly polarized components, the polarization of the beam can be defined as:

$$P = \frac{|E_+|^2 - |E_-|^2}{|E_+|^2 + |E_-|^2}$$  \hspace{1cm} (3.22)
3.4.2 X-ray Magnetic Circular Dichroism

In a magnetic material, the spin-up and spin-down density of states (DOS) are separated by the exchange splitting. The resulting imbalance of spin-up and spin-down electrons forms the magnetic moment. X-ray magnetic circular dichroism (XMCD) is the polarization dependence of the absorption, which originates from the difference in the number of available states in the spin-up and spin-down channels. XMCD forms the basis for magnetic contrast in many x-ray techniques.

![Diagram of XMCD mechanism](image)

Figure 3.6: The X-ray Magnetic Circular Dichroism effect is a reflection of the imbalance in the number of unoccupied states between the two spin channels. Depending on the polarization (photon spin) of the incident x-rays, domains with magnetization parallel (cyan) or anti-parallel (pink) to the incident photon spin exhibit different absorption.

Let us illustrate the XMCD mechanism with L-edge absorption, a transition from the 2p to the 3d shell. Circularly polarized light carry angular momentum, as defined by the photon spin. The angular momentum can be transferred to the excited photoelectron during the absorption process, resulting in spin-up or spin-down photoelectrons, depending on the polarization of the incident light. Because spin flips are forbidden in an electric dipole transition, a spin-up photoelectron from the 2p shell can only be excited into an unoccupied state in the spin-up 3d shell, and vice versa for spin-down photoelectrons. The imbalance in the number of unoccupied states in
the two spin channels manifests itself in the x-ray absorption spectra. The effect is maximal when the magnetization and the photon spin are aligned.

Using circularly polarized x-rays at the $L_3$ edge, magnetic images taken with transmission x-ray imaging techniques will thus show three distinct shades of gray - darker regions corresponding to where the magnetization is parallel to the photon spin (cyan curve, higher absorption), brighter regions corresponding to where the magnetization is anti-parallel to the photon spin (pink curve, lower absorption), and intermediate regions corresponding to where the magnetization is in-plane (black curve, average absorption).

Note that the $L_3$ and $L_2$ absorption edges have opposite spin-orbit coupling, $L+S$ and $L-S$ respectively, leading to a sign change in the absorption dichroism between the two peaks in the XMCD spectra.

### 3.4.3 Natural Basis for Perpendicularly Magnetized Films

From an incident wave at normal incidence, differences between systems with in-plane magnetization and perpendicular out-of-plane magnetization result in a different choice for the proper basis system. These differences arise from the direction of the quantization axis, which lies along the magnetization direction of the sample. A thin film with perpendicular anisotropy positioned in the $x - y$ plane has its quantization axis in $z$. For a wave at normal incidence, the propagating direction $z$ is thus aligned to the quantization axis. The natural basis for the radiation in this case is circularly polarized light. An intuitive explanation for this can be seen by considering the differences between incident linearly polarized light versus incident circularly polarized light for such a film with perpendicular magnetization.
An incident wave linearly polarized in \( x \) can be broken down into its right and left circularly polarized components:

\[
E_{\text{in}}(x, y, z) = A_x \sin(2\pi z)\hat{\epsilon}_x
\]
\[
= A_x \sin(2\pi z) \frac{1}{\sqrt{2}}(\hat{\epsilon}_- - \hat{\epsilon}_+)
\]
\[
= \frac{A_x}{\sqrt{2}} \sin(2\pi z)\hat{\epsilon}_- - \frac{A_x}{\sqrt{2}} \sin(2\pi z)\hat{\epsilon}_+
\]

Let us assume that we are at an absorption resonance, where the dispersion is zero. The sample exhibits only absorption dichroism. For the component of right circularly polarized (RCP) light, the magnitude of the transmitted field is \( A_+ \). For the component of left circularly polarized (LCP) light, the magnitude of the transmitted field is \( A_- \). The wave emerging from the sample is then:

\[
E_{\text{out}}(x, y, z) = \frac{A_-}{\sqrt{2}} \sin(2\pi z)\hat{\epsilon}_- - \frac{A_+}{\sqrt{2}} \sin(2\pi z)\hat{\epsilon}_+
\]
\[
= \frac{A_-}{2} \sin(2\pi z)\hat{\epsilon}_x - i\frac{A_+}{2} \sin(2\pi z)\hat{\epsilon}_y
\]
\[
= \frac{A_- - A_+}{2} \sin(2\pi z)\hat{\epsilon}_x - i\frac{A_- + A_+}{2} \sin(2\pi z)\hat{\epsilon}_y
\]

where we have used Equation (3.21) to convert from the circular basis to the linear basis. We see that the transmitted wave has now gained a vertically polarized component, \( \hat{\epsilon}_y \). Absorption dichroism thus leads to an elliptically polarized outgoing wave, with the major and minor axes of the ellipse aligned along the \( x \) and \( y \) axes, as shown in Figure 3.7(a).

In the case of pure dispersion dichroism, the RCP and LCP components of the incident wave experience different phase shifts, but are attenuated equally. The wave emerging from the sample remains linearly polarized, with the polarization axis rotated. This effect is also known as Faraday rotation, and is shown in Figure 3.7(b).
Effect of Absorption
Dichroism

Effect of Dispersion
Dichroism

Figure 3.7: Effects on the polarization for absorption and dispersion dichroism.

For a sample with magnetic domains with uniaxial magnetization along the propagation direction, the XMCD effect generally results in both absorption dichroism and dispersion dichroism. In other words, incident linearly polarized light emerges as elliptically polarized light, where the ellipticity depends solely on the absorption dichroism, and the tilt of the major axis depends on the dispersion dichroism.

On the other hand, incident circularly polarized light will emerge attenuated, but still as pure circularly polarized light:

\[
E_{\text{in}}(x, y, z) = A_{z0} \sin(2\pi z)\hat{\epsilon}_+
\]

\[
E_{\text{out}}(x, y, z) = A_{z0} \sin(2\pi z)\hat{\epsilon}_+
\]

Thus for samples with perpendicular out-of-plane magnetization and incident waves at normal incidence, the natural polarization basis is circularly polarized light. This polarization dependence is exploited in many imaging techniques, as we shall see with the experiments in Chapter 4 and 5.
3.5 Diffraction Theory

In a typical diffraction experiment, a wave of wavelength $\lambda$ is incident on a sample with features of size $a$. The transmission at the sample plane is given by $f(x, y)$. The exit wave from the sample plane is propagated to the detector plane located a distance $D$ away. The diffraction at the detector plane is given by $F(k_x, k_y)$. The coordinates $x$ and $k_x$ form a Fourier pair such that $k_x = \frac{x}{\lambda}$. The diffraction intensity measured is the squared amplitude of the wave, or $|F(k_x, k_y)|^2$.

![Diagram of transmission diffraction geometry](image)

Figure 3.8: Typical transmission diffraction geometry.

In the farfield or Fraunhofer regime ($a^2/D\lambda \ll 1$), the diffraction $F(k_x, k_y)$ is given by the Fourier transform of the transmission function $f(x, y)$ of the sample plane [31, 32]:

$$F(k_x, k_y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y)e^{-2\pi i (k_x x + k_y y)} dx dy \quad (3.23)$$
3.5.1 Diffraction from 1D Apertures

Let us begin with the illustrative case of diffraction from 1D apertures. For the case of a single slit of width \(a\), the transmission function is given by:

\[
f(n) = \begin{cases} 
1 & -\frac{a}{2} < x < \frac{a}{2} \\
0 & \text{otherwise}
\end{cases}
\] (3.24)

Diffraction from this single slit has the well-known form:

\[
F(k) = \int_{-a/2}^{a/2} e^{-2\pi ikx} dx
= \frac{e^{i\pi ka} - e^{-i\pi ka}}{2\pi ik}
= \frac{\sin \pi ka}{\pi k}
\] (3.25)

The diffraction intensity is given by \(|F(k)|^2\). From this, it is immediately obvious that changes in the transmission affect the diffraction intensity quadratically, i.e. when the overall transmission is halved, the diffraction intensity is reduced by a factor of 4.

We note here that the most commonly encountered 2D aperture is a circular aperture, which is also often employed in our experiments. For a circular aperture of radius \(a\), the intensity is given by the Airy pattern:

\[
I(r) = \left(\frac{\pi a^2}{\lambda D}\right) \left(2 \frac{J_1(kar/D)}{kar/D}\right)^2
\] (3.26)

where \(\lambda\) is the wavelength, \(D\) is the sample to detector distance, \(k\) is the wavenumber, \(J_1\) is the Bessel function of the first kind of order one, and \(r\) is the distance from the center in the detector plane. The Airy pattern is depicted in Figure 3.8 above.
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For the case of two slits each of width \( a \), whose edges are separated by \( b \) as shown on the left of Figure 3.9, the transmission function is given by:

\[
f(n) = \begin{cases} 
1 & -\frac{b}{2} - a < x < -\frac{b}{2}, \frac{b}{2} < x < \frac{b}{2} + a \\
0 & \text{otherwise}
\end{cases}
\]

Diffraction from this double slit gives:

\[
F(k) = \int_{-\frac{b}{2} - a}^{-\frac{b}{2}} e^{-2\pi ikx} dx + \int_{\frac{b}{2}}^{\frac{b}{2} + a} e^{-2\pi ikx} dx
\]

\[
= \frac{1}{-2\pi ik} \left[ e^{\pi ikb} \left( 1 - e^{2\pi ik a} \right) + e^{-\pi ikb} \left( e^{-2\pi ik a} - 1 \right) \right]
\]

\[
= \frac{1}{-2\pi ik} \left[ e^{\pi ikb} e^{\pi ik a} \left( e^{-\pi ik a} - e^{\pi ik a} \right) + e^{-\pi ikb} e^{-\pi ik a} \left( e^{-\pi ik a} - e^{\pi ik a} \right) \right]
\]

\[
= \frac{1}{\pi k} \left[ e^{\pi ik(a+b)} \sin(\pi ka) + e^{-\pi ik(a+b)} \sin(\pi ka) \right]
\]

\[
= \frac{\sin(\pi ka)}{\pi k} \left( e^{\pi ik(a+b)} + e^{-\pi ik(a+b)} \right)
\]

\[
= 2a \frac{\sin(\pi ka)}{\pi ka} \cos(\pi k(a + b))
\]

Diffraction intensities for the single and double slits, are shown in Figure 3.9.

In Figure 3.9: Diffraction from a single slit compared to diffraction from two slits with equal transmission.
For the double slit, the $2a \frac{\sin(\pi ka)}{\pi ka}$ term represents the diffraction from a single slit and provides the overall envelope for the diffraction. The $\cos(\pi k(a + b))$ term represents the interference between the two slits, and gives rise to additional intensity modulations, or fringes, in the diffraction.

### 3.5.2 Double Slits with Dichroic Transmission

Let us take our example one step further, and consider diffraction from two slits with different transmissions. The transmission function is given by:

$$f(n) = \begin{cases} 
\tau_{NM} + \tau_M & -\frac{b}{2} - a < x < -\frac{b}{2} \\
\tau_{NM} - \tau_M & \frac{b}{2} < x < \frac{b}{2} + a \\
0 & \text{otherwise}
\end{cases}$$

with the constraints $\tau_M < \tau_{NM}$ and $\tau_{NM} + \tau_M \leq 1$. Here, $\tau_{NM}$ represents the average transmission, while $\tau_M$ represents the transmission dichroism between the two slits. The resulting diffraction is very similar to the double slit case, with slight modifications:

$$F(k) = \frac{\sin(\pi ka)}{\pi k} \left[ (\tau_{NM} + \tau_M) e^{\pi ik(a+b)} + (\tau_{NM} - \tau_M) e^{-\pi ik(a+b)} \right]$$

$$= a \frac{\sin(\pi ka)}{\pi ka} \left[ \tau_{NM} (e^{\pi ik(a+b)} + e^{-\pi ik(a+b)}) + \tau_M (e^{\pi ik(a+b)} - e^{-\pi ik(a+b)}) \right]$$

$$= 2a \frac{\sin(\pi ka)}{\pi ka} \left[ \tau_{NM} \cos(\pi k(a + b)) + i\tau_M \sin(\pi k(a + b)) \right]$$

The overall envelope in the diffraction is still determined by the $2a \frac{\sin(\pi ka)}{\pi ka}$ term in front, representing diffraction from a single slit. The cosine term is identical to the form of the double slit with equal transmission, with an additional scaling factor $\tau_{NM}$. However, there is an additional imaginary term with scaling factor $\tau_M$. The diffraction is no longer purely real because the transmission function is now asymmetrical. Diffraction intensities for $\tau_M = 0, 0.25\tau_{NM}, 0.5\tau_{NM}, 0.75\tau_{NM}$, and $\tau_{NM}$ are shown in Figure 3.10.
Figure 3.10: Diffraction from two slits with total dichroic transmission \( \tau_{NM} \pm \tau_M \), where \( \tau_{NM} \) is a constant that represents average transmission.

The effect of the additional imaginary sine term, which is exactly \( \pi/2 \) out of phase with the cosine term, is to reduce the contrast of the interference fringes. Note that \( \tau_M \cos (\pi k(a + b)) + i\tau_M \sin (\pi k(a + b)) \) is the equation of a circle, which has a constant magnitude of \( \tau_M \). Thus for \( \tau_M = \tau_{NM} \), the diffraction simplifies to that of a single slit, and the interference fringes disappear. For \( \tau_M = 0 \), the cosine term attains its maximum oscillation amplitude between \( \pm \tau_{NM} \). The diffraction in this case is identical to that of the double slit each with transmission \( \tau_{NM} \). The maxima in the diffraction intensity depend only on \( \tau_{NM} \). On the other hand, the minima depend only on \( \tau_M \).
The effect of the imaginary sine term can be quantified by the fringe visibility, defined as:

\[
\text{Fringe Visibility} = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} = \frac{\tau^{2}_{NM} - \tau^{2}_{M}}{\tau^{2}_{NM} + \tau^{2}_{M}}
\]

For the case of a double slit with equal transmission \((\tau_{M} = 0)\), the interference effect is maximized, and the fringe visibility is 100%. For the case of a single slit \((\tau_{M} = \tau_{NM})\), there is no interference, and the fringe visibility is 0%. The fringe visibility is plotted for dichroic transmission \(0 \leq \tau_{M} \leq \tau_{NM}\) in Figure 3.11. For a wide range of \(\tau_{M}\), the fringe visibility is essentially linear as a function of \(\tau_{M}\).

Figure 3.11: Fringe visibility as a function of difference in transmission \(\tau_{M}\) for two slits of transmission \(\tau_{NM} + \tau_{M}\) and \(\tau_{NM} - \tau_{M}\), where \(\tau_{NM}\) is a constant.
3.5.3 Double Slits with Complex Transmission

Let us complete our thought experiment by fully generalizing the transmission from two slits to allow for complex transmission, i.e. to consider the effects of both absorption ($\beta$) and dispersion ($\delta$). The generalized transmission function is:

$$f(n) = \begin{cases} 
\tau_{NM} + \tau_M + i(\delta_{NM} + \delta_M) & -\frac{b}{2} - a < x < -\frac{b}{2} \\
\tau_{NM} - \tau_M + i(\delta_{NM} - \delta_M) & \frac{b}{2} < x < \frac{b}{2} + a \\
0 & \text{otherwise}
\end{cases}$$

(3.32)

where $\delta_{NM}$ represents the average dispersion, and $\delta_M$ represents the dichroic dispersion between the two slits. The resulting diffraction is:

$$F(k) = 2a \sin(\pi ka) \left[ (\tau_{NM} + i\delta_{NM}) \cos(\pi k(a + b)) + (-\delta_M + i\tau_M) \sin(\pi k(a + b)) \right]$$

(3.33)

As we saw in the previous section, the maximum of the diffraction depends on the $\cos(\pi k(a + b))$ term, while the fringe visibility depends on the $\sin(\pi k(a + b))$ term. Thus the diffraction intensity depends on $|\beta_{NM} + i\delta_{NM}|^2$. The fringe visibility is given by:

$$\text{Fringe Visibility} = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = \frac{|\beta_{NM} + i\delta_{NM}|^2 - |\delta_M + i\tau_M|^2}{|\beta_{NM} + i\delta_{NM}|^2 + |\delta_M + i\tau_M|^2}$$

(3.34)

The factor of $i$ between $\tau$ and $\delta$ indicates that the transmission and absorption terms are orthogonal to the dispersion terms. In other words, when we consider the squared amplitude, the two optical constants contribute equally to the contrast in the diffraction pattern.

