Structural dynamics of the metal-insulator transition in VO$_2$: an ultrafast electron diffraction study with radio-frequency compressed electron pulses

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Abstract

In this thesis the design and implementation of an ultrafast electron diffractometer with radio frequency compression capabilities is presented. In addition, the results of ultrafast electron diffraction (UED) measurements on the semiconductor to metal phase transition in vanadium dioxide (VO$_2$) are shown. The ability to perform UED measurements on ultrafast time scales is first demonstrated by observing the expansion and coherent oscillation of the crystal lattice in thin film, single crystal gold. The evolution of the spatio-temporal charge density in ultrashort pulses was then studied using electron-laser cross correlation measurements mediated by the ponderomotive force. These measurements were compared with particle tracing simulations and theoretical models. Similar electron-laser cross correlation measurements were also performed in order to characterize the behaviour of a novel radio-frequency (RF) pulse compression technique. Using an RF cavity, an oscillating, 3 GHz electric field is synchronized to the electron pulse arrival time and allows for the compression of high bunch charge electron pulses ($\sim$0.1 pC) to 334±10 fs. This represents a bunch charge increase of $10^2$-$10^3$ over previous ultrafast electron sources that provide a sub 500 fs impulse response. Finally, the semiconductor to metal transition in VO$_2$ was studied using RF compressed electron pulses. Here, distinct ultrafast structural and electronic phase transitions were observed providing insight into the long standing debate surrounding the roles of electron-electron interactions and electron-lattice interactions in this phase transition.
Résumé

Cette thèse présente la conception et la construction d’un appareil de diffraction électronique ultra-rapide capable de compression radiofréquence. De plus, les résultats de mesures de diffraction ultra-rapide de délectrons (DUE) lors de la transition de phase semiconducteur-métal du dioxyde de vanadium (VO$_2$) sont présentés. La possibilité de mesures DUE à l’échelle ultra-rapide est démontrée, dans un premier temps, en observant l’expansion et les oscillations cohérentes du réseau cristallin d’une couche mince d’or monocristallin. L’évolution spatio-temporelle de la densité de charges dans les pulses ultra-courts a ensuite été étudiée grâce aux mesures de corrélation croisée électron-laser médiées par la force pondéromotrice. Ces mesures ont été comparées aux simulations de trajectoires de particules et aux modèles théoriques. Des mesures de corrélation croisée électron-laser similaires ont également permis de caractériser une technique novatrice de compression de pulses par radiofréquences (RF). Dans cette cavité RF, un champ électrique oscillant à 3 GHz est synchronisé avec l’arrivée du pulse délectrons, ce qui permet la compression de paquets délectrons de haute charge ($\sim 0.1pC$) à 334±10 fs. Ce résultat représente une augmentation de la charge de paquet d’un facteur 10$^2$-10$^3$ en comparaison des précédentes sources d’électrons capables de générer des pulses de moins de 500 fs. Finalement, la transition de phase semiconducteur-métal du VO$_2$ a été étudiée grâce à ces pulses d’électrons compressés par RF. Des transitions de phases structurelles et électroniques distinctes ont été observées à l’échelle ultra-rapide, permettant d’éclairer le débat de longue date au sujet du rôle des interactions électron-électron et électron-réseau lors de cette transition de phase.
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Preface

The work presented in this thesis describes my contribution to the design and implementation of an ultrafast electron diffractometer. Much of the work presented in chapter three has been published in Morrison, V. R., Chatelain, R. P., Godbout, C., & Siwick, B. J. (2013). *Direct optical measurements of the evolving spatio-temporal charge density in ultrashort electron pulses*. Optics Express, 21(1), 21. The results from chapter four have been published in Chatelain, R. P., Morrison, V. R., Godbout, C., & Siwick, B. J. (2012). *Ultrafast electron diffraction with radio-frequency compressed electron pulses*. Applied Physics Letters, 101(8), 081901, where both Robert Chatelain and I have contributed equally. My contribution to these measurements consists of the design and implementation of the electron-laser cross correlation technique as well as conducting cross correlation measurements. All simulations of the behaviour of the radio-frequency compression cavity are courtesy of Robert Chatelain.
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CHAPTER 1