Contributions from differences in dispersion to the diffraction contrast is the basis for phase imaging [33]. By tuning the x-ray energy to the maximum of the dispersion, which occurs near the inflection point for the absorption, radiation damage in the sample can be greatly reduced while maintaining high imaging contrast.
3.6 Transmission through a Magnetic Sample

For a purely magnetic sample, the absorption depends on the alignment between the magnetization in the domains, and the photon spin of the incident x-rays, as a result of the XMCD effect discussed in section 3.4. Consider a magnetic thin film with large perpendicular anisotropy, where the magnetization in the domains point either in or out of the sample plane. For circularly polarized x-rays, the XMCD effect leads to distinct transmissions for domains where the magnetization is aligned and anti-aligned to the photon spin. When the incident x-rays are switched to the opposite polarization, domains where the magnetization were previously aligned to the photon spin are now anti-aligned, as shown by the up and down arrows in Figure 3.12.

![Figure 3.12: Transmission profile of a purely magnetic sample for left circular, right circular, and linearly polarized light.](image)

The transmission profile for LCP and RCP x-rays are thus mirror images of each other. The transmission for linearly polarized light, which is a linear combination of LCP and RCP in equal amounts, exhibits no absorption dichroism.

From this, the connection between diffraction from a magnetic sample and diffraction from two slits with unequal transmission in Section 3.5.2 is immediately clear. $\tau_{NM}$ represents the non-magnetic contrast in the transmission, or the average transmission within the sample aperture. $\tau_{M}$ represents the transmission dichroism between magnetic domains which originates from the XMCD effect. The diffraction intensity depends quadratically on the average transmission, while the fringe visibility, or speckle contrast is determined by the magnetic contrast between the 'up' and 'down' magnetic domains.
3.7 Diffraction in Transmission Geometry

Building on the basis of the previous section, we see that calculating the far-field diffraction from a sample is a two step process as shown in Figure 3.13. In the first step, a transmission mask at the sample plane is calculated by breaking the sample down into its component layers. The wavelength and polarization dependent optical constants and the thickness of each layer determines its contribution to the absorption. In the second step, the propagation of the diffracted wave from the sample plane to the detector plane is calculated using the Fourier transform.

Our experimental samples are typically magnetic thin films sputter deposited on 100 nm thick SiN membranes. The SiN membrane is supported by 300 μm of Si, with a window typically 250 by 250 μm etched into the Si to expose the membrane. Approximately 1 μm of Au is sputter deposited on the backside of the SiN membrane to form an opaque mask for the x-rays. Using the focused ion beam (FIB), an aperture of 1 - 3 μm in diameter is then drilled into the Au layer to define a sample aperture. The sample cross-section can be seen in the inset of Figure 3.13.

Figure 3.13: Simulating the scattered diffraction from a magnetic thin film is a two step process: (1) The transmission profile at the sample plane is calculated. (2) The diffracted wave is propagated to the detector plane in the far-field through a Fourier transform.
As an example, the simulated transmission profiles for LCP and RCP light for a 50 nm Co/Pd multilayer thin film with a 2 μm Au aperture are shown in Fig 3.14. From Section 3.6, we know that the dichoric magnetic contrast for the two cases are exact inverses of each other.

![Simulated sample transmission of a 50 nm Co/Pd multilayer thin film for left circularly polarized light (left panel) and for right circularly polarized light (right panel). Associated diffraction for each polarization is shown below, with the intense transmitted beam at the center obscured by a beamstop.](image)

Figure 3.14: Simulated sample transmission of a 50 nm Co/Pd multilayer thin film for left circularly polarized light (left panel) and for right circularly polarized light (right panel). Associated diffraction for each polarization is shown below, with the intense transmitted beam at the center obscured by a beamstop.

In the diffraction pattern, speckles that arise from interference of wavefronts from different regions of the sample are clearly visible. Up until now, we have assumed ideal, coherent illumination of our samples, where the incident wave exhibits a known phase relationship over the entire sample aperture. Only with coherent illumination can scattering from different regions of the sample interfere and form a coherent superposition, resulting in speckles. The speckle pattern thus reflects the exact real-space structure of the sample [34, 35]. In reality, the extent of the coherence of the incident beam is given by its transverse coherence, typically a few μm at a synchrotron beamline [36].
The diffraction intensity for a magnetic sample is a combination of the magnetic and charge scattering contributions given by

$$I = |c + m|^2 = |c|^2 + |m|^2 + 2|c||m| \cos \Delta \phi,$$

where $c$ represents the charge scattering contribution, $m$ the magnetic scattering contribution, and $\Delta \phi$ the phase of the charge-magnetic interference [37]. For our samples, charge contrast is largely due to the difference in absorption between the Co/Pd film within the sample aperture and the opaque Au background. The charge scattering is thus dominated by the Airy diffraction rings of the circular Au aperture. Magnetic contrast arises from the dichroic absorption in the magnetic domains, giving rise to magnetic speckles at a scattering length scale corresponding to the periodicity of the domains.

![Figure 3.15: (a) Simulated scattering for linearly polarized light (left) and for circularly polarized light (right). In the case of linear polarization, the charge and magnetic scattering simply superimpose. In the case of circular polarization, the charge and magnetic scattering can interfere. The interference is visible as gaps in the Airy ring pattern.](image)

For linearly polarized light, the polarization of charge and magnetic scattering are orthogonal as we saw in Section 3.2.1, and the two types of scattered waves do not interfere. Thus the Airy disc pattern and the magnetic speckles are simply superimposed in the final diffraction as shown on the left of Figure 3.15. On the other hand, for circularly polarized light, interference between charge and magnetic scattering can occur. The magnetic speckles thus break up the Airy rings as shown on the right panel of Figure 3.15.
Much of the information contained in scattering can be understood by considering the relationship between a transmission profile and its Fourier transform. Small features result in high frequency components in the scattering, and thus a ring at high \( q \) in the diffraction. Information about the characteristic length scales in the system is thus encoded in the diffraction pattern. Speckles originate from the interference between different regions of the sample. Thus the size of the speckles reflects the number of scatterers in the field of view. The directionality of scattering means that the orientation of the magnetic speckles can also provide information about preferential orientations in the sample. These examples are illustrated in Figure 3.16, where different magnetic domains and the corresponding magnetic scattering are shown. To accentuate the magnetic signal, the intense transmitted beam at the center has been blocked, as it would be by the beamstop in an experiments.

![Figure 3.16: Comparison of magnetic scattering for simulations of different domain widths and orientations.](image)
3.8 Transmission Experimental Geometry

Our experiments are typically performed in the transmission geometry. Through a comparison with Figure 3.3, we see that the scattering angle between $k$ and $k'$ remains $2\theta$. Thus knowing the sample to detector distance $d$, the pixel size of the detector $p_s$, and the pixel position $p$, we can relate features in the diffraction pattern to a specific scattering vector $q$ as shown in Figure 3.17. The real space length scale is then given by $l = 2\pi/q$.

\[
q = k - k'
\]

Figure 3.17: Schematic of the transmission geometry typically used in our experiments. Features in the diffraction pattern can be related to specific length scales in the sample.

Let us illustrate this with two calculations for a typical experiment at the Co L3 edge (780 eV x-rays, $\lambda = 1.59$ nm) using the Princeton Instruments MTE2048 detector, which has 2048 pixels of 13.5 $\mu$m by 13.5 $\mu$m in size, with a sample to detector distance of 490 mm.

First, let us calculate the Airy disc pattern for a 1.5 $\mu$m diameter sample aperture. As given in Equation (3.26), the spatial dependence of the diffraction from a circular aperture has the form:

\[
I(r) \propto \left(2\frac{J_1(kar/D)}{kar/D}\right)^2
\]  
(3.35)
The minima of the pattern occurs at the zeros of $J_1(kar/D)$. The first dark ring thus occurs at:

$$kar/D = 3.8317$$

$$\frac{2\pi}{1.59 \text{ nm}} \frac{0.75 \mu m \cdot r}{490 \text{ mm}} = 3.8317$$

$$r = 0.63 \text{ mm}$$

Since the pixel size is 13.5 μm, the first dark ring is thus observed 47 pixels out from the center. The scattering angle here is $2\theta = \tan^{-1}(0.63 \text{ mm} / 490 \text{ mm}) = 0.074^\circ$, which corresponds to a scattering vector of $q = 4\pi \sin \theta/\lambda = 4\pi \sin (0.037^\circ)/1.59 \text{ nm} = 0.0051 \text{ nm}^{-1}$.

Let us now calculate the magnetic scattering ring for worm domains of 100 nm width. The periodicity of such domains is 200 nm, which corresponds to a scattering vector of $q = 2\pi / 200 \text{ nm} = 0.0314 \text{ nm}^{-1}$. Using $q = 4\pi \sin \theta/\lambda$, this corresponds to a scattering angle of $\theta = 0.2278^\circ$. From $\tan(2\theta) = r/D = r / 490 \text{ mm}$, the scattering ring is 3.92 mm from the center, or in pixel 291.

We shall see later on in the experiments, the very different $q$ for the Airy pattern, representing the charge scattering from the sample aperture, and the speckles representing the magnetic scattering from the magnetic worm domains makes it possible to separate out the charge and magnetic contributions in the diffraction.
3.9 Reconstruction of Real Space Images

Although diffraction patterns can reveal a great deal about the characteristics of the sample, the interpretation of diffraction patterns is not always straight-forward. In many cases, it is more intuitive to have a real space image of the sample, similar to that obtained with real space imaging techniques such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM). We have seen from the previous section that the farfield diffraction at the detector plane is the Fourier transform of the transmission profile at the sample plane. It is thus tempting to suggest that an inverse Fourier transform of the farfield diffraction would reproduce the transmission profile. Unfortunately, reconstructing the real-space image from the diffraction is not so trivial. The reason is that detectors only record intensity, or the squared magnitude of the wave fields. Information about the phase of the wave field is invariably lost. This is known as the phase problem in imaging.

Let us consider a sample with transmission $t_s(x, y)$ illuminated by a spatially coherent monochromatic plane wave with amplitude $E_i$. The transmitted electric field as shown in Figure 3.18(a) is given by:

$$E_t(x, y) = E_i t_s(x, y) = s(x, y)$$  \hspace{1cm} (3.37)

The electric field profile in the far field is a Fourier transform of $E_t(x, y)$:

$$E_d(X, Y) = F\{E_t(x, y)\} = S(X, Y)$$  \hspace{1cm} (3.38)

However, only the intensity, or the square of the amplitude, is recorded by the detector. Hence the diffraction intensity as shown in Figure 3.18(b) is given by:

$$I_d(X, Y) = |S|^2$$  \hspace{1cm} (3.39)

A Fourier inversion of the recorded diffraction intensity as shown in Figure 3.18(c)
thus produces the auto-correlation of the transmitted field:

\[
F^{-1}\{I_d(X,Y)\} = F\{|S|^2\} = s \otimes s^* \tag{3.40}
\]

Figure 3.18: (a) The sample transmission profile is given by \(s(x,y)\). (b) The resulting far field diffraction intensity recorded is given by the squared magnitude of the Fourier transform of (a). The phase information of the diffracted wave has been lost. (c) An inverse Fourier transform on the diffraction intensity results in the auto-correlation of (a).

Two common techniques of solving the phase problem are holography and phase retrieval methods. Both techniques were first developed and demonstrated for optical lasers, then extended to the x-ray regime for synchrotron sources. For the scope of the present thesis, we will focus on the features in the diffraction pattern of a hologram for the technique of Fourier Transform Holography (FTH) [32, 36, 38].
The essence of holography is to encode the phase information of the wave diffracted from the sample via interference with a reference wave. Let us consider a sample with two apertures - a sample aperture with transmission \( t_s(x,y) \), and a much smaller reference aperture with transmission \( t_r(x,y) \). Illumination by a spatially coherent monochromatic plane wave with amplitude \( E_i \) results in a transmitted electric field as shown in Figure 3.19(a) given by:

\[
E_t(x, y) = E_i(t_s(x, y) + t_r(x, y)) = s(x, y) + r(x, y) \quad (3.41)
\]

The electric field profile in the far field is the Fourier transform of this:

\[
E_d(X,Y) = F\{E_t(x,y)\} = S(X,Y) + R(X,Y) \quad (3.42)
\]

Figure 3.19: (a) The sample transmission profile consists of a sample aperture \( s(x,y) \) and a reference aperture \( r(x,y) \). (b) The resulting far field diffraction intensity recorded is given by the squared magnitude of the Fourier transform of (a), or \( |S + R|^2 \). (c) An inverse Fourier transform on the diffraction intensity results in two auto-correlation terms and two cross-correlation terms.
The diffraction intensity recorded by a detector as shown in Figure 3.19(b) is the square of the amplitude of the field profile:

\[ I_d(X,Y) = |S + R|^2 = SS^* + SR^* + RS^* + RR^* = |S|^2 + |R|^2 + SR^* + RS^* \]

This sample transmission profile is similar to a double pinhole separately vertically. As a result, the interference between the wave diffracted from the sample aperture and from the reference aperture can be clearly seen as horizontal interference fringes in the diffraction. Taking the inverse Fourier transform of the recorded diffraction produces the reconstruction as shown in Figure 3.19(c) given by:

\[ F^{-1}\{I_d(X,Y)\} = s \otimes s^* + r \otimes r^* + s \otimes r^* + r \otimes s^* \]

The first two terms are the auto-correlation of the sample and reference apertures respectively, located at the center of the inverse Fourier transform. But there are two additional off-axis terms - the cross-correlation between the sample and the reference and its conjugate pair. Due to the delta-function like nature of the reference aperture, the cross-correlation is essentially a replica of the sample transmission profile. In other words, we have obtained a reconstruction of the real space image of the sample.

An attractive feature of Fourier transform holography is its potential for single shot imaging. As we shall see in Chapter 5, combined with the emergence of ultra-intense x-ray sources such as the Linac Coherent Lightsource (LCLS), FTH enables us to capture the nanoscale ferromagnetic order of solid state samples with a single x-ray pulse.
Chapter 4

Time Resolved Coherent X-ray Diffraction

Since the discovery of ultrafast demagnetization in 1996, the field of femtomagnetism has grown rapidly. Time-resolved techniques, both in the optical and the x-ray regime, are becoming ever more important for the study of laser-induced magnetization dynamics. From a scientific perspective, the fundamental mechanisms and limits behind the manipulation and control of magnetization are of great interest. From a technological perspective, the operational bounds of our devices are set by the time scale at which dynamic processes cease to be repeatable [11]. To explore these limits therefore requires knowledge of the spatial and time correlation of excited states.

Until very recently, femtomagnetism has largely been driven by all-optical pump-probe techniques, because of the dominance of optical techniques in the time domain, where femtosecond optical pulses can be generated from commercially available laser systems. These systems allow ultrafast magnetic excitations and the study of their evolution on the macroscopic scale through the magneto-optical Kerr or Faraday effect. However, the spatial resolution of optical techniques is limited by the wavelength to a few hundred nm, obscuring the details on the atomic to mesoscopic length scales. The last few years have seen intense efforts to integrate femtosecond optical laser systems with synchrotron-based x-ray techniques to fill this void.
4.1 Optical Pump X-ray Probe Techniques

Well established techniques such as resonant magnetic scattering [35] and coherent diffractive imaging [32, 33] have long been used to provide access to spatially resolved information on the magnetic correlations in a sample, down to atomic length scales. In principle, by gating a single x-ray pulse, time-resolved experiments at 3rd generation synchrotron sources such as the Stanford Synchrotron Radiation Lightsource (SSRL) can achieve a time resolution of 50 ps [39]. Even shorter x-ray pulses, on the order of 10s of femtoseconds, can be generated with a novel technique known as femtoslicing [40]. Femtoslicing has been combined with XMCD spectroscopy in several femt magnetism experiments to separate the ultrafast quenching of the spin and orbital moments [20, 41]. The major drawback with the femtoslicing technique is the greatly reduced flux, which has precluded time-resolved scattering. The XMCD spectra for the above experiments were taken over a period of weeks.