Introduction

Our understanding of the emergent properties of bulk materials in the condensed phase, the molecular changes involved in a chemical reaction, or the function of a biological macro-molecule all result, in part, from our ability to probe their structure on the atomic length scales of their constituent particles. In order to fully understand the behaviour of these systems, we need to be able to study them on both the relevant length and time scales. To probe structure at the atomic level we need spatial resolution better than the interatomic distances of interest, generally on the order of one Ångstrom ($10^{-10}$ m). The characteristic time scale of motion on this length scale is on the order of 100 fs, or approximately the time it would take an atom to move one Ångstrom at the speed of sound ($\sim 10^3$ m/s). Just as a movie is made, frame by frame, with a shutter speed capable of freezing the motion being filmed, we need to be able to determine structural information throughout a transition with an effective shutter speed faster than that of the dynamics being observed.

Dramatic progress has been made on both of these fronts over the course of the past century. Since x-ray diffraction was first discovered by von Laue in 1912,
diffraction techniques (including x-ray, electron and neutron scattering) have become commonplace and provide the sub-Ångstrom spatial resolution required to study the three-dimensional structure of matter in equilibrium. In addition, electron microscopy and scanning probe microscopy now allow us to image matter at atomic length scales. The long acquisition times of these techniques, however, limit their ability to determine structure dynamically on the ultrafast time scales of atomic motion.

A method to study matter on these ultrafast time scales remained elusive until the advent of mode-locked lasers in the 1960s [1, 2]. In normal laser operation, e.g., continuous wave or Q-switched, there is no phase relationship between the various modes of the laser cavity and a generally continuous output is produced. By mode-locking, or phase-locking, a laser, a fixed phase relationship between the longitudinal cavity modes is introduced. This results in a single pulse oscillating in the laser cavity and a pulsed output allowing for the production of laser pulses in the picosecond and femtosecond regime [3]. These laser pulses provided, for the first time, the ability to initiate a transition and then probe the ensuing dynamics on the same time scale as the induced atomic motion. These advances led to the first observation of a molecular transition state by Dantus et al. in 1987 [4].

Due to the increase in laser intensity that accompanied this remarkable decrease in laser pulse length, non-linear optical processes, such as second harmonic generation (SHG), sum frequency generation (SFG) and super continuum generation, became easily achievable. Although these nonlinear processes have many useful applications, the nonlinear effect of self-focusing, a result of an intensity dependent index of refraction, limited the ability to produce high energy pulses, i.e., with sufficient intensity intracavity pulses would focus in the gain medium, damaging it.
This obstacle was overcome by Strickland and Mourou in 1985 by developing the chirped pulse amplification (CPA) method which involved first stretching the ultrashort pulse, amplifying this lower intensity stretched pulse, and then compressing the pulse back to an ultrashort duration [5]. By using dispersive elements, such as gratings and prisms, to stretch the pulse, a linear position-frequency relationship, or chirp, is introduced. This chirp is then removed using similar elements after the amplification has taken place. Previous to this, ultrashort laser oscillators were able to produce pulses with energies on the order of a nJ and peak intensities on the order of \(10^{12} \text{ W/cm}^2\) [6]. In contrast, femtosecond amplifiers now routinely produce pulses with energies in the 1 mJ to 1 J range, an amplification factor of \(10^6\)-\(10^9\). The ability to control pulses lengths through the manipulation of the position-momentum distribution is a concept that will also be applied to the creation of the ultrashort, ultrabright, electron pulses discussed later in this thesis.

Following these advances, numerous ultrafast spectroscopic techniques were introduced which used both optical pumps and probes [7–9]. The simplest, time resolved transient absorption spectroscopy, employs a pump-probe approach where the sample dynamics after photo-excitation are probed after a given delay with an optical probe. Visible and ultraviolet probe pulses, in the 1 eV - 5 eV energy range, are sensitive to the evolution of electronic states, whereas infrared (IR) probes, with energies on the order of 100 eV, are sensitive to the vibrational states of the sample. These pump-probe spectrosocopies have been used with great success to study a wide variety of phenomena including chemical reactions in both the gas [4] and liquid phase [10], phase transitions in correlated materials [11] and the function of proteins [12]. Similarly, time resolved photo-electron spectroscopy follows the dynamics along a reaction coordinate by determining the time dependent kinetic energy
spectrum of photo-emitted electrons; here, the delayed probe is used to ionize the sample [13].