For time-resolved optical pump x-ray probe experiments at a synchrotron, a major bottleneck has been the mismatched repetition rate between the optical laser pump and the synchrotron x-ray probe. Synchrotron storage rings have a typical repetition rate of a few hundred MHz. At SSRL, the SPEAR3 storage ring has a revolution frequency of 1.28 MHz. Up to 372 electron bunches can be filled in the ring at once, resulting in a repetition rate of 476 MHz. The typical operation of the synchrotron utilizes a 'camshaft fill', where each cycle consists of 279 small bunches of 0.36 mA separated approximately 2.1 ns apart, in addition to a large camshaft bunch of 20 mA as shown in Figure 4.1(a).

On the other hand, the repetition rate of high intensity, femtosecond optical lasers that can supply the requisite energy per pulse to trigger excitations is typically a few kHz. This restriction meant that less than 0.1% of the x-ray flux of the synchrotron was utilized. The recent development of high power, high repetition rate femtosecond optical lasers have dramatically improved the situation, leading to high repetition rate optical-pump x-ray-probe setups [42, 43]. Our group, in collaboration with the Lindeneng group at Stanford, has developed such a time-resolved setup for the coherent scattering endstation at SSRL beamline 13-3 to study magnetization dynamics on the
Figure 4.1: (a) SSRL typically operates in camshaft fill mode with 280 x-ray bunches. (b) Special four bunch mode for time-resolved experiments.

picosecond time scale. We use a 5.12 MHz repetition rate long cavity Ti:Sapphire laser phase locked to the revolution clock of SSRL (1.28 MHz) to capture a much larger fraction of the coherent flux. When operating SSRL in four bunch mode with high filling as shown in Figure 4.1(b), we obtained a coherent flux of $2 \times 10^6$ photons/$\mu$m$^2$/s, or 10% of the flux under normal operations. With this greatly enhanced flux, we were able to directly observe magnetization relaxation in Co/Pd multilayer samples with 50 ps time resolution down to 50 nm spatial resolution [44].
4.2 Real versus Reciprocal Space Imaging of the Demagnetization Process

For observing the demagnetization process, coherent scattering has several advantages over real-space imaging techniques such as transmission electron microscopy (TEM) and scanning transmission x-ray microscopy (STXM). First of all, coherent scattering is a full field technique, unlike the two techniques above, which are both raster scan techniques. With scattering, information about the entire sample is captured in a single snapshot. Secondly, as we shall see below, even if the contrast in real space averages out as the system relaxes via many unique paths, the length scale information in scattering is preserved.

Let us consider the two extreme possibilities for the demagnetization process, one in which the recovery always follows the same path, and one in which the recovery is stochastic and follows a different path each time.

The first case is when the optical excitation induces only a small perturbation of the magnetic domains from their equilibrium configuration. Initially, the magnetization of the sample is out-of-plane. When the sample is hit with an optical excitation, the sample is slightly demagnetized, equivalent to a redistribution of a small portion of the magnetization from out-of-plane to a random orientation. On average, the magnetization in the domains acquire a small in-plane component and become slightly canted. However, as the perturbation is small, the domain configuration has a strong tendency to return to its original state. In effect, the remaining out-of-plane component of the magnetization act as pinning sites. The overall domain configuration thus does not change very much.

The second case is when the excitation is strong enough to completely demagnetize the sample. Following each excitation, the sample starts from random magnetization and follows a unique relaxation path to a different equilibrium domain configuration. The overall characteristics of the configurations, such as the domain width, are determined by material parameters. Each final state domain configuration creates a different speckle pattern in the recorded diffraction.

As an example, using typical material parameters for a 50 nm Co/Pd multilayer
film, the equilibrium domain configuration was simulated with OOMMF for multiple random initial magnetization. The resulting real and reciprocal space image for a single run, and averaged for 5, 20, and 50 different runs are shown in Figure 4.2.

Figure 4.2: Equilibrium domain configuration for a 50 nm Co/Pd multilayer film simulated with OOMMF, with the corresponding magnetic scattering pattern. The different panels show the real and reciprocal space images for a single configuration, and for the average of 5, 20, and 50 configurations.

For the averaged real space image, the magnetic contrast disappears with an increasing number of runs. For the reciprocal space image, the individual magnetic speckles average out to a diffuse ring, but information about the characteristic length scales in the sample is retained. Note that to simulate experimental conditions, a cross-shape beamstop has been included in the diffraction.
CHAPTER 4. TIME RESOLVED COHERENT X-RAY DIFFRACTION

The characteristic length scale encoded in the diffraction ring can reveal the $q$-dependence of the underlying mechanisms of the recovery process following optical demagnetization. Time evolution of the magnetization in a sample starting from a random initial state, i.e. complete demagnetization, is shown in the top row in Figure 4.3, with the associated diffraction pattern for each time point shown below. Note that the central transmitted beam has been blocked, as is done by the beamstop in our experiments.

![Diffraction Patterns](image)

Figure 4.3: OOMMF simulation of evolution from random magnetization to equilibrium domain configuration.

Initially, after full demagnetization, the magnetization orientation in the sample is random, resulting in isotropic scattering. As the magnetization coalesces into domains, the length scales become more well defined, resulting in a ring in the scattering. Simulations show that the time scale for recovery of the magnetization depends largely on the degree of disorder in the magnetic state after excitation [45]. For complete demagnetization, recovery of the magnetization is thus extremely slow, due to considerable frustration in the initially random magnetization orientation. Eventually, the magnetic domains relax into an equilibrium configuration as determined by the material parameters. The associated scattering is largely concentrated at a specific $q$, corresponding to the periodicity of the domains.
4.3 Experiment Setup

The optical pump, x-ray probe experiment was conducted with the coherent scattering endstation at SSRL beamline 13-3. The sample consisted of a $[\text{Co}(0.5\text{nm})\text{Pd}(0.7\text{nm})]_{15}$ multilayer thin films sputter deposited on a 200 by 200 $\mu$m $\text{Si}_3\text{N}_4$ membrane at 3 mTorr Ar pressure. This sample has out-of-plane worm domains of approximately 100 nm in width, as shown in the MAD Holography reconstruction in Figure 4.4a [46]. For this system, quasi-static magnetization changes in an external field have been studied [47], but its response to laser excitation had not been previously explored.

Figure 4.4: Schematic of optical pump x-ray probe experimental setup. a) Sample magnetization reconstructed using MAD Holography[46]. b) Overhead schematic of experimental geometry.

The schematic experimental setup is shown in Figure 4.4. A long cavity Ti:Sapphire laser at 800 nm is in-coupled at 90 degrees to the coherent scattering chamber through a viewport with an anti-reflection coating optimized for 800 nm. A small optical breadboard with a focus and scanning mirror stage sits in between the experiment chamber and the pump laser. The sample, tilted at 30 degrees, is excited by a 50 fs
optical pump pulse from the optical laser, then probed after a variable delay $t$, ranging from -40 ps to +3 ns, with a circularly polarized coherent x-ray pulse of approximately 50 ps FWHM at the Co $L_3$ edge (778.8 eV). Using the highest laser fluence available, the pump laser is focused to a spot size of less than 20 by 20 $\mu m$, corresponding to a fluence of approximately 5 mJ/cm$^2$ at the sample. The time-resolved small angle diffraction pattern is captured with a Princeton Instruments MTE1340 soft x-ray CCD detector. The optical-pump and x-ray-probe beam geometry are shown Figure 4.4b.

There are several experimental considerations in a pump-probe experiment. The first is the volume overlap between the pump and the probe beams, to maximize the signal that comes from the excited region. At SSRL beamline 13-3, the x-ray probe size is approximately 220 by 70 $\mu m$, much larger than the optically excited region. To confine the probe size, 800 nm of Au is first deposited on the back side of the sample, then a 3 $\mu m$ aperture is milled with a focused ion beam as described in [32, 36]. The opaque gold mask ensures that the x-rays probe an area with uniform laser fluence, and also facilitates heat dissipation from the high repetition rate pump laser. The size of the 3 $\mu m$ aperture was chosen to ensure that the incident x-ray beam would be coherent over the probed area.

A second consideration is the repetition rate of the pump and probe. Ideally, the pump and probe should have the same repetition rate, in order to maximize the signal. During normal operations at SSRL, the synchrotron operates at 476 MHz. With a 5.12 MHz optical pump laser, the ratio of pump pulses to probe pulses is approximately 1:100. In other words, only 1% of the x-ray probe pulses observe an excited state. When we used this optical pump x-ray probe setup during normal operations, the change in the diffraction was too weak to be detected. Instead, a special four bunch fill pattern was requested during an accelerator physics shift at SSRL. Because the synchrotron revolution clock runs at 1.28 MHz, a four bunch fill pattern is perfectly synchronized to the 5.12 MHz optical pump laser.
4.4 Time Resolved Magnetic Scattering

Prior to the excitation, the sample has its full out-of-plane magnetization. The reference diffraction, taken with negative time delay, where the optical excitation arrives after the x-ray probe pulse, thus sees the full magnetization. At time zero, upon optical excitation, the magnetization suddenly decreases, resulting in a sharp drop of magnetic contrast as is seen in ultrafast demagnetization experiments. The magnetization slowly recovers as the sample relaxes back to its equilibrium configuration. Depending on the time delay of the probe along the relaxation process, a reduced magnetization is observed.

In this experiment, the time-dependent scattering intensity is given by:

$$I(t) = |c|^2 + |m(t)|^2 + 2|c||m(t)| \cos \Delta \phi$$  \hspace{1cm} (4.1)

where $c$ represents the charge scattering, which is time-independent as long as the sample aperture does not change during the experiment, $m(t)$ the time-dependent magnetic scattering, and $\Delta \phi$ the phase of the charge-magnetic interference.

Changes in the scattering can be calculated by comparing patterns from the pumped sample at time delays of interest, $t = -40 \text{ ps}$ to $+3 \text{ ns}$, to a reference pattern from the unperturbed sample. In a pump-probe experiment, this typically involves a comparison between laser on and laser off measurements. When this scheme was attempted, thermal heating effects on the sample resulted in expansion and contraction of the Au aperture for laser on and laser off shots, resulting in visibly different charge Airy diffraction rings.

The scheme was altered to a laser early versus laser late comparison in order to maintain a constant heat load on the sample and render the charge scattering time-independent. For laser early shots, the optical pump pulse arrives before the x-ray probe pulse, resulting in diffraction patterns of the excited state. For laser late shots, the optical pump pulse arrives 1 ns after the x-ray probe pulse, resulting in reference diffraction patterns of the unperturbed sample. Subtraction of the reference diffraction thus allows for removal of the time-independent charge scattering $|c|^2$ from time delay diffractions.
If the magnetization reduces from $m_s \rightarrow m_t$ with $m_s - m_t = \Delta m(t) > 0$, the scattered intensity for the pump probe and reference images are respectively:

\[ I(t) = |c|^2 + |m_o - \Delta m(t)|^2 + 2|c||m_o - \Delta m| \cos \Delta \phi(t) \quad (4.2) \]
\[ I(t_{\text{ref}}) = |c|^2 + |m_o|^2 + 2|c||m_o| \cos \Delta \phi(t_{\text{ref}}) \quad (4.3) \]

Subtracting the two measurements, we obtain:

\[ I(t) - I(t_{\text{ref}}) = |m_o - \Delta m(t)|^2 - |m_o|^2 + 2|c|(|m_o - \Delta m| \cos \Delta \phi(t) - |m_o| \cos \Delta \phi(t_{\text{ref}})) \quad (4.4) \]

The normalized difference in scattering intensity is given by:

\[ \Delta I_{\text{norm}} = \frac{I(t_{\text{ref}}) - I(t)}{I(t_{\text{ref}}) + I(t)} \quad (4.5) \]

Since the magnetic scattering is more than an order of magnitude less than the charge scattering even on resonance [3], $|m|/|c| \ll 1$, and equation (4.5) above reduces to:

\[ \Delta I_{\text{norm}} = \frac{2|c|(|m_o - \Delta m| \cos \Delta \phi(t) - |m_o| \cos \Delta \phi(t_{\text{ref}}))}{2|c|^2} \]
\[ = \frac{|m_o - \Delta m| \cos \Delta \phi(t) - |m_o| \cos \Delta \phi(t_{\text{ref}})}{|c|} \quad (4.6) \]
4.4.1 Experimental Data

Normalized diffraction patterns $\Delta I_{\text{norm}}$ for given time delays are shown in Figure 4.5. A clear build up in the normalized difference signal is observed, with the maximum signal seen at +60 ps. As the magnetization recovers, the difference signal fades away. The slightly negative background in the normalized difference is a result of the overall reduction of the out-of-plane component magnetization during demagnetization.

![Figure 4.5: Normalized change in magnetic scattering at various time delays. The q range extends out to 0.125 nm$^{-1}$. The stable speckle configuration indicates that the underlying domain structure is maintained.](image)

The continued presence of speckles in a given $q$ range indicates that the domain configuration is maintained during the exposure. In other words, in Equation (4.6), $\Delta \phi(t)$ is approximately constant, so that $\Delta \phi(t) \approx \Delta \phi(t_{\text{ref}})$. If the domain configuration changed from shot to shot, the resulting speckle arrangement would be different for each shot. These diffractions would then average out to a diffuse ring in the accumulated exposure, as discussed in Section 4.2.
The normalized difference in equation 6.4.2 thus simplifies to:

$$\Delta I_{\text{norm}} = \frac{|\Delta m| \cos \Delta \phi}{|c|}$$  (4.7)

The reduction in magnetization, $\Delta m$, can be deduced once the saturation magnetization $m_s$ is known. For the case of $I_+$ and $I_-$ (left and right circular polarization), the magnetization is equivalent to the saturation magnetization $m_s$, with only a phase difference of $\pi$ between the two polarizations, representing the contrast reversal, as explained in Section 3.6. Using equation (4.5), the normalized difference for the static images taken with LCP and with RCP is:

$$\frac{I_+ - I_-}{I_+ + I_-} = \frac{2|c||m_s|| \cos \Delta \phi - 2|c||m_s|| \cos(\Delta \phi + \pi)}{2|c|^2} = \frac{2|c||m_s|| \cos \Delta \phi + 2|c||m_s|| \cos \Delta \phi}{2|c|^2} = \frac{2|m_s| \cos \Delta \phi}{|c|}$$  (4.8)

Figure 4.6: Demagnetization curve from $\Delta I_{\text{norm}}$, which is proportional to deviation from $M/M_s = 1$. The line is a fit to the data with Koopman’s micro three temperature model [48], which indicates a maximum demagnetization of 20-25%. The curve is broadened by convolution with the 50 ps x-ray pulse width.
Dividing equation (4.7) by equation (4.8) thus results in $\Delta m/2m_s$. Hence with this additional normalization, the demagnetization can be deduced from the intensity in the normalized difference images. The demagnetization curve is shown in Figure 4.6.

The $q$-dependent scattering intensity can be calculated by integrating the normalized difference images as a function of $q$, and is shown in Figure 4.7a. The signal is strongest near 100 nm, corresponding to magnetization reduction within the domains following the initial excitation.

![Figure 4.7](image)

Figure 4.7: a) The $q$-dependent scattering intensity in the normalized difference images for different time delays. b) Time correlation of the asymmetry, with the signal at 0 ps as the reference. Inset c) The scattering intensity at +60ps consists of a time delay independent, or static intensity at low $q$, and a time delay dependent, or changing intensity at high $q$.

The nature of coherent scattering makes it possible to determine the relative size of the repeatable and non-repeatable portions of the dynamics using the pixel-to-pixel correlation between the diffraction patterns of different time delays. We calculate the
normalized time correlation function given by:

\[
G(t, q) = \frac{I_n'(q)}{\|I_n'(q)\|} \cdot \frac{I_n'(q) - \langle I_n(q) \rangle}{\|I_n'(q)\|},
\]

(4.9)

where \( I_n'(q) = I_n(q) - \langle I_n(q) \rangle \) and \( I_n(q) \) consists of the measured intensities within an annulus 5 pixels wide centered with respect to the diffraction pattern and stepped across in steps of one pixel [49]. As shown in Fig. 4.7b, the time correlation is centered around the magnetic scattering peak, and drops to zero for length scales below 65 nm. The \( q \)-dependent intensity thus has two contributions, a portion centered around the length scale of the domain width with sizable correlation and independent of time delay, and a second portion at higher \( q \) that is completely uncorrelated. One possible explanation is that after optical excitation, memory of the initial domain magnetization is retained in a low \( q \) portion of the sample, but the magnetization fluctuates on smaller length scales along the domain boundaries.