Multi-dimensional spectroscopies, which use more than two pulses, can provide additional information on the transitions and coupling between states in multilevel systems that can be unresolvable using a standard pump-probe approach. 2D IR spectroscopy has been used extensively to study biological molecules and the pulse sequences used are optical analogs to those used in nuclear magnetic resonance (NMR) spectroscopy [14]. Many advances in structural biology have resulted from NMR spectroscopy but the long acquisition times associated with the technique prevent it from probing matter on ultrafast time scales. In contrast, sub picosecond IR pulses can be easily generated allowing 2D IR spectroscopy to probe such systems as the ultrafast dynamics of water [15] and the light harvesting dynamics of photosynthesis [16].

Ultrafast spectroscopy has also been extended to the far-infrared or terahertz (THz) regime. Various techniques exist for producing these THz pulses which provide the ability to probe the ultrafast dynamics of low energy (meV) phenomena [17]. These techniques have provided insight into a variety of systems including the dynamical photo-conductivity of inorganic semiconductors and correlated materials and the relaxation dynamics of liquids and solutions [18]. Although the various types ultrafast spectroscopy can provide a wealth of information on the behaviour of systems on ultrafast time scales, their relatively long wavelengths ($\gg 1 \, \text{Å}$) have prevented them from providing direct structural information.

1.1 Ultrafast Diffraction

Ultrafast diffraction is a stroboscopic, or “pump-probe”, technique (Fig. 1–1) that results from combining the temporal resolution of ultrafast spectroscopy with
the high spatial resolution of modern diffraction techniques. As such, there are two obvious choices for the structural probe; x-rays and electrons. Both electron and x-ray approaches are currently being employed and enormous strides have been made recently in the experimental capabilities of each [19–26]. These two probes differ both in how they interact with matter and how the pulses are generated. As a result, each possess different strengths as an ultrafast structural probe.

![Figure 1-1: Schematic diagram of the pump-probe geometry used in ultrafast diffraction. The sample dynamics are first initiated using an ultrashort laser pulse. The sample is then probed after a known delay with an ultrashort electron/x-ray pulse and the resulting diffraction pattern is recorded.](image)

The ability to measure the structural dynamics of a transition rests on detecting a sufficient number of electrons or x-rays so that the structure of the sample can be resolved at each time delay. This can be accomplished by either repeating the measurement a large number of times with a low brightness probe or, in contrast, increasing the probe brightness and using a correspondingly lower number of measurements, ideally a single shot, for each time delay. For many systems the dynamics of interest are either irreversible or cannot be cycled quickly. If ultrafast diffraction is limited to using only low brightness probes, the number of system that can be studied is significantly reduced.
When considering the interaction between the structural probe and the sample, electrons have a significant inherent advantage over x-rays. The scattering cross-section of x-rays is approximately $10^5$-$10^6$ times less than that of electrons and, therefore, much brighter x-ray pulses are required to produce the same number of scattering events [27]. This allows electron diffraction to use significantly thinner samples than x-ray diffraction, typically less than 100 nm depending on the electron energy used. Further, this allows for the use of samples with a thickness on the order of the optical penetration depth of the initiating light pulse in most cases, providing a uniform sample excitation with the pump pulse. For larger samples in the micron to millimetre thickness range, commonly used in x-ray diffraction measurements, uniform optical excitation of the sample is often not possible. The diffraction pattern produced following the optical excitation of such a sample has contributions from regions with differing excitation fluences. This must be taken into account during the analysis and contributes to a lower signal to noise ratio.

The drawback of this high scattering cross section is the difficulty encountered when preparing samples for use in time resolved electron diffraction measurements. Preparing samples that are on the order of 100 nm thick can be very challenging and limits what types of materials can be studied. In addition, dynamical diffraction effects are often present in electron diffraction measurements and complicate the analysis; this limits the types of samples to which electron diffraction techniques can be applied.