By multiplying the \( q \)-dependent correlation and \( q \)-dependent intensity together, we can identify the correlated, elastic portion of the scattering as shown in Figure 4.7c. The remaining scattering is attributed to a fluctuating, non-correlated portion. The small size of the elastic component suggests that the pump fluence is in a borderline regime where irreversible changes of the domain structure are emerging. During recovery, as hot electrons scatter off domain walls, angular momentum transfer leads to fluctuations of the magnetic order and motion of the magnetic domain boundaries. These fluctuations lead to progressive loss of correlation for length scales below 65 nm.

In this experiment, we were unfortunately limited by the pump fluence. In the future, it would be interesting to explore the fluence dependence of the demagnetization process. As the pump fluence is increased, the fluctuating portion should increasingly govern the relaxation process, leading to a loss of correlation on longer length scales.
4.5 Summary and Future Outlook

In conclusion, we have demonstrated picosecond time resolved coherent x-ray scattering experiments at a synchrotron [44]. Time-resolved diffraction data taken on Co/Pd multilayer samples show that after excitation by a femtosecond optical pulse, the magnetic contrast is sharply reduced, followed by a slow magnetization recovery over a nanosecond time scale. The speckle pattern remains stable during the recovery, indicating that the spatial arrangement of magnetic domains in the sample is maintained. Pixel-to-pixel correlation is used to separate the dynamic scattering intensity into an elastic portion at low $q$, corresponding to a disordering of spins within the individual domains which retains the initial domain structure, and a fluctuating portion at high $q$ attributed to motions of magnetic domain boundaries during relaxation.

Even though time resolved optical pump, coherent x-ray probe experiments have been demonstrated at SSRL with four bunch mode, accelerator physics shifts remain a specialized mode of operation scheduled only once every two weeks. The logical next step is to implement time-resolved coherent scattering for normal operations of the synchrotron. By taking advantage of the large spacing around the camshaft bunch, a fast gate-able detector can be used to isolate the camshaft pulse. Due to the lack of fast, gate-able detectors in the soft x-ray regime, a multi-channel plate is needed to convert x-ray photons into optical photons via a phosphor screen, which is then imaged by a fast gate-able detector operating in the optical regime.

Picosecond time resolved coherent scattering experiments at 3rd generation synchrotron sources will enable the study of many dynamic processes. Of special interest to the magnetism community is the all-optical switching process, which can occur on picosecond time scales [50, 51]. At SSRL, efforts are under way to improve the time resolution of synchrotron x-ray pulses. By reducing the current in each bunch in a mode of operation known as low-alpha, the repulsive force between the electrons is reduced and x-ray pulses of approximately 1 ps can be produced [52].

Due to the limited coherent flux even at third generation synchrotrons, direct
imaging of the dynamics remains challenging. Time-resolved experiments at synchrotrons will thus be restricted to statistical and correlation studies. In the future, time-resolved laser pump x-ray probe experiments at X-ray Free Electron Laser (XFEL) facilities, such as the Linear Coherent Lightsource, will provide access to sub-picosecond dynamics with the potential for single shot imaging as we shall see in Chapter 5. Time-resolved coherent scattering experiments at 3rd generation synchrotrons will complement experiments at XFELs, allowing a wide range of dynamics to be probed with nanometer scale resolution over the femtosecond to nanosecond time scale.
Chapter 5

Ultrafast Demagnetization and Single Shot Imaging at LCLS

Much has been written about the Linac Coherent Light Source (LCLS), the first x-ray free electron laser (XFEL) in the world [9]. For our purposes, the most important characteristics that distinguish LCLS from conventional x-ray sources such as third generation synchrotron sources are its peak brightness, its femtosecond x-ray pulses, and its full transverse coherence. The number of photons in a single x-ray pulse at LCLS is approximately $10^{13}$ per eV. In comparison, at a 3rd generation synchrotron like SSRL, the number of photons in a pulse is approximately $10^5$ per eV. The x-ray pulse width at LCLS ranges from 10-300 fs, compared with approximately 50 ps at SSRL. In combination, these two factors result in a peak brightness at LCLS that is a factor of $10^{11}$ larger than at SSRL, opening the door to the exploration of many nonlinear x-ray-matter interactions. For the purposes of coherent scattering, LCLS has an additional advantage - it is a laser, and hence the pulses are almost fully transversely coherent [53]. Thus unlike at a synchrotron, no coherence aperture is necessary to filter the incident beam, and the full intensity of the beam can be utilized. Altogether, these unique properties enable experiments at LCLS that are not possible anywhere else.

I will address three scientific problems using the unique time resolution and high peak brightness of LCLS: 1) Studying the process of ultrafast demagnetization on a
nanometer lengthscale and femtosecond time scale, 2) Investigating the potential for single shot imaging of a nanoscale magnetic state, and 3) Exploring nonlinear x-ray effects in a solid state sample at extreme x-ray intensities.

For ultrafast demagnetization, the primary goal is to capture the evolution of $q$-dependent spin waves within the first picosecond of an optical excitation. The spin lattice relaxation following demagnetization would provide important insights into the underlying mechanisms of angular momentum transfer in the ultrafast demagnetization process, a topic of considerable controversy in the literature [25, 28, 48]. For single shot imaging, we take advantage of the high peak brightness of LCLS and the photon efficient technique of Fourier transform holography (FTH) to capture the nanoscale ferromagnetic structure of a magnetic sample with a single x-ray pulse. This technique can in principle be combined with the ultrafast demagnetization experiments to provide images of the intermediate states during the demagnetization process. Lastly, we investigate the onset of nonlinear x-ray effects by using the ultra-bright x-ray pulses of LCLS. The first two topics are addressed in this chapter, while nonlinear x-ray effects are discussed in Chapter 6.
5.1 Ultrafast Demagnetization in Co/Pd

The experiments were performed at the Soft X-ray Material Science (SXR) hutch at LCLS on the Resonant Coherent Imaging (RCI) endstation using transmission geometry coherent imaging, as shown in Figure 5.1. At LCLS, the optical pump laser is first expanded to approximately 2 inches in diameter, then coupled into the endstation with a focusing mirror at 45 degrees. A hole in the center of the mirror allows the XFEL beam to pass through. The optical pump and laser probe pulses are thus co-linear at LCLS.

The samples are again the ideal model system of Co/Pd as studied previously at SSRL. \([\text{Co}_{0.5\text{nm}}/\text{Pd}_{0.7\text{nm}}]_{40}\) multilayer thin film with a 1.5 nm Ta, 3 nm Pd base layer was sputter deposited on 100 nm thick SiN membrane windows supported on a Si frame. The multilayer was capped with 2 nm of Pd to prevent corrosion. The membrane windows are approximately 200 x 200 μm. Small angle coherent scattering patterns from these samples are shown in Figure 5.2 for a laser fluence of 12 mJ/cm².

Without the strong, Airy-disc charge scattering from an Au sample aperture, the diffraction is dominated by magnetic scattering from the perpendicular worm domains in the sample. As explained in Section 3.7, the \(q\) of the magnetic ring corresponds to the periodicity of the magnetic domains, approximately 100 nm. For this experiment, the x-ray focus was approximately 80 x 80 μm. Compared to the SSRL pump probe experiment in Chapter 4, a large number of scatterers are illuminated by the incident beam, resulting in very small speckles, which appear almost as a diffuse ring. Due to the small size of the speckles, it is not possible to distinguish whether the
configuration of the speckles changes, which would reflect changes in the magnetic domain configurations. The magnetic scattering intensity is constant for negative delays, decreases dramatically at time zero, reaches a minimum at 1 ps, and recovers slowly over picosecond time scales.

![Figure 5.2: Coherent scattering diffractions of Co/Pd multilayer thin film samples from the first optical pump x-ray probe experiment at LCLS. The q range extends out to 0.157 nm⁻¹. The colorbar indicates the number of photons.](image)

As discussed in Section 3.5 the integrated diffraction intensity in the magnetic scattering ring is proportional to $\tau_{avg} \cdot |m|^2$, where $\tau_{avg}$ is the average transmission of the sample, and $m$ the magnitude of the magnetization in the up and down domains. The full magnetic signal is given by the diffraction of the unperturbed sample at negative delay times. Using the time resolved scattering patterns, a demagnetization curve similar to that obtained with optical pump-probe experiments can be calculated as shown in Figure 5.3. This set of data was taken over a 30 minute run at LCLS, in stark contrast to the SSRL optical pump x-ray probe data in Figure 4.6, which was
taken over a 12 hour accelerator physics shift.

Figure 5.3: Coherent scattering diffractions of Co/Pd multilayer thin film samples from the first optical pump x-ray probe experiment at LCLS.

The magnetization is reduced to approximately 50% of its initial value within the first picosecond, indicating that a significant amount of energy is pumped into the system, followed by a slow recovery over the pico- to nanosecond time scale. A fit to the data was calculated using two exponential functions, one for the ultrafast demagnetization within the first picosecond, and one at longer time scales representing magnetization recovery. The fit indicates a total decay time constant of 495 fs for the demagnetization. This value is a convolution of several contributions - the intrinsic demagnetization time, the 80 fs x-ray probe pulse, and the jitter between the optical and x-ray pulses.
In many femtosecond pump-probe experiments, both the pump and probe pulses are derived from the same laser source by means of a beam-splitter and path-length delay lines. With such setups, jitter in the attosecond regime have been demonstrated [54]. The situation is more difficult at LCLS, where the optical pump laser and the XFEL probe need to be actively synchronized. LCLS employs both conventional feedback techniques that synchronize the optical pulse with respect to the radio frequency (RF) driving the linear accelerator, and also a pair of resonant RF phase cavities that measure the arrival of the electron bunches at the exit of the undulator to provide shot-to-shot adjustments [55]. The jitter depends on many parameters, and is sensitive to minor changes in beam transport optics and feedback electronics. For the jitter between the optical and x-ray pulses at LCLS, values between 140 - 400 fs FWHM have been reported [55, 56, 57]. The jitter measured for our setup was approximately 300 fs. Since our original experiments, a shot-to-shot optical cross-correlator has been implemented in the SXR experimental hutch which reduces the jitter between optical and x-ray pulses down to $130 \pm 20$ fs FWHM [58].

Taking into account the 80 fs width of the x-ray probe pulses, and the approximately 300 fs jitter, the intrinsic demagnetization time for these Co/Pd multilayers is then 380 fs. This time scale is comparable, though slightly longer than the demagnetization time of 220 - 280 fs observed for interstitial Co/Pd samples with optical pump femtoslicing XMCD probe experiments at BESSY [41]. We note that optical pump-probe measurements which rely on the Magneto-Optical Kerr Effect (MOKE) are not possible on Co/Pd multilayers, as contributions from domains with opposite magnetization within the probe spot effectively cancels out the MOKE signal.

The $q$-resolved scattering intensities for all time delays are plotted in Figure 5.4. Most of the scattering was collected for delay times within 2 ps of time zero. Scattering patterns were thus binned with varying bin sizes: 200 fs bins for delay times between -400 fs and 2 ps, 500 fs bins for delays between 2 ps to 4 ps, and 2 ps bins for delays between 4 ps to 10 ps. Other than changes in the peak intensity, no significant wavevector resolved changes in scattering were observed. No shift in the $q$ of the magnetic peak is observed.
There are several possible explanations for these results. The first possibility is that the pump fluence was not high enough to demagnetize the sample completely. If the optical excitation does not penetrate the entire sample, which is approximately 50 nm thick, the deep lying layers would retain their initial magnetization. Thus even though the layers close to the surface may be completely demagnetized, the magnetization of the deep lying layers can act as pinning sites during the recovery, restoring the domains to their initial configuration after each excitation. The second possibility is that changes on small length scales do occur, but the scattering features are beyond the range covered by the detector, which extends down to a length scale of approximately 40 nm.

The first ultrafast demagnetization experiment at LCLS thus did not reveal any new information about the underlying microscopic mechanisms. Nevertheless, we proceeded on to the second goal - single shot imaging of the magnetic domains as a proof of principle experiment that the nanoscale magnetic state of a sample can be captured with a single, intense x-ray pulse prior to sample damage.
5.2 Single Shot Imaging

Single shot molecular imaging was one of the early drivers behind the push for building an XFEL. For biomolecules, the destruction mechanism of concern is the Coulomb explosion of the molecule which occurs on the 10-fs time scale. In 2000, a simulation was published which suggested that by using x-ray pulses of only a few femtoseconds, this damage process could be outrun [59]. In other words, with ultrashort high fluence x-ray pulses, a single shot diffraction pattern of the unperturbed sample can be obtained before damage sets in. The authors further proposed that this concept could be combined with spray injection techniques to obtain single shot x-ray diffraction on nanocrystals. This concept was recently demonstrated at LCLS for nanocrystals of photosystem I, a large membrane protein complex [60].

The situation is more complicated for magnetic imaging, which is intimately connected to the electronic structure. Even before the Coulomb explosion, atoms in the sample will experience electronic damage through the faster processes of photoabsorption and photoionization [61, 62]. The onset of this radiation damage to the valence electron structure thus sets the time frame in which the image of the magnetic state needs to be captured. Utilizing the photon efficient technique of FTH as discussed in Section 3.9, we successfully imaged the nanoscale ferromagnetic arrangement in a Co/Pd multilayer sample with a single high intensity x-ray pulse from LCLS [63]. We further demonstrated that x-ray induced electron and spin dynamics can be outrun by using x-ray pulses shorter than 80 fs. The results will only be briefly discussed here as they are covered comprehensively in references [63, 64].

The experimental setup is the typical transmission geometry for FTH as shown in Figure 5.5. Single x-ray pulses of either 80 or 360 fs from LCLS are passed through an x-ray grating monochromator tuned to the Co L3 edge at 778.8 eV, with a bandwidth of 1 eV. The monochromatized beam is then focused to a spot size of approximately 10 x 10 μm² at the sample plane.
The samples are the same as for the ultrafast demagnetization experiment in the previous section, with the addition of an integrated sample-holographic mask [32]. On the side of the membrane opposite to the Co/Pd multilayer thin film, an 800 nm thick Au film is sputtered, forming a layer opaque to the x-rays. A spectro-holography mask consisting of a single 1.45 μm diameter sample aperture and five 100 nm diameter reference apertures arranged in a pentagon as shown in Figure 5.5(a) are cut in the sample with a dual-beam focused ion beam instrument from FEI [63]. Diffraction from the sample is captured by a soft x-ray CCD detector located 490 mm downstream of the sample.

Figure 5.5: Experimental setup for single shot imaging at LCLS with Fourier transform holography. (a) Scanning electron microscopy image of integrated spectro-holography mask with single 1.45 μm diameter sample aperture and five 100 nm diameter reference apertures. (b) The resulting diffraction is captured by a soft x-ray CCD detector located 490 mm downstream of the sample. (c) Single shot image of the nanoscale magnetic structure from a Fourier transform of the diffraction. Light and dark regions correspond to domains with opposite out-of-plane magnetization directions [63].
Currently, LCLS only produces linearly polarized x-ray pulses. To reconstruct a magnetic image with FTH, the interference between charge and magnetic diffractions is essential. To produce this mixing, the linearly polarized x-rays are sent through a thin magnetic Co film, which produces a transmitted beam that is elliptically polarized through the XMCD effect. The two main drawbacks of these polarizer films are the strong absorption and the fact that they are inevitably tuned to particular absorption edges \[38, 65\]. In our case, the Co polarizers produces 40% polarization with 4% transmission. Future upgrades to the undulator system at LCLS will enable full polarization control and render the polarizer unnecessary, increasing the flux at the sample by two orders of magnitude.

By taking the Fourier transform of the diffraction, each reference produces an independent reconstruction of the sample through the cross-correlation. Summing over multiple references significantly improves the signal-to-noise-ratio in the reconstruction \[66\]. The reconstruction of the nanoscale magnetic structure for a single 80 fs x-ray pulse is shown in Figure 5.5(c). Light and dark regions correspond to 100 - 150 nm wide domains with opposite out-of-plane magnetization directions. The 10% - 90% criteria on the domain walls indicates a resolution of 80 nm, limited by the size of the reference apertures and the photon flux within a single x-ray pulse with the use of the polarizer.

We investigated the damage induced by the x-rays by analyzing the charge-magnetic contrast ratio of the reconstructions as a function of pulse intensity for 80 and 360 fs x-ray pulses. Charge contrast is related to the average transmission while magnetic contrast is related to the dichroic transmission between domains of opposite magnetization as discussed in Section (3.7). For 360 fs pulses, we observed slight decreases in the charge-magnetic contrast as shown in Figure 5.6, indicative of changes to the sample’s spin structure via x-ray induced demagnetization. For 80 fs pulses, the charge-magnetic contrast remained proportional to the incident fluence up to the most intense shot at 28 mJ/cm\(^2\), or approximately \(4.7 \times 10^{11}\) W/cm\(^2\). These results indicate that electronic damage induced by intense x-ray pulses can be outrun by using pulses shorter than 80 fs.
CHAPTER 5. ULTRAFAST DEMAGNETIZATION

Figure 5.6: Charge-magnetic contrast as a function of fluence for 80 and 360 fs single x-ray pulses. For 80 fs pulses, the contrast scales linearly with incident x-ray fluence. For 360 fs pulses, a marginal decrease in the contrast is observed at high x-ray fluences. The red line is a calculation of the expected contrast taking into account photon induced ultrafast demagnetization [63].

The characteristic time scale for the laser induced demagnetization in Co/Pd has been reported to be 220 - 280 fs [41]. Increasing the incident fluence leads to a higher degree of demagnetization and slower recovery times, but does not significantly alter the demagnetization time constant [45, 48]. Although no data on demagnetization with x-ray excitations exists, we can estimate the demagnetization effects of x-rays by comparison with optical pulses that deposit an equivalent amount of energy in the sample. We assume a fluence independent demagnetization time constant of 280 fs, and a minimum in the demagnetization curve that decreases linearly with increasing fluence until complete demagnetization. The resulting estimate for the charge-magnetic contrast is shown as the red curve in Figure 5.6. These results indicate that x-ray induced damage to the electronic structure can be outrun by using x-ray pulses shorter than 80 fs.
The success of single-shot imaging on a solid sample makes coherent diffraction an attractive tool for the time-resolved study of nanoscale femtosecond dynamics. By combining a pump-probe setup with single-shot imaging, individual real-space snapshots of a dynamical process can be captured. Currently, the resolution of single shot imaging remains photon-limited. But we should note that for non-magnetic single shot imaging, the polarizer is not necessary, and the incident flux can be increased by two orders of magnitude. The resolution can thus be greatly enhanced. At the same time, at these high intensities, the exploration of nonlinear effects in the x-ray regime becomes possible, as we shall see in Chapter 6.
Chapter 6

Nonlinear X-ray-Matter Interactions

The nonlinear response of matter subjected to intense electromagnetic fields, essential for the operation of lasers, has led to an extraordinary range of applications in nonlinear laser spectroscopy [67]. Ultrafast nonlinear spectroscopy, encompassing diverse techniques such as coherent anti-stokes Raman scattering (CARS), four wave mixing (FWM), and transient grating spectroscopy (TGS), has become a cornerstone technique for exploring microscopic interactions and dynamical processes [68]. The transfer of these nonlinear spectroscopic techniques to the x-ray regime have long been proposed [69, 70]. X-rays offer several key advantages over optical radiation, including smaller wavelengths, larger penetration depths, chemical and elemental specificity, and the ability to separate charge and spin degrees of freedom. Yet until recently, the requirements of intense, sub-picosecond x-ray pulses have prevented the systematic investigation of nonlinear x-ray-matter interactions. At a typical third generation synchrotron, due to the relatively low photon flux and long x-ray pulses, there is at most a single photon in a sample at a given instant in time. With the emergence of XFELs such as the LCLS which are capable of producing intense, coherent, femtosecond x-ray pulses, such experiments are now becoming possible.

Early nonlinear x-ray-matter experiments at LCLS have focused on the response of isolated atoms and molecules to intense x-ray pulses, due to the ease of replenishing
samples. Reported experiments include the creation of hollow-atoms through sequential photoionization [62, 71, 72, 73], induced Rabi oscillations [74], and an atomic x-ray laser based on atomic population inversion [75]. These experiments were typically performed in the continuum, far away from resonances, and utilized x-ray intensities of more than $10^{18}$ W/cm$^2$ to overcome the weak scattering cross-section of gas phase samples.

A second important class of materials which presents intriguing possibilities for nonlinear x-ray-matter interactions are solid state samples. Solids offer atomic densities that are higher by three to four orders of magnitude than typical gases. Furthermore, by tuning to the strong resonant absorption edges in the soft x-ray regime, the interaction strength can be enhanced by another three orders of magnitude. Taken together, these two factors suggest that resonant nonlinear x-ray effects in solids should be achievable at considerably lower intensities. The critical question to whether nonlinear spectroscopic techniques will be useful in solids is whether these effects appear below the sample damage threshold. Unlike with gas phase samples or spray injected nanocrystals, solid state samples cannot be easily replaced. The determination of this threshold is thus of great importance.

In this chapter, I will begin with an introduction to nonlinear susceptibility, and estimates of the nonlinear susceptibility in the x-ray regime. I will then discuss a nonlinear x-ray effect that has attracted a considerable amount of interest, and which has the potential to greatly expand our understanding of materials - stimulated Resonant Inelastic X-ray Scattering (RIXS). The first experimental indications of stimulated RIXS, in the intensity dependent changes to single shot coherent diffraction at LCLS will be presented. An explanation of the observed nonlinear changes to the refractive index using a theory based on stimulated RIXS will be discussed next. Finally, I will end with thoughts on future stimulated RIXS experiments.
6.1 Nonlinear Susceptibility

When an electromagnetic wave propagates through a material, charged particles within the medium are displaced from their equilibrium positions, creating induced dipole moments which then radiate. The induced dipole moment per unit volume is known as the polarization. At low field intensities, the induced polarization depends linearly on the applied field:

\[ P(t) = \varepsilon_0 \chi^{(1)} E(t) \]  

(6.1)

where \( \varepsilon_0 \) is the permittivity of free space, and \( \chi^{(1)} \) is the linear susceptibility. The susceptibility can thus be viewed as a modification to the permittivity of the material \( \varepsilon \) from its vacuum value \( \varepsilon_0 \), through the relation:

\[ \varepsilon = \varepsilon_0 (1 + \chi) \]  

(6.2)

In materials where the magnetic permeability \( \mu = \mu_0 \), as is the case with non-magnetic materials or for most materials in the x-ray regime, the susceptibility has a simplified relation to the refractive index:

\[ n = \frac{\varepsilon_0}{c} = \sqrt{\frac{\varepsilon \mu}{\varepsilon_0 \mu_0}} = \sqrt{\frac{\varepsilon}{\varepsilon_0}} = \sqrt{1 + \chi} \]  

(6.3)

The susceptibility is thus a complex quantity, and related to the absorption (\( \beta \)) and dispersion (\( \delta \)) optical constants through:

\[ n(\omega) = 1 + \delta(\omega) - i\beta(\omega) = \sqrt{1 + \chi(\omega)} \approx 1 + \frac{1}{2}(\chi'(\omega) + i\chi''(\omega)) \]  

(6.4)

where \( \chi'(\omega) \) and \( \chi''(\omega) \) are the real and imaginary parts of the susceptibility.
At sufficiently high electric fields, any material will exhibit a nonlinear response. The induced polarization is then expressed as a power series with respect to the electric field:

\[ P = \sum_{n} \varepsilon_o \chi^{(n)} E^n = \varepsilon_o \chi^{(1)} E + \varepsilon_o \chi^{(2)} E^2 + \varepsilon_o \chi^{(3)} E^3 + \ldots \]  

Higher order terms involve the interaction of multiple wave fields. For example, processes that depend on \( \chi^{(2)} \) are three-wave mixing processes. Two incident frequencies at \( \omega_1 \) and \( \omega_2 \) mix to produce a third frequency given by \( \omega_3 = \omega_1 \pm \omega_2 \). The size of the higher order terms decreases rapidly. In the optical regime, for many materials typical values for the nonlinear susceptibilities are \( \chi^{(2)} \sim 10^{-12} \) m/V and \( \chi^{(3)} \sim 10^{-22} \) m²/V² [76]. But under certain conditions, the second-order susceptibility \( \chi^{(2)} \) can be zero or negligible compared to the third-order susceptibility \( \chi^{(3)} \). One such example is in materials that possess inversion symmetry, such as gases or homogeneous materials, where the second-order susceptibility vanishes.

In the case of resonant x-ray scattering, the second-order susceptibility leads to a three-wave mixing process that connects the ground state to a particular resonance as shown in the energy diagram on the left side of Figure 6.1. This process is weak because it requires the assistance of a virtual state, which is represented by the dashed line.

Figure 6.1: Left: Energy diagram for three-wave mixing process. Right: energy diagram for stimulated Raman scattering.
The third-order susceptibility leads to four-wave mixing processes. Note that while energy conservation dictates that three-wave mixing must result in an elastic process, four-wave mixing can lead to inelastic processes. As an example, the energy diagram for stimulated Raman scattering, which will be discussed in Section 6.3, is shown on the right side of Figure 6.1. Raman scattering links the ground state to a low-lying excited state separated from the ground state by $\Omega$ through an intermediate state. Stimulated Raman scattering is a special degenerate case of four-wave mixing where only two frequencies are present. Because all the states in this process are real, the process can be resonantly enhanced. As we shall see in the next section, this resonant enhancement is the reason why the contribution from resonant $\chi^{(3)}$ is orders of magnitude larger than that from non-resonant $\chi^{(2)}$. 
6.2 Estimates of Nonlinear Susceptibility

An estimate of the third-order susceptibility can be made with the simple centrosymmetric anharmonic oscillator presented by Boyd [70, 76]. Let us begin with the case of linear susceptibility. The Lorentz model of the atom, in which the atom is treated as a harmonic oscillator, provides a good description of the behaviour for linear optical properties near resonances. In this simple model, the electron is connected to the nucleus via a spring. In the presence of an applied field, the electron oscillates due to the Lorentz force, while the nucleus remains fixed due to its much larger mass. The restoring force is linear with the displacement of the electron from its equilibrium position and given by:

$$\vec{F}_{\text{restoring}} = -m_e\omega_0^2 \vec{x}$$  \hfill (6.6)

where $m_e$ is the mass of the electron, and $\omega_0$ is the resonance frequency. The resulting potential is a parabola, as shown in blue in Figure 6.2. The electron oscillates within this potential at the frequency of the applied electric field.

![Potential energy function for a harmonic oscillator (blue) and for an anharmonic oscillator (red).](image)

Figure 6.2: Potential energy function for a harmonic oscillator (blue) and for an anharmonic oscillator (red).

We can generalize the treatment to higher orders by considering the addition of nonlinear terms. First, let us consider the addition of a second-order term. The restoring force becomes:

$$\vec{F}_{\text{restoring}} = -m_e\omega_0^2 \vec{x} - m_e\alpha \vec{x}^2$$  \hfill (6.7)
where \( a \) characterizes the strength of the nonlinearity. Following the derivation in [76], we obtain a non-resonant second-order susceptibility of:

\[
\chi^{(2)}_{\text{Non-resonant}} = \frac{Ne^3}{\epsilon_0 m_e^2 d} \frac{1}{\omega_0^3}
\]  

(6.8)

where \( N \) is the atomic number density, and \( d \) the atomic spacing. Typical optical energies are on the order of \( \hbar \omega = 1 - 3 \text{ eV} \), while soft x-ray energies are approximately two orders of magnitude larger, on the order of \( \hbar \omega = 200 - 1000 \text{ eV} \). From equation (6.8), the difficulty of observing nonlinear x-ray effects is immediately clear - the higher order terms scale inversely with frequency. In this case, \( \chi^{(2)} \), scales as \( 1/\omega_0^4 \), which leads to a rapidly diminishing nonlinear susceptibility in the x-ray regime. For Co at its L3 edge (780 eV) we obtain a value for non-resonant \( \chi^{(2)} \) of \( 1.5 \times 10^{-19} \text{ m/V} \) (see Appendix A).

Let us now consider the case where the first significant nonlinear term is the third-order susceptibility. With the addition of a third-order term, the restoring force becomes:

\[
\vec{F}_{\text{restoring}} = -m_e \omega_0^2 \vec{x} + m_e b \vec{x}^3
\]  

(6.9)

where \( b \) characterizes the strength of the nonlinearity. The resulting potential thus includes a correction term \( -m_e bx^4/4 \), and is shown in red in Figure 6.2. Using this centro-symmetric anharmonic potential and following the derivation in [76], we obtain a non-resonant third order susceptibility of:

\[
\chi^{(3)}_{\text{Non-resonant}} = \frac{Ne^4}{32 \epsilon_0 m_e^3 d^2} \frac{1}{\omega_0^6}
\]  

(6.10)

Again, inserting the parameters for Co, we obtain a value for non-resonant \( \chi^{(3)} = 1.1 \times 10^{-34} \text{ m}^2/\text{V}^2 \), which is more than ten orders of magnitude smaller than typical \( \chi^{(3)} \) values in the optical regime (see Appendix A).
Fortunately, as in the optical regime, \( \chi^{(3)} \) can be enhanced by many orders of magnitude by tuning the incident beam to a resonance of the material. Using the same anharmonic potential above, we obtain for the resonant case [76]:

\[
\chi_{\text{Resonant}}^{(3)} = \frac{Ne^4}{32\epsilon_0 m_e d^2 \omega_0^2 \Omega^4}
\]

where \( \Omega \) is the amount of detuning from resonance. For the experimental setup of \( \omega_0 = 780 \text{ eV} \) and \( \Omega = 1 \text{ eV} \), the lower bound estimated of resonant \( \chi^{(3)} \) is \( 1.3 \times 10^{-24} \text{ m}^2/\text{V}^2 \), more than \( 10^{10} \) times larger than non-resonant \( \chi^{(3)} \) (see Appendix A). Other authors have done more detailed calculations for \( \chi^{(3)} \) at the C K-edge at 284 eV, and have obtained estimates of \( 10^{-20} \) to \( 10^{-21} \text{ m}^2/\text{V}^2 \) at this lower energy [69, 70]. These values are comparable to the third-order susceptibility in the optical regime, which suggest that observing resonant nonlinear x-ray effects in the soft x-ray regime should be possible.

Let us wrap up this section by calculating a rough estimate for the relative contributions of \( \chi^{(2)} \) and \( \chi^{(3)} \) to the induced polarization by using Equation (6.5). Consider the case of an 100 fs x-ray pulse of 100 mJ/cm\(^2\), which corresponds to an electric field of \( 2.74 \times 10^9 \text{ V/m} \) (see Appendix A). The contributions from \( \chi^{(2)} \) and \( \chi^{(3)} \) are then:

\[
\chi^{(2)}E = (1.5 \times 10^{-19} \frac{m}{V})(2.74 \times 10^9 \frac{V}{m}) = 4.1 \times 10^{-10}
\]

\[
\chi^{(3)}E^2 = (1.3 \times 10^{-24} \frac{m^2}{V^2})(2.74 \times 10^9 \frac{V}{m})^2 = 9.6 \times 10^{-6}
\]

In other words, at this x-ray intensity, the contribution from \( \chi^{(3)} \) is more than a factor of \( 10^4 \) larger than the contribution from \( \chi^{(2)} \), which can be neglected.
6.3 Resonant Inelastic X-ray Scattering

One potential nonlinear technique in the x-ray regime that has attracted much attention is stimulated resonant inelastic x-ray scattering [69, 70]. Its spontaneous analog, resonant inelastic x-ray scattering (RIXS), is a powerful synchrotron-based technique for studying the low lying excitations in materials, including the important spin excitations in magnetic systems [77, 78, 79, 80]. The main drawback of RIXS is its low efficiency, typically a factor of $10^5$ lower than elastic scattering. RIXS measurements at third generation synchrotrons can thus take several days or even weeks.

The optical analog of inelastic x-ray scattering is Raman scattering. A pump wave at frequency $\omega_0$ is incident on a sample. Most of the wave is scattered elastically, or through Rayleigh scattering, and photons of the same wavelength are re-emitted. But a small fraction of the incident wave undergoes Stokes scattering, where photons of lower energy at frequency $\Omega - \omega_0$ are emitted as shown in Figure 6.3(a). The difference in frequencies between the pump wave and the Stokes wave, $\Omega$, corresponds to a low-lying electronic transition or vibrational mode of the system. The Raman process

![Figure 6.3](image_url)

Figure 6.3: (a) In the Raman scattering process, an incident photon at frequency $\omega_0$ is converted to a photon of lower energy at frequency $\Omega - \omega_0$ and a low-lying excitation in the sample at $\Omega$. (b) With stimulated Raman scattering, the downward transition to the low-lying excitation is stimulated by a second beam with matching frequency $\Omega - \omega_0$. 
is thus an inelastic light scattering process. One advantage of the Raman process is that it provides a way to probe low-lying excitations which cannot be directly accessed from the ground state due to symmetry.