Radiation damage is also a factor which also needs to be considered when performing structural dynamics measurements. In this regard, electrons are much less damaging to samples than x-rays. For biological samples, both the ratio of inelastic to elastic scattering and the energy deposited per inelastic scattering event is higher
in 1.5 Å x-rays in comparison with 80 - 500 keV electrons [28]. More simply, x-rays deposit \(\sim 1000\) times more energy per elastic scattering event than electrons in biological samples.

From the perspective of pulse production, electrons have a significant advantage over x-rays. The photo-electric effect allows electron pulses to be generated at photocathodes quite easily with a quantum efficiency of \(\sim 10^{-5}\) [29]; the initial pulse length and number of electrons scale with the pulse length and intensity of the generating optical pulse. This allows for the production of electron pulses with a large number of electrons and is limited mainly by the available laser power. However, the primary challenge facing UED is providing this high brightness and short pulse duration at the sample. As electrons are charged particles, space-charge effects cause the pulses to broaden rapidly during propagation towards the sample, increasing the pulse duration [30]. Thus, when performing UED measurements there is a trade-off between pulse duration and flux. Nevertheless, UED has been used successfully to study various phenomena with sub-500 fs time resolution without the use of additional pulse compression techniques [24,31].

The production of x-ray pulses, in comparison with electron pulse production, suffers from complementary technical challenges. Similar to UED pulse production, x-ray pulses can be generated using ultrashort laser pulses to create a laser induced plasma in a gas or solid [32,33]. These plasmas can produce pulses of Cu-K\(\alpha\) radiation in the 100 fs to 1 ps range [34, 35]. Unlike electron pulses though, these x-ray pulses don’t broaden as they propagate and maintain their short pulse duration. The primary challenge facing plasma generated x-ray pulses is brightness; x-rays produced in a laser induced plasma are emitted over a large solid angle which limits the brightness which can be achieved at the sample.
In contrast with plasma based sources, synchrotrons are able to produce high brightness, polychromatic (1-100 keV) pulses but with much longer pulse durations, on the order of 100 ps. Although these pulses lack the sub-ps time resolution required to study many processes of interest, time resolved synchrotron measurements have been successfully employed in samples ranging from laser induced phase transitions in semi-conductors [36] to the structural dynamics of a functioning protein [21].

Finally, x-ray free electron lasers (XFEL), which have just come online in the past few years [20], represent an enormous step forward for ultrafast x-ray diffraction. These facilities accelerate electrons into the GeV energy range and, using a series of undulators, can produce pulses on the order of 10 fs in duration with more than $10^{12}$ photons per pulse. The costs associated with XFELs are enormous though, and require a large investment of resources. In contrast with these high brightness x-ray sources, ultrafast electron diffractometers are significantly cheaper to build due to the low acceleration energy and laser pulse intensity requirements. DC linear accelerators can be manufactured or purchased commercially and commercially available, table top laser amplifiers provide sufficient laser intensity to both generate the electron pulses and initiate sample dynamics.

1.2 Timeline of UED

The first measurement that demonstrated the ability to probe structural dynamics on the picosecond time scale was the reported melting of aluminum by Williamson and Mourou in 1984 [37]. They used $\sim 20$ ps electron pulses with approximately $10^4$ electrons per pulse. These electron pulses were photo-emitted from a cathode and accelerated to 25 kV. Although, ultimately, the degree of heating was less than reported (i.e., only a loss of diffraction was observed, they did not observe the diffraction signature characteristic of the liquid phase), the methods demonstrated here were the first
step towards the various ultrafast diffraction techniques which would be employed in the coming years.

Following the work of Williamson and Morou [37], UED was implemented in a geometry using molecular beams to produce gas-phase samples by the Zewail group at Caltech [38–40]. In this geometry, the structural dynamics of isolated molecules were studied with a time resolution of $\sim 10$ ps [41, 42]. The time resolution of UED is often limited when studying gas-phase samples due to the large sample volume and the velocity mismatch between laser and electron pulses, i.e., the relative delay between the electron pulse and the laser pulse changes as they propagate through the sample. The Zewail group followed their gas-phase work with UED in a reflection geometry on condensed matter samples [43, 44]. This reflection geometry, similar to the measurements performed on gaseous samples, suffered from a decreased time resolution as a result of the velocity mismatch between the laser pulse and electron pulse as it travels across the surface of the sample at a grazing angle. This loss in time resolution was later remedied using pulse tilting techniques which allowed for sub-picosecond time resolution for UED measurements in reflection geometry [45, 46].