Raman scattering, as with inelastic x-ray scattering, has low scattering efficiencies. However, the Raman process can be stimulated by coupling in a second beam of the correct frequency to drive the down transition into a low lying state, as shown in Figure 6.3(b). With stimulated Raman scattering, gains of up to $10^7$ have been reported in the optical regime [70, 76]. Thus in principle, stimulated RIXS should also enhance the RIXS signal by many orders of magnitude. The most important question is the threshold at which stimulated RIXS occurs. If it is below the threshold for irreversible changes to the sample, stimulated RIXS would open up an entirely new range of materials for study, and revolutionize the field of RIXS.
6.4 Experimental Results

In our experiment, we used coherent x-ray diffraction to measure changes to the refractive index of a Co/Pd multilayer thin film caused by intense, ultrashort x-ray pulses tuned resonantly to the Co L3 resonance. At fluences approaching 300 mJ/cm$^2$, we detected a five order of magnitude increase of inelastic scattering compared to the spontaneous inelastic scattering, a strong indication of stimulated RIXS. These results provide the first important benchmarks for the threshold of stimulated RIXS, and open an avenue for using nonlinear ultrafast spectroscopy to study low energy excitations.

Besides the spectroscopic prospects of stimulated RIXS, the impact of nonlinear effects on coherent x-ray diffraction is also critical. The importance of diffraction for structural determination of matter is well known. The feasibility of both nanocrystallography and single shot imaging at a XFEL has recently been demonstrated [60, 63]. At the same time, calculations have shown that nonlinear effects such as core ionization can significantly impact the coherent diffraction [81, 82]. The threshold we establish for the onset of nonlinear effects in a solid thus places important limitations on the usefulness of coherent diffraction for structural determination.

6.4.1 Experiment Setup

The experiments were performed at the SXR experimental hutch of LCLS using the RCI chamber. Electron bunches of 80 fs duration are sent through a series of undulators to produce x-ray pulses near the Co L3 absorption edge at 778.8 eV with a bandwidth of 6 eV. Two recent experiments have suggested that the duration of the x-ray pulse may be up to a factor of two shorter than the electron bunch [56, 62]. This shorter pulse length is corroborated by calculations done by Alberto Lutman of the Accelerator Research group at SLAC, whose statistical analysis in the spectral domain shows that nominal 80 fs electron bunches correspond to x-ray pulses of 50-60 fs [83].

Downstream of the undulator, the x-rays pass through a gas attenuator with two pulse-energy monitors, which provide a shot-by-shot analysis of the total pulse energy.
By using the gas attenuator, the x-ray pulse energy can be varied over three orders of magnitude, enabling measurements as a function of pulse energy with otherwise identical pulse parameters. The final spectral bandwidth of the x-rays is set by the exit slits on a grating monochromator. For our experiment, the bandwidth was approximately 1 eV FWHM.

The monochromatic beam is focused by a pair of bendable Kirkpatrick-Baez (KB) mirrors to a 10 μm diameter FWHM spot at the sample plane. Samples consist of the same Co/Pd multilayer samples with integrated sample-holographic masks as used for the single shot imaging experiments described in Section 5.2. Due to the lack of charge-magnetic interference with linear polarization, a real space reconstruction is not possible through FTH. In this case, the advantage of using a spectro-holographic mask is that it provides an additional check of the incident shot-to-shot pulse intensity at the sample plane through the intensity of the reference-reference cross-correlations, as will be discussed in Section 6.4.2.

Small angle coherent diffraction patterns of the samples were recorded with a Princeton Instruments MTE-2048 CCD camera, which has 2048 by 2048 pixels of 13.5 by 13.5 μm², placed 490 mm downstream of the sample. For each sample, a baseline diffraction was obtained with 360 x-ray pulses at a low intensity of approximately $1 \times 10^{10}$ W/cm² at two energies - before the Co L3 resonance (765 eV), and at one of three energies near the Co L3 resonance (778.0, 778.8, or 779.7 eV). The gas attenuation was then reduced, and a single shot high intensity diffraction with intensity ranging between $1 \times 10^{12} - 10^{13}$ W/cm² was taken at the same energy near the Co L3 resonance. The sample is destroyed by this high intensity x-ray pulse.

A schematic of the experimental setup is shown in Figure 6.4. Incident x-rays of 50-60 fs width are linearly polarized along the horizontal x axis. As described in Section 3.7, charge scattering arises from the differences in electron distribution between the circular sample aperture and the opaque Au mask of the background, and forms an Airy diffraction pattern. It retains the same polarization plane as the incident wave. Magnetic scattering arises from the differences in spin distribution between magnetic domains of opposite magnetization, shown as light and dark stripes, and have polarization orthogonal to the incident wave. Since the polarizations of the
Figure 6.4: The charge and magnetic scattering exhibit different polarization behaviour - the charge scattering retains the same polarization as the incident light, while the magnetic scattering has polarization orthogonal to the incident light. As explained in Section 3.7, for linearly polarized light, charge and magnetic scattering do not interfere and are simply superimposed on the detector.

Charge and magnetic scattered waves are orthogonal, the waves do not interfere on the detector. The resulting diffraction is thus a superposition of the purely resonant magnetic speckles and the non-resonant charge rings. Near the Co L3 resonance at 778.8 eV, the diffraction consists of a mixture of charge and magnetic scattering as shown in Figure 6.4. On the other hand, the diffraction at 765 eV exhibits no magnetic contrast, and consists of pure charge scattering because the XMCD effect exists only near resonance (see Section 3.4). Once the wavelength difference is taken into account, this pre-edge diffraction provides an estimate of the charge scattering contribution near resonance, enabling us to separate the charge and magnetic contributions in the near resonance diffraction.
6.4.2 Fluence Calculations

For single x-ray pulses, the intensity monitors in the upstream gas chamber provides a measurement of the pulse energy to within 20%. The focus spot size for specific settings of the Kirkpatrick-Baez mirrors can be characterized by examining imprints in lead tungstate targets [84]. These two measurements, along with the beamline transmission, provide a good estimate of the XFEL beam intensity at the sample. Typically, a more accurate assessment can be made by placing a photodiode at the sample position. Unfortunately, the tightly focused beam used in our experiment saturates these photodiodes even for low intensity shots.

The coherent diffraction in the low intensity regime at LCLS is expected to scale linearly with intensity, similar to the situation at third-generation synchrotrons such as SSRL. Thus the comparison of diffraction patterns from the same samples taken at SSRL and at LCLS provides an alternative measure of the incident photon flux at LCLS. At SSRL, the fairly large x-ray beam size and low fluences enables the incident photon flux at the sample position to be measured directly with a photodiode. For the SXUV Si photodiode produced by International Radiation Detectors (IRD), the responsivity is 0.255 A/W at 780 eV. This translates to 199 electrons for each 780 eV photon. Using a SXUV photodiode at the sample position, the incident photon flux at SSRL is measured to be approximately $1.2 \times 10^{11}$ photons/s. At SSRL, the vertical and horizontal exit slits of the beamline were adjusted to produce a beam size of approximately 220 μm by 90 μm at the sample plane as measured by knife edge scans. With a sample aperture of 1.45 μm diameter, the flux incident on the sample is thus:

$$\text{Photons}_{\text{SSRL}} = \text{Incident Flux} \times \frac{\text{Area of Aperture}}{\text{Area of Beam}}$$

$$= 1.2 \times 10^{11} \text{photons/s} \times \frac{\pi (0.725\mu m)^2}{220\mu m \times 90\mu m}$$

$$= 1.01 \times 10^7 \text{photons/s} \quad (6.13)$$
Coherent diffraction from the [Co(0.5nm)Pd(0.7nm)]₄₀ multilayer thin films are shown in Figure 6.5. Data taken at SSRL is shown on the left for an accumulation of one second; data taken at LCLS is shown on the right for an accumulation of 360 x-ray pulses. The diffraction patterns have been re-scaled to cover the same q-range. Due to the elliptical shape of the beam at SSRL, the coherence is better in the horizontal direction as compared to in the vertical direction. Coherence in the LCLS pattern is visibly better, as a result of the high transverse coherence of the XFEL beam [53].

Figure 6.5: Coherent scattering diffractions of Co/Pd multilayer thin films with integrated holographic masks. Data taken at SSRL is shown on the left. Data taken at LCLS is shown on the right. The diffraction patterns have been re-scaled to cover the same q-range.

For this particular set of diffraction patterns, using the counts from the first charge ring unobstructed by the beamstop as highlighted by the red circles in Figure 6.5, the ratio of the counts between the two images (SSRL:LCLS) is 1:2.06. The incident photon flux for a single x-ray pulse at LCLS is thus:

\[
\text{Photons}_{\text{LCLS}} = \frac{\text{Photons}_{\text{SSRL}} \times 2.06}{360 \text{ shots}} = 5.74 \times 10^4 \text{ photons}
\]
The single shot fluence is then:

\[
\text{Fluence} = \frac{5.74 \times 10^4 \text{ ph} \times 778.8 \text{ eV/ph} \times 1.6 \times 10^{-16} \text{ mJ/eV}}{\pi (0.725 \times \mu m)^2} = 0.43 \text{ mJ/cm}^2
\]

Calculating the fluence for high intensity single shots at LCLS is more complicated. At high intensities, the assumption that the coherent scattering pattern will be similar to those taken at SSRL no longer holds. Although an estimate of the flux on the sample can be made by using the gas chamber intensity monitor, the beamline transmission, and the focus spot size, the error of this estimate is likely to be large. A more accurate measurement of the single shot pulse intensity can be achieved by exploiting the spectro-holography mask structure of the sample. As demonstrated in Section 3.9, a sample transmission profile that includes both a sample aperture and a reference aperture generates sample-reference cross-correlation terms in addition to the sample-sample and reference-reference auto-correlation terms in the reconstruction. We can extend this to a case of two reference apertures in the transmission profile as shown in Figure 6.6:

Figure 6.6: (a) Transmission profile with sample aperture and two reference apertures labeled a and b. (b) Resulting diffraction. (c) Reconstruction from inverse Fourier transform of diffraction.
The additional reference generates a conjugate pair of reference-reference cross-correlations in the reconstruction, denoted by $a \otimes b$ in Figure 6.6. The intensity of each reference-reference cross-correlations is equal to twice the flux that passes through the reference holes. Because the reference apertures are drilled completely through the sample, this intensity is unaffected by changes in the sample itself, and thus serves as an excellent measure of the pulse intensity at the sample plane.

As with the other cross-correlation terms in the Fourier transformed image, the positions of these reference-reference cross-correlations are determined by the geometry of the reference apertures in the transmission profile. For the case above where the two references are separated horizontally by a distance $R$, the reference-reference cross-correlations appear at a horizontal distance $R$ from the center of the reconstruction. Thus by knowing the geometry of the transmission profile, we can pinpoint the exact pair of reference apertures that contribute to a particular reference-reference cross-correlation. A transmission profile corresponding to the actual experimental sample, five reference apertures arranged in a pentagon around the sample aperture, is shown in Figure 6.7. Simulated diffraction using the transmission profile of (a) is shown in (b).

Figure 6.7: (a) Transmission profile with sample aperture and five reference apertures labeled a-e. (b) Resulting diffraction with band-pass filter applied. (c) Reconstruction from inverse Fourier transform of simulated diffraction. (d) Reconstruction from experimental diffraction.
To mimic the processing of the experimental data, the diffraction is band-pass filtered. Removed low $q$ corresponds to the beamstop at the center of the detector, while removed high $q$ corresponds to a high pass filter applied to reduce edge effects from the finite detector area. The reconstruction from the simulation is shown in (c). As a comparison, the reconstruction from the experimental data is shown in (d), showing excellent correspondence. To fully visualize the cross-correlations, the intense central part of the reconstruction arising from the auto-correlations have been blocked out to increase the dynamic range.

Note that although the intensity of the reference-reference cross-correlation in the Fourier transformed image is proportional to the flux going through the reference hole, it does not provide an absolute measure of this incident intensity. Determination of the single shot pulse intensity is thus a two step process. In the first step, the absolute pulse intensity of the low intensity diffraction is calculated by a comparison with synchrotron diffraction data taken at SSRL. In the second step, the ratio between the reference-reference cross-correlations in the reconstructions for the low and high intensity diffractions is then used to calculate the absolute pulse intensity of the high intensity diffraction.
6.4.3 Analysis of Experimental Results

We observed significant nonlinear changes to the diffraction pattern as a function of x-ray pulse intensity, indicative of nonlinear changes to the index of refraction. The low and high intensity diffraction patterns from two representative samples are shown below in Figure 6.8. In the low intensity reference diffractions in Figure 6.8(a) and (d), the magnetic speckles are clearly visible and distinctly separated from the Airy rings of the charge scattering. The experimentally observed high intensity diffractions are shown in Figure 6.8(b) and (e). We note three key observations: 1) a dramatic reduction in the intensity of the magnetic speckles, 2) a reduction in the charge scattering at high intensity, and 3) both of the previous effects are highly dependent on the pulse intensity.

![Coherent diffraction patterns for two representative samples. a) Low intensity baseline reference diffraction for Sample A. b) High intensity single shot diffraction for Sample A. c) $q$-dependent intensity for a and b. d) Low intensity baseline reference diffraction for Sample B. e) High intensity single shot diffraction for Sample B. f) $q$-dependent intensity for d and e. The colourbars are linear and indicate number of photons. The images extend out to $q = 0.055$ nm$^{-1}$.](image)
To better visualize these intensity dependent nonlinearities, we plot the normalized charge and magnetic scattering intensities. In the case of linear scaling, as is the situation at SSRL, the expected high intensity pattern should correspond to a low intensity pattern multiplied by the ratio of the two intensities. In other words, when the incident intensity is doubled, the counts in the diffraction doubles, but the pattern remains the same. Using the intensity ratio between the reference-reference cross-correlations in the low and the high intensity diffractions, the low intensity patterns are scaled to provide a reference pattern at high intensity that assumes linear scaling. A comparison of this expected high intensity diffraction with the experimentally observed high intensity diffraction reveals deviations from linearity.

The $q$-dependent intensity for the expected high intensity diffraction for linear scaling (blue) and the experimentally observed high intensity diffraction (red) are shown in Figure 6.8(c) and (f) for the two samples. Note the evenly spaced peaks with decreasing intensity corresponding to the Airy rings of the charge scattering coming from the circular sample aperture, and the increased intensity near $q = 0.03 \text{ nm}^{-1}$ corresponding to the magnetic scattering from the periodic magnetic domains. For the $40 \text{ mJ/cm}^2$ high intensity single shot in, only a slight deviation from linear behaviour is observed in (c). For the $272 \text{ mJ/cm}^2$ high intensity single shot, a significant decrease in intensity as compared to linear scaling is observed in (f).

As mentioned previously, the pre-edge diffraction pattern, which consists only of charge scattering, can be used to separate the charge and magnetic contributions in the diffraction. The pre-edge scattering pattern is first re-scaled to account for the difference in wavelength with the on resonance diffraction, then normalized to the on resonance scattering by using the intensity in the first fully visible charge ring from the Airy pattern. This normalized image is a good approximation of the charge scattering on resonance. By subtracting the charge contribution, the magnetic contribution of the on resonance image can be isolated.
6.5 Discussion of Experimental Results

The normalized charge and magnetic scattering are plotted as a function of x-ray pulse intensity in Figure 6.9 for three photon energies near the Co L3 absorption resonance - pre-edge (778.0 eV), on resonance (778.8 eV), and post-edge (779.7 eV). The normalized charge and magnetic scattering both deviate from a linear scaling with x-ray pulse intensity, as would be given by a line at 1. Instead, both charge and magnetic scattering decrease significantly with increasing x-ray pulse intensity, with the onset of the nonlinearity in magnetic scattering at a lower threshold. The observed effect is also strongly dependent on the photon energy. For both charge and magnetic scattering, the nonlinearities are much stronger at 778.0 eV than at 779.7 eV.

Figure 6.9: Normalized charge and magnetic scattering as a function of x-ray pulse intensity for three energies near the Co L3 resonance. The magnetic scattering clearly exhibits a much stronger nonlinear behaviour as compared to the charge scattering.
6.5.1 Exclusion of Ultrafast Demagnetization

Let us first address the dramatic decrease of the magnetic scattering intensity. One potential explanation for this reduction is the same mechanism behind laser-induced ultrafast demagnetization [19], as discussed in Section 2.2, which involves an ultrafast channel of angular momentum dissipation out of the spin system. In Co/Pd systems, femtoslicing XMCD experiments at BESSY have shown that the time scale for this transfer is 220-280 fs [41], which is significantly longer than the 50 - 60 fs pulses used in our experiment. The major difference between the two experiments is the photon energy of the excitation source - 1.5 eV ($\lambda = 800$ nm) at BESSY, and 780 eV ($\lambda = 1.59$ nm) at LCLS. At LCLS, the resonant x-ray excitation creates a distribution of highly energetic electrons near 780 eV. These hot electrons then thermalizes within 10-100 fs down to the Fermi level. This electron cascade eventually results in many low energy electrons near the Fermi level. As the cascade proceeds, the limited amount of empty states near the Fermi level becomes a bottleneck. Thus the number of excitations is not expected to be significant during the first 50 - 60 fs. The absence of demagnetization on short time scales is corroborated by the single shot imaging experiments discussed in Section 5.2, which demonstrated that x-ray induced electronic damage can be outrun by using x-ray pulses shorter than 80 fs [63].

In addition to the time scale, neither the energy dependence nor the changes in charge scattering intensity in the experiment can be explained by ultrafast demagnetization. At the two selected near-resonance energies (pre-edge at 778.0 eV and post-edge at 779.7 eV), the first order absorption is similar, and thus a similar amount of energy is deposited in the system at the two photon energies. Yet the two display vastly different behavior in both charge and magnetic scattering intensities, suggesting that photon-induced demagnetization cannot be the underlying mechanism. Lastly, demagnetization cannot account for the observed reduction in charge scattering, indicative of an increase of absorption in the sample. With demagnetization, the filling of empty states near the Fermi level would actually result in reduced absorption as the number of available states for the absorption transition is reduced.
6.5.2 Nonlinear Contributions to the Refractive Index

To understand the experimental results, we need to examine the formation of the diffraction pattern. As explained in Section 3.7, the diffraction is intimately connected to the transmission profile of the sample, governed by the spatially dependent refractive index of the sample. In transmission geometry, due to the relative size of the absorption cross-section and the scattering cross-section (see Section 3.3), the diffraction contrast is dominated by absorption. The average absorption determines the charge contribution in the diffraction, while the dichroic absorption between the magnetic domains due to the XMCD effect determines the magnetic contribution.

As discussed in Section 3.1, absorption of a sufficiently energetic photon can eject an inner shell electron from the atom, leaving behind a core hole. In a simple atomic model, this is a one-electron transition connecting the wave functions of two states, $|a\rangle$ and $|b\rangle$ [8]. The initial wave function is given by:

$$|a\rangle = |R_{n,c}(r); c, m_c, s, m_s\rangle$$

where $R_{n,c}(r)$ is the radial component of the core shell, $n$ is the principle quantum number, $c$ is the orbital quantum number, and $s, m_s$ describes the spin state of the electron. The final wave function is given by:

$$|b\rangle = |R_{n',l}(r); l, m_l, s, m_s'\rangle$$

where $R_{n',l}(r)$ is the radial component of the valence state, and $n', l$ are the principle quantum number and orbital quantum number of that shell. The transition matrix element connecting these two states is then given by the dipole operator $P$ through:

$$\langle b | P | a \rangle = \delta(m_s', m_s) \sum_{m_c, m_l, p} \langle R_{n',l}(r) | r | R_{n,c}(r) \rangle \sum_{m_c, m_l, p} \langle l, m_l | e_p | c, m_c \rangle$$

$$= \langle b | P | a \rangle$$

$$= \delta(m_s', m_s) \sum_{m_c, m_l, p} \langle R_{n',l}(r) | r | R_{n,c}(r) \rangle \sum_{m_c, m_l, p} \langle l, m_l | e_p | c, m_c \rangle$$
where the first term represents the spin part, the second term the radial part, and the third term the angular part of the transition matrix element. As evident from the \( \delta(m'_s, m_s) \) term, the dipole operator preserves spin. The radial part of the transition matrix element is the overlap between the wave functions of the initial and final states. It is typically included as a single multiplicative constant used to scale theoretical calculations to experimentally observed absorption intensities. The angular part of the transition matrix element contains the full polarization dependence and gives rise to the dipole selection rules.

A theoretical calculation for the first-order absorption can be done for the 2p\(_{3/2}\) to 3d transition at the Co L3 edge by considering the transition matrix elements that connect one of the four filled 2p\(_{3/2}\) states \((m_j = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2})\) to one of the five possible empty 3d states \((3d_{xy}, 3d_{xz}, 3d_{yz}, 3d_{x^2-y^2}, 3d_{z^2-r^2})\) [8]. Photon energy dependence around the resonance is accounted for with the spin-dependent Co density of states, shown in Figure 6.10 below:

![Density of States](image)

Figure 6.10: Spin-dependent Co density of states.

The calculated absorption reproduces the shape of experimentally measured absorption spectrum. Light green shading represents the largely filled states below the...
Fermi level at 778.0 eV. Because absorption maps out the available empty states, its peak is centered above the Fermi level, near the center of mass of the empty states. Due to differences in the available states between the two spin channels, the absorption exhibits dichroism for left and right circularly polarized light (LCP and RCP) - the origin of the XMCD effect. The absorption can be re-written as the first-order susceptibility $\chi''(\omega)$ using equation (6.4), and is shown in the bottom panel of Figure 6.11. The dispersion is calculated from the absorption spectrum using the Kramers-Kronig relations. Note that at the absorption resonance, the dispersion vanishes.

In a similar fashion, resonant scattering can be calculated by considering transitions that connect an initial $2p_{3/2}$ state to an intermediate $3d$ state, and back to a $2p_{3/2}$ state [8]. Scattering can be considered as a coherent two step process. In the first step, an incident photon is absorbed, exciting an electron from the $2p_{3/2}$ state to

Figure 6.11: Top: Third order nonlinear susceptibility. Bottom: First order susceptibility, corresponding to the refractive index $n$. The real part of the susceptibility $\chi'(\omega)$ corresponds to dispersion, while the imaginary part $\chi''(\omega)$ corresponds to absorption.
the 3d state, leaving behind a core hole. In the second step, the excited state decays back to the ground state, accompanied by the emission of a photon. The coherent scattering matrix element is given by:

\[
D_{lm} = \sum_n \langle b | P_2 | n \rangle \langle n | P_1 | a \rangle \frac{\omega_{na} - \omega_1 - i\gamma_{na}}{\omega_{na} - \omega_1 - i\gamma_{na}}
\]

where \( \omega_1 \) is the incident photon energy, \( \omega_{na} = \omega_n - \omega_a \) is the difference in energy between the ground state and the intermediate state, \( \gamma_{na} \) is the lifetime of the intermediate state, and \( R^2 \) represents the strength of the radial matrix element. In the case of inelastic scattering, the excited state does not decay back into the true ground state, but rather, a low-lying excitation of the system. In other words, \( a \neq b \). The emitted photon is of a lower energy than the absorbed incident photon.

Because inelastic scattering is a four-wave mixing process, it is related to the third-order susceptibility. As can be seen from the top panel of Figure 6.11, \( \chi^{(3)} \) is many orders of magnitude smaller than \( \chi^{(1)} \). Thus typically, it has a negligible contribution to the optical constants. Note that this more detailed calculation yields a \( \chi^{(3)} \) that is two to three orders of magnitude larger than the simple estimate of \( \chi^{(3)} \) using the anharmonic oscillator model in Section (6.2). \( \chi^{(3)} \) exhibits a dichroism opposite to \( \chi^{(1)} \), because any inelastic scattering process that involves a spin-flip always acts to reduce the imbalance of spins.

From the first and third-order susceptibility as plotted in Figure 6.11, and the field dependence given in Equation (6.5), the absorption as a function of field intensity can be calculated using:

\[
\chi^{n(To)}(\omega) = \chi^{n(1)}(\omega) + \chi^{n(3)}(\omega) E(\omega)^2
\]

At low field intensities, the absorption depends only on the first-order absorption given by \( \chi^{n(1)} \), which dominates over the absorption due to spontaneous inelastic scattering from \( \chi^{n(3)} \). But at sufficiently high field intensities, absorption due to inelastic scattering becomes significant due to its \( E^2 \) dependence.
means that we must take into account the structure of the incident XFEL pulses in
calculating the intensity dependent changes to the coherent diffraction pattern.
6.5.3 FEL Pulse Structure Simulation

Our model of nonlinear susceptibility takes into account the time-dependent pulse structure of the Self-Amplified Spontaneous Emission (SASE) FEL pulses with a simple model. Simulations have shown that the pulse structure of the FEL in the time domain is highly non-Gaussian, but rather a flat top function with peaks at the leading and trailing edges, also known as a double-horn structure [83]. The spiked structure means that the peak intensity can be many times larger than the average intensity, an important consideration for intensity dependent nonlinear effects. Furthermore, the number of spikes depends on the monochromator bandwidth. In general, the smaller the bandwidth, the fewer the number of spikes.

In order to account for the effects of the FEL pulse structure on the stimulated scattering data, a MATLAB simulation of the FEL pulse structure was created based on the theory laid out in [85]. A simplified version of the model is outlined below.

The origin of the SASE process is shot noise, or the random arrival time of electrons at the entrance of the undulator. The electron beam current is given by:

\[ I(t) = (-e) \sum_{k=1}^{N} \delta(t - t_k), \tag{6.19} \]

where \(-e\) is the electron charge, \(N\) is the number of electrons in a bunch, \(\delta(...)\) is the delta-function, and \(t_k\) is the random arrival time of the electron to the undulator entrance. The Fourier transform of the electron beam current is:

\[ \mathcal{I}(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} I(t) dt = (-e) \sum_{k=1}^{N} e^{i\omega t_k}, \tag{6.20} \]
In the linear high-gain regime, field at the exit of a SASE FEL can be written as:

\[ \overline{E}(\omega) = H_{\text{mono}}(\omega - \omega_0)H_{\text{FEL}}(\omega - \omega_0)\overline{I}(\omega) \]  \hspace{1cm} (6.21)

where \( H_{\text{mono}} \) is the transmission function of the monochromator, and \( H_{\text{FEL}} \) is the transmission function of the FEL. For a Gaussian profile of the monochromator line,

\[ |H_{\text{mono}}|^2 = \exp\left[ -\frac{(\omega - \omega_0)^2}{2\sigma_{\text{mono}}^2} \right] \]  \hspace{1cm} (6.22)

where \( \sigma_{\text{mono}} \) is the bandwidth of the monochromator. To a good approximation, the transmission function of the FEL is also Gaussian in the high-gain linear limit,

\[ |H_{\text{FEL}}|^2 = \exp\left[ -\frac{(\omega - \omega_0)^2}{2\sigma_{\text{FEL}}^2} \right] \]  \hspace{1cm} (6.23)

where \( \sigma_{\text{FEL}} \) is the bandwidth of the FEL. For LCLS, \( \sigma_{\text{FEL}} \) is 0.25 - 0.5% of the energy. The effect of \( H_{\text{mono}} \) and \( H_{\text{FEL}} \) can be seen as Gaussian filters on the wide-band input signal that arises from shot noise. For typical numbers, \( \sigma_{\text{FEL}} \ll \sigma_{\text{mono}} \).

Simulated spectrum \( E(\omega) \) before and after the monochromator is shown in Figure 6.12 for \( \omega_0 = 780 \text{ eV}, \sigma_{\text{mono}} = 0.6 \text{ eV}, \sigma_{\text{FEL}} = 0.5\% \omega_0, \) and a pulse length of 80 fs.
Figure 6.12: Simulated SASE FEL spectra before and after the monochromator. The solid red line indicates the average FEL spectra before the monochromator. The overall transmission function is dominated by $H_{\text{mono}}$.

From $\overline{E}(\omega)$, the pulse structure in the time domain can be calculated with a simple Fourier transform. The simulated SASE FEL pulse structure in the time domain is shown in Figure 6.13.

![Pulse Structure Pre-mono](image1)

![Pulse Structure Post-mono](image2)

Figure 6.13: Simulated FEL pulse structure in the time domain before and after the monochromator.

Two other statistical properties of the pulse structure are important - the number
of spikes and the coherence time. The coherence time determines the width of each coherent spike within the x-ray pulse envelope, and is approximately:

\[ \tau_c = \frac{\sqrt{\pi \hbar}}{\sigma_{\text{mono}}} \]  

(6.24)

The number of spikes is then given by \( T/\tau_c \), where \( T \) is the overall x-ray pulse length.

For the set of parameters given above, the average number of spikes in a pulse is 17.8, with a coherence time of 4.6 fs.

I would like to thank Jacek Krzywinski, a research scientist at LCLS, for pointing me to reference [85], and for fruitful discussions as I worked through the FEL pulse simulation.
6.5.4 Impact on Absorption Cross-Sections

The nonlinear contributions from stimulated inelastic scattering to absorption is evident in a plot of the relevant cross-sections. As discussed in Section 3.3, the elastic scattering cross-section is many orders of magnitude smaller than the absorption cross-section. By definition, elastic scattering does not contribute to absorption - the re-emitted photon is of the same energy as the absorbed photon, and no energy is left behind in the system. Only inelastic scattering contributes to absorption. As shown in Figure 6.14, the spontaneous inelastic scattering cross-section (dotted line) is approximately five orders of magnitude smaller than the absorption cross-section (dashed line). Thus typically the contribution of inelastic scattering to absorption is negligible. This small inelastic scattering cross-section is also the source for the low efficiency of RIXS.

![Figure 6.14: Contributions to the total absorption cross-sections by the various x-ray processes as a function of x-ray intensity.](image)
However, as in the optical regime, inelastic scattering can be greatly enhanced with a stimulating beam of the correct frequency (see Section 6.3). In our experiment, the incident beam contains a range of frequencies due to its 1 eV FWHM bandwidth. This energy spread mimics the two beam condition of stimulated Raman scattering - a portion of the incident beam creates core holes through absorption, while a second portion of the beam at lower photon energy stimulates the decay of these excited states into available low-lying states rather than the ground state.

Using the calculated susceptibilities in Figure 6.11, a 60 fs SASE XFEL pulse with a 1 eV FWHM bandwidth from Section 6.5.3, the Co density of states, and the intensity dependence as given by Equation (6.18), the stimulated inelastic scattering cross-section (solid green line) is calculated and shown in Figure 6.14. Stimulated inelastic scattering increases exponentially with intensity, and becomes comparable to absorption at approximately $1 \times 10^{13}$ W/cm$^2$. Thus for the single shot intensities used in our experiment, $1 \times 10^{12} - 10^{13}$ W/cm$^2$, the nonlinear contribution to absorption from stimulated inelastic scattering will be significant.

As explained in Section 6.5.2, the sign of the dichroism in the nonlinear susceptibility $\chi^{(3)}$ is reversed as compared to the first order susceptibility. As the third order contribution to the absorption becomes ever more significant with increasing intensity, the dichroic absorption between LCP and RCP disappears. Thus the amount of magnetic scattering decreases with increasing x-ray pulse intensity. This effect is evident in the total absorption shown in Figure 6.14, given by the sum of spontaneous absorption and inelastic scattering and shown for LCP and RCP as the solid blue and solid red lines respectively. The reduction in the magnetic contrast resulting from the reduced dichroism is much stronger than the reduction in the charge contrast resulting from increased total absorption.
6.5.5 Comparison of Theory and Experiment

Using the x-ray pulse intensity dependence of the index of refraction for a 60 fs SASE XFEL pulse with a 1 eV FWHM bandwidth, the resulting changes to the charge and magnetic contrast, and hence the intensity of charge and magnetic scattering in the farfield is calculated. Curves for three different incident photon energies at 778.0 eV, 778.8 eV, and 779.7 eV are shown along with the experimental observations in Figure 6.15 below. The calculations are consistent with our observations, and correctly predict the photon energy dependence.

![Intensity-dependence Charge Scatt.](image1)

![Intensity-dependence Magnetic Scatt.](image2)

Figure 6.15: Normalized charge and magnetic scattering as a function of x-ray pulse intensity. The theoretical calculations show excellent agreement with the experimental observations and correctly predict the photon energy dependence.