The aforementioned studies were all highly reversible and, as such, could be repeated a large number of times with low charge electron pulses in order to achieve adequate statistics. In contrast, it was the work of Siwick et al. which first measured an irreversible phase transition, the melting of aluminum, with sub-500 fs time resolution [24]. The nature of this transition required that a new sample be used for each electron pulse. This work, by the Miller group at the University of Toronto, was followed by subsequent studies of the structural dynamics in various solid-state samples including a non-thermal phase transition in silicon [47], bond-hardening in gold [25] and the optical suppression of charge density waves [48].
Following the early work which used uncompressed pulses and electron energies of <100 keV, UED has diversified in both its methodology and its application. Still, one of the primary goals remains the production of high-brightness, temporally short electron pulses. Currently, relativistic electron sources are being developed for use in UED [49–51]. The use of electron pulses with electron energies on the order of MeV and velocities near c reduces longitudinal space-charge broadening and may offer pulse durations in the 10 fs regime and transverse coherences large enough to study proteins [52]. These MeV UED setups require a larger of investment of resources than their non-relativistic, table-top counterparts and radiation safety becomes an issue due to the amount of ionizing radiation generated by these high energy electrons.

An alternative to reducing space-charge effects is to employ pulse compression techniques which reduce the pulse duration after first letting it broaden. As electron pulses propagate they naturally develop a linear position-momentum correlation, as can be seen in Fig. 1–2 [30]. While initially uncorrelated, this linear position-momentum relationship develops rapidly, resulting in the fast electrons being located at the front of the pulse and the slow electrons at the back. These types of correlations are routinely used when stretching or compressing optical pulses and similar methods can be applied to electron pulses, i.e., if this linear distribution is reversed the pulses will compress ballistically during propagation. This can be achieved passively with a reflectron [53–55], or actively, by using a radio-frequency (RF) compression cavity [23, 56, 57]. Relectrons are effectively electrostatic mirrors and the manipulation of the position-momentum distribution is accomplished by having an energy dependent path length through the reflectron. A similar passive approach, which uses a spherical electrostatic capacitor to reverse the position-momentum relationship has also been proposed [58]. In contrast with these passive techniques, RF compression cavities are
actively synchronized to the arrival of electron pulses and have oscillating electric fields in the propagation direction of the electron beam. These cavities apply a time-dependent force to the electron bunch resulting in the reversal of the position-momentum relationship; these cavities will be discussed at length in chapter 4.

The work presented in this thesis focuses on i) the development and implementation of an ultrafast electron diffractometer with RF cavity based pulse compression capabilities, ii) the characterization and simulation of the evolution of electron pulses as they propagate and iii) the use of this diffractometer to study the semi-conductor to metal transition in VO$_2$. My initial work focused on the implementation of the
diffractometer in a compact geometry without pulse compression capabilities. In this geometry, time-resolved measurements on gold were performed in order to ensure the correct operation of the diffractometer. Measurements using electron-laser pulse cross correlation methods and simulations were also performed in order to study the evolution of the internal charge density of ultrashort electron pulses [59]. Following this, an RF compression cavity was integrated into the diffractometer. Our work on the production and characterization of RF compressed electron pulses represents a dramatic improvement in UED instrument performance [23]. Finally, the semi-conductor to metal transition in VO$_2$ was studied using RF compressed electron pulses. These measurements, for the first time, identify the photo-induced transition to a meta-stable metal-like state, without the accompanying change in crystal structure which is normally associated with this transition. This was accomplished by measuring a charge redistribution within a static crystal lattice, a phenomenon which had not previously been observed using ultrafast structural techniques. These UED measurements were supported by time-resolved IR transmittance measurements. The results demonstrate the effectiveness of UED at probing the dynamics of electron density redistribution on ultrafast timescales in addition to providing direct structural information on the dynamics of the crystal lattice.
References