The photon energy dependence can be explained by considering impulsive stimulation with an incident beam of 1 eV bandwidth, where the energy spread of the incident beam enables it to both excite up-transitions and stimulate decays. In the stimulated scattering process, the up excitation is related to the number of unoccupied states (analogous to x-ray absorption), while the down transition is related to the number of filled states (analogous to x-ray emission). Thus for impulsive stimulation, the stimulated signal is maximal when the photon energy of the incident beam
optimally overlaps with both the filled and the unoccupied states - when it is centered at the Fermi level. On resonance (778.8 eV), the photon energy of the incident beam is 0.8 eV above the Fermi level. Although the up excitation is relatively strong due to the large fraction of unoccupied states, the stimulated process is limited by the small fraction of the filled states accessible by the decay transition. Moving to the pre-edge (778.0 eV), the photon energy of the incident beam is centered at the Fermi energy. The up excitation is weaker due to the reduced number of unoccupied states, but the decay transition is enhanced by the increase in the number of accessible filled states. Thus the stimulated effects are enhanced in both the charge and spin channels. Similarly, moving above the edge (779.7 eV) decreases the overlap with the filled states, and restricts the decay transition.
6.6 Future Experiments

Though the observed x-ray intensity and photon energy dependent changes to the charge and magnetic diffraction is consistent with a nonlinear contribution to the optical constants via the third order susceptibility, the experiment which was performed does not provide conclusive proof of stimulated inelastic scattering. For impulsive stimulation, where the incident beam acts as both the pump and the stimulating beam due to its relatively broad energy bandwidth, the stimulated signal is in the forward direction. The ideal experiment to detect a stimulated process thus requires energy-resolving the directly transmitted beam. In a coherent diffraction experiment, the transmitted beam is typically blocked by a beamstop in order to protect the detector pixels from damage. Information from the transmitted beam is thus lost.

An ideal spectroscopy experiment would involve first taking a baseline spectrum of the inelastic scattering at low x-ray intensities. The incident x-ray pulse intensity would then be increased, and the spectrum measured as a function of incident intensity. Stimulated inelastic processes would be detected as increases in the spectral weight of the inelastic peaks. Due to the relative intensities between the directly transmitted beam and the inelastic beam in the forward direction, detecting an enhancement of the inelastic beam will be difficult. Rather than a transmission experiment, measuring the reflected beam may be more suitable. As the elastic beam is highly suppressed in reflection, enhancements in the inelastic peak should be clearly visible. The sample in this case should be an insulator, which has well defined inelastic peaks. These inelastic peaks must be clearly separated from the elastic peak, but within the bandwidth of the incident beam. One candidate system is cobalt oxide, which has been well-studied with RIXS, and shows strong inelastic peaks within 2 eV of the elastic peak [86, 87]. Such an intensity dependent spectroscopic experiment has been proposed, and will receive beamtime at LCLS.
6.7 Conclusions

In summary, we have observed strong indication of stimulated resonant inelastic x-ray scattering in a solid with a single high intensity x-ray pulse from LCLS by exploiting the large resonant scattering cross-section enhancements. The x-ray pulse intensity dependent changes to both the charge and the magnetic contributions to the coherent diffraction pattern, as well as their photon energy dependence, is consistent with a significant nonlinear contribution to the refractive index from enhanced inelastic scattering. The stimulated inelastic scattering contribution is five orders of magnitude larger than spontaneous inelastic scattering. A spectroscopy experiment at LCLS has been planned to confirm the existence and thresholds for stimulated RIXS.

Stimulated effects at XFELs will be the foundation for the emerging field of nonlinear x-ray optics and spectroscopy. In the future, we envision that stimulated scattering experiments can be performed at XFEL facilities in a two beam geometry - the first pulse acts as the pump and creates core holes, while the second pulse injects stimulating photons with the requisite properties, such as photon energy and polarization, to drive specific radiative decay channels. Stimulated intensity enhancements would revolutionize the field of RIXS, enabling the illumination of electronic communication between different atoms in a system [69, 70], or pump-probe time-resolved RIXS experiments.
Chapter 7
Summary and Outlook

Coherent x-ray diffraction is one of the most powerful tools for studying a wide range of material systems due to the many unique advantages of x-rays. In this dissertation, we have discussed two sets of experiments based on coherent x-ray diffraction - time-resolved optical pump x-ray probe experiments, and nonlinear x-ray effects at high x-ray intensities.

The shift towards time-resolved studies at synchrotrons and x-ray free electron laser (XFEL) sources by utilizing pump-probe techniques have opened up new avenues of exploring dynamics on the femtosecond to picosecond time scales. In this thesis, we demonstrated the potential for time-resolved laser pump x-ray probe at synchrotrons for studying magnetization dynamics. We looked at the picosecond relaxation dynamics in the labyrinth-like magnetic domains of a Co/Pd multilayer thin film following excitation by a femtosecond optical pulse [44].

The emergence of XFELs such as the Linac Coherent Light Source has greatly expanded the realm of experimental possibilities. For the first time, we can now image a sample with a single x-ray pulse [60, 63]. We showed that the information obtained at a XFEL can be complementary to that obtained at a third generation synchrotron with our measurements of the ultrafast demagnetization process. Without a doubt, time-resolved techniques will continue to grow and play increasingly important roles in the next decades.

At the same time, x-ray free electron lasers have also enabled the exploration of
nonlinear x-ray-matter interactions. Already, numerous nonlinear x-ray effects have been demonstrated [62, 75, 88]. Nonlinear spectroscopy in the optical regime has been a powerful toolbox for probing of microscopic interactions and dynamical processes. The extension of these nonlinear spectroscopic techniques to the x-ray regime has long been proposed.

One of the most promising nonlinear x-ray techniques is stimulated resonant inelastic x-ray scattering (RIXS), analogous to stimulated Raman scattering in the optical regime. In the second half of this thesis, we demonstrate strong indications of stimulated RIXS in our high intensity single shot coherent diffraction experiment at LCLS. By exploiting the strong resonant enhancements of the third-order susceptibility, we detected significant nonlinear changes in the coherent diffraction as a function of x-ray pulse intensity. These observations are consistent with calculated intensities for a stimulated inelastic scattering process.

To confirm these findings, an intensity-dependent spectroscopy experiment at LCLS in reflection geometry will be conducted in the near future. If the threshold for stimulated Raman scattering is indeed below the sample damage threshold, it will serve as a viable nonlinear x-ray spectroscopic techniques. The development of such x-ray will revolutionize our understanding of materials. For the x-ray community, the future certainly looks bright!
Appendix A

Estimates of Nonlinear Susceptibility

A.1 Non-Resonant $\chi^{(2)}$ for X-ray Wavelengths

As discussed in Section (6.1), second-order nonlinear processes involve the mixing of three waves. Two incident frequencies at $\omega_1$ and $\omega_2$ can mix to produce a third frequency given by $\omega_3 = \omega_1 \pm \omega_2$. Using the non-centrosymmetric anharmonic oscillator model in Boyd, the second-order susceptibility is given by:

$$
\chi^{(2)}(\omega_1, \omega_2, \omega_1 + \omega_2) = \frac{Ne^3\omega_0^2}{\epsilon_0 m_e^2 d} \frac{1}{D(\omega_1)D(\omega_2)D(\omega_1 + \omega_2)} \tag{A.1}
$$

where $N$ is the atomic density, $e = 1.9 \times 10^{-19}$ C is the electron charge, $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the permeability of free space, $m_e = 9.1 \times 10^{-31}$ kg is the electron mass, $d$ is the atomic spacing, $\omega_0$ is the resonance frequency, and $D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\omega_j \gamma$ where $\gamma$ is the linewidth of the incident radiation.

In the non-resonant case, $D(\omega_j) \approx \omega_0^2$. Thus non-resonant $\chi^{(2)}$ is given by:

$$
\chi^{(2)}(\omega_1, \omega_2, \omega_1 + \omega_2) = \frac{Ne^3\omega_0^2}{\epsilon_0 m_e^2 d} \frac{1}{\omega_0^4} = \frac{Ne^3}{\epsilon_0 m_e^2 d} \frac{1}{\omega_0^4} \tag{A.2}
$$
which is the expression given in Equation (6.8). For Co, \( N = 90 \text{ atoms/nm}^3 \) and \( d = 0.17 \text{ nm} \). For the Co L3 edge, \( \hbar \omega_0 = 780 \text{ eV} \) \( (\omega_0 = 1.185 \times 10^{18} \text{ rad/s}) \). The approximate value of the non-resonant \( \chi^{(2)} \) is thus:

\[
\chi^{(2)} = \frac{(90 \times 10^{27} \frac{1}{m^3})(1.6 \times 10^{-19} \text{C})^3}{(8.85 \times 10^{-12} \text{F/m}) (9.1 \times 10^{-31} \text{kg})^2 (0.17 \times 10^{-9} \text{m}) (1.185 \times 10^{18} \text{rad/s})^4} = 3.6864 \times 10^{-28} \frac{2.4567 \times 10^{-9}}{V} = 1.5 \times 10^{-19} \text{m}^2 \text{V}^2
\]

(A.3)

A.2 Non-resonant \( \chi^{(3)} \) for x-ray wavelengths

Using the centrosymmetric anharmonic oscillator model in Boyd, the third-order susceptibility is given by:

\[
\chi^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p) = \frac{Ne^4\omega_0^2}{\epsilon_0 m_e^2 d^2} \frac{1}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}
\]

(A.4)

As shown in Section (6.1), Raman scattering corresponds a degenerate case of four wave mixing where only two frequencies, \( \omega_1 \) and \( \omega_2 \), are present. In this case, \( \chi^{(3)} \) is given by:

\[
\chi^{(3)} = \frac{Ne^4\omega_0^2}{\epsilon_0 m_e^2 d^2} \left( \frac{1}{\omega_0^2 - \omega_1^2 - 2i\gamma\omega_1} \right)^2 \left( \frac{1}{\omega_0^2 - \omega_1^2 - 2i\gamma\omega_1} \right)^2
\]

(A.5)

In the non-resonant case, \( D(\omega_j) \approx \omega_0^2 \). And the above equation simplifies to:

\[
\chi^{(3)} = \frac{Ne^4\omega_0^2}{\epsilon_0 m_e^2 d^2} \frac{1}{\omega_0^2} = \frac{Ne^4}{\epsilon_0 m_e^2 d^2} \frac{1}{\omega_0^2}
\]

(A.6)

which is the expression given in Equation (6.10). For Co, \( N = 90 \text{ atoms/nm}^3 \) and \( d = 0.17 \text{ nm} \). For the Co L3 edge, \( \hbar \omega_0 = 780 \text{ eV} \) \( (\omega_0 = 1.185 \times 10^{18} \text{ rad/s}) \). The
approximate value of the non-resonant $\chi^{(3)}$ is thus:

$$\chi^{(3)} = \frac{(90 \times 10^{27} \frac{1}{m^3})(1.6 \times 10^{-19} C)^4}{(8.85 \times 10^{-12} F/m)(9.1 \times 10^{-31} kg)^3(0.17 \times 10^{-9} m)^5(1.185 \times 10^{18} \text{rad/s})^6} = 5.8982 \times 10^{-47}$$

$$= \frac{5.8982 \times 10^{-47}}{5.336 \times 10^{-13}}$$

$$= 1.1 \times 10^{-34} \frac{m^2}{V^2}$$

(A.7)

### A.3 Resonant $\chi^{(3)}$ for x-ray wavelengths

In the resonant case, $\omega_1 = \omega_0$ and $\omega_2 = \omega_0 - \Omega$, where $\Omega$ represents the detuning from resonance. Let us assume that $\omega_0 \gg \gamma, \Omega$ the linewidth of the incident radiation, $\gamma$, is approximately equal to $\Omega$. Equation (A.5) then simplifies to:

$$\chi^{(3)} = \frac{N e^4}{32 \epsilon_0 m_e^4 d^2} \frac{1}{\omega_0^2 \Omega^4}$$

(A.8)

Using the same parameters for Co, and $\hbar \omega_0 = 780 \text{ eV} (\omega_0 = 1.185 \times 10^{18} \text{ rad/s})$, with an incident beam of bandwidth $\hbar \Omega = 1 \text{ eV} (\Omega = 1.52 \times 10^{15} \text{ rad/s})$, we obtain an estimate for the resonant third-order susceptibility $\chi^{(3)}$:

$$\chi^{(3)} = \frac{N e^4}{32 \epsilon_0 m_e^4 d^2} \frac{1}{\omega_0^2 \Omega^4}$$

$$= \frac{(90 \times 10^{27} \frac{1}{m^3})(1.6 \times 10^{-19} C)^4}{32(8.85 \times 10^{-12} F/m)(9.1 \times 10^{-31} kg)^3(0.17 \times 10^{-9} m)^2(1.185 \times 10^{18} \text{rad/s})^2(1.52 \times 10^{15} \text{rad/s})^4}$$

$$= 5.8982 \times 10^{-47}$$

$$= \frac{5.8982 \times 10^{-47}}{4.623 \times 10^{-23}}$$

$$= 1.3 \times 10^{-24} \frac{m^2}{V^2}$$

$$= 1.3 \times 10^{-20} \frac{cm^2}{V^2}$$

(A.9)
A.4 Calculation of electric field strength

Let us calculate the electric field strength for a 100 fs pulse of 100 mJ/cm²:

Fluence 100 mJ/cm² = 1000 J/m²

The energy density $U$ is given by:

$$U = \frac{1000 \text{ J/m}^2}{c \cdot t} = \frac{1000 \text{ J/m}^2}{(3 \times 10^8 \text{ m/s})(100 \times 10^{-15} \text{s})} = 3.33 \times 10^7 \text{ J/m}^3 \quad (A.10)$$

The energy density is related to the electric field through:

$$U = \frac{1}{2} \epsilon_0 E^2$$

$$3.33 \times 10^7 \text{ J/m}^3 = \frac{1}{2}(8.85 \times 10^{-12} \text{ F/m}) E^2$$

$$E^2 = 7.53 \times 10^{18} \text{ V}^2 \text{ m}^2$$

$$E = 2.74 \times 10^9 \text{ V/m}$$
Appendix B

Fluence to Photon Flux Conversion

\[
100 \text{ mJ} \times \frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} \times \frac{1 \text{ photon}}{778.8 \text{ eV}} = 8.03 \times 10^{14} \text{ photons}
\]

\[
1 \text{ cm}^2 = (1 \times 10^7 \text{ nm})^2 = 1 \times 10^{14} \text{ nm}^2
\]

\[
100 \text{ mJ/cm}^2 = 8.03 \times 10^{14} \text{ photons/cm}^2 = 8 \text{ photons/nm}^2
\]
Appendix C

Pulse Illumination Profile

Though the reference-reference cross-correlations largely served as excellent measures of the single shot pulse intensities, certain samples exhibited additional complexities. One such reconstruction where only four pairs of reference-reference cross-correlations and their conjugate pairs are observed is shown in Figure C.1:

Figure C.1: Experimental reconstruction showing partial illumination.
APPENDIX C. PULSE ILLUMINATION PROFILE

For this reconstruction, the reference apertures can be divided into two groups - $a,b$ and $c,d,e$. Interference between reference apertures within the same group is strong, as seen by the intense reference-reference cross-correlations in the reconstruction. However, interference between reference apertures from different groups is very weak, and are nearly invisible in the reconstruction. The lack of interference suggests that two pulses illuminate the sample at different points in time as shown in Figure C.2. One pulse illuminates references $a$ and $b$, and produces a strong $a\otimes b$ cross-correlation. A separate pulse illuminates references $c$, $d$, and $e$, and produces strong $c \otimes d$, $c \otimes e$, and $d \otimes e$ cross-correlations. The reconstruction is essentially a superposition of two individual reconstructions.

Figure C.2: The lack of certain reference-reference cross-correlation pairs indicates that the sample is illuminated by two temporally separated beams. The resulting reconstruction is a superposition of the two individual reconstructions.
Due to the strong evident for an illumination from two temporally separated beams, a beam illumination profile was calculated using two Gaussian beams using an iterative fitting algorithm. An initial illumination profile is assumed, then the diffraction and resulting reconstruction are calculated. Adjustments are made to the illumination profile to minimize the difference between the simulated and experimental reconstruction. The estimated beam profile, simulated reconstruction, and experimental reconstruction, are shown in Figure C.3.

![Figure C.3](image)

**Figure C.3:** Left: Fourier transform of experimental diffraction, showing four pairs of intense reference-reference cross-correlations. Center: Simulated double beam illumination for best fit. Right: Resulting Fourier transform of simulated illumination, showing excellent correspondence with experimental observations.
Bibliography


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I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

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