CHAPTER 2

The Ultrafast Electron Diffractometer

UED is a stroboscopic technique that uses an ultrafast laser pulse to initiate dynamics in a sample and an ultrashort electron pulse to follow the ensuing dynamical evolution of the material. By repeating this measurement for many pump-probe delays the structural evolution of the sample can be determined. In order to achieve this capability an ultrafast electron diffractometer relies on the integration and synchronization of many individual components including, but not limited to, an electron source, an ultrafast laser system and an imaging electron detector. In this chapter the design, parameters and operation of our table-top diffractometer will be presented along with a brief introduction to the theory of electron diffraction. The results of measurements on femtosecond laser-induced lattice dynamics in single crystal gold will be shown as an example of the capabilities. The implementation and characterization of the RF compression cavity will not be addressed in this chapter but is the focus of Chapter 4.
2.1 Optical Setup

The diffractometer was designed to allow two modes of operation, one in a compact geometry and the second with pulse compression capabilities. The optical setup of the ultrafast electron diffractometer in the compact geometry is shown in Fig. 2–1. The source of the ultrashort laser pulses is a Newport Spitfire Pro XP CPA laser amplification system. The femtosecond laser pulses are originally created in a Newport Tsunami, a titanium sapphire (Ti:sapph) passively mode-locked laser oscillator; it produces $\sim$5 nJ, $\sim$100 fs pulses with a repetition rate of $\sim$ 75 MHz. The Tsunami has one of the cavity end mirrors attached to a motorized linear stage providing the ability to change the cavity length which in turn gives us control of the pulse repetition rate. This capability is required for correct synchronization of the RF cavity and will be addressed in Chapter 4. In the compact geometry this parameter is unimportant and is left unchanged at approximately 75 MHz. These low energy pulses from the Tsunami are then used to seed the Spitfire Pro XP Ti:sapph CPA regenerative amplifier. This amplifier outputs 3 mJ, 35 fs pulses centered at 800 nm with a maximum pulse repetition rate of 1 kHz (3 W total output power); the repetition rate can be reduced as required. All subsequent laser and electron pulses used in the diffractometer are generated from these laser pulses.

Following the generation of the ultrashort laser pulses the laser light is split equally into three lines: the UED line, the infrared spectroscopy line and the optical parametric amplifier (OPA) line. In the diffractometer setup a 50/50 beam splitter is used to send 500 mW into a pump line that consists of a variable optical delay, a waveplate/polarizer combination, a focusing lens and any required non-linear optical crystals (Fig. 2–1). The optical delay consists of a gold coated retroreflector, an optical component that reflects light in a direction parallel to the incident wave
Figure 2–1: Schematic diagram of the ultrafast electron diffractometer in compact geometry. The incoming laser pulse (1 mJ, 35 fs, 800 nm) is split into the pump line and the probe line. After being sent through a variable delay, the pulses in the pump line are used to generate 400 nm light in a BBO crystal. They are then focused to the desired size at the sample position. The pulses in the probe line are first attenuated using a half waveplate and polarizing beam splitter before generating 266 nm light using two BBO crystals. The 266 nm is then filtered from the remaining 800 nm and 400 nm light by a prism compressor before being focussed on the high-voltage DC photocathode. The photo-emitted electrons then travel to the sample position and are focused at the CCD camera using a variable magnetic lens.

vector, mounted on a linear delay stage. This stage has a range of 20 cm which provides a variable pump-probe delay of ~1.3 ns and a minimum step size of ~1 μm, equivalent to a minimum temporal step size of ~5 fs. For the measurements presented in this thesis, the pump used was either the original 800 nm wavelength or
400 nm pulses produced using type I second harmonic generation (SHG) in a single beta barium borate (BBO) crystal.

The remaining 500 mW of power is sent into the probe line and is used to generate the electron pulses. Here, the 800 nm pulses are attenuated to the desired pulse energy using a waveplate-polarizer combination, and are sent through a BBO crystal which converts some of the 800 nm light into 400 nm light. The 400 nm pulses are produced through type I SHG and are polarized orthogonal to the 800 nm pulses [1]. Due to the different group velocities of 800 nm and 400 nm light the pulses temporally separate as they travel through the BBO crystal. This relative delay is removed by the use of birefringent calcite crystal in which 800 nm light has a lower group velocity than the 400 nm light, reversing the pulse separation. These two pulses, now temporally overlapped, then pass through a second BBO crystal and using type II sum frequency generation (SFG), 266 nm (UV) pulses polarized orthogonal to the 800 nm pulses are produced. The UV pulses need to be isolated from the remaining 800 nm and 400 nm light to remove the risk of photo-cathode damage and the production of secondary electron pulses from these relatively high intensity pulses. This is accomplished by using a prism compressor configuration (Fig. 2–1) where the UV pulses takes a unique path and the 800 nm and 400 nm pulses can be blocked. The UV pulses pass through a focusing lens before entering the sample chamber. Here they are reflected into the electron gun chamber and onto the centre of the photo-cathode.

2.2 The DC Electron Source

The electron source is held in a cylindrical vacuum chamber with a vacuum of approximately $10^{-7}$ Torr, achieved using a turbo pump. A commercial high voltage feedthrough, rated for 100 kV, enters through the top of the source chamber and is
connected to the high voltage power supply. The high voltage power supply used is a Heinzinger PNChp. This power supply can produce voltages as high as 150 kV, with a voltage stability of 0.001%, or 1 V, at 100 kV. This level of stability results in an arrival time jitter of <10 fs for the cathode-sample distances used in the compact geometry and an acceleration voltage of 100 kV.

The original electron gun design (Fig. 2–2) was based on a design by the group of Prof. Jom Luiten at the Technical University in Eindhoven, Netherlands [2]. The key features of this source design are the large hole in the anode that allows for front side illumination of the photo-cathode and the linear extraction fields along the beam axis at the centre of the photo-cathode. In this original design the photo-cathode

![Diagram of the original electron gun. A PEEK cone (white), supported a stainless steel (hatched) housing for the photo-cathode (gray).](image_url)
and its housing were held away from the anode (the flange of the source chamber) at a distance of 6 mm using a conical piece of polyether ether ketone (PEEK). The cathode, indicated in grey in the figure, was originally a standard convex lens that had a gold coating approximately 1 µm thick sputtered onto it; this design was to facilitate back surface illumination if needed. The high voltage source is connected to the back of the photo-cathode. The surface of the cathode housing and the anode were polished using various polishing pastes, with diamond grit sizes down to 5 µm, in order to obtain as smooth a surface as possible. The surfaces were then washed with solvents in order to remove the polish residue.

If a high voltage gap is to achieve optimal insulating capabilities, it must first be conditioned. There are several ways that can be achieved; we used a combination of two methods, “current” conditioning and “spark” conditioning [3]. Current conditioning involves slowly incrementing the voltage in small steps which results in a decrease in frequency of current spikes or micro-discharges. Here, micro-protrusions that result in high electric fields can be thermally blunted from electron emission. In addition, particles that loosely adhere to the surface will be removed at the lowest voltage possible and their velocity as they impact the opposing electrode will ideally be low enough to not initiate a breakdown event. Spark conditioning occurs when arcs between the cathode and anode erode away locations of high field emission. The conditioning was accomplished by using a software algorithm which slowly increased the voltage until a breakdown event occurred before reseting; this was implemented by Robert Chatelain.

After attempting to condition the electron source, two problems were encountered. The first being that the breakdown events experienced at the cathode had the potential to damage the thin film cathode and visible holes could be seen. The
second issue encountered was one of surface tracking, i.e., certain breakdown events would result in a sustained current being present, limiting the ability to increase the voltage. Visual inspection of the PEEK cone revealed small tracks in the surface where, presumably, this current was travelling. A discussion of the various breakdown mechanisms is beyond the scope of this thesis but a general mechanism is that of an electron cascade across the insulating surface [4]. Field emitted electrons can collide with the insulator, releasing additional electrons and resulting in an electron cascade mechanism. This causes a breakdown of the high voltage gap and can damage the surface of the insulator. These events permanently damaged the PEEK cone and another design for the source was pursued.

Charging of the insulator surface due to the deposition of field emitted electrons can result in an increased likelihood of a surface tracking event. In order to reduce this, the new design incorporated metal shields to reduce the amount of field emitted electrons incident upon the insulator. The insulating material in the new design is Macor, a machinable, highly-insulating ceramic, with excellent vacuum properties and the cathode to anode distance along the surface of the insulator was increased. The new design can be seen in Fig. 2–3. This is the electron source design used for all measurements presented in this thesis.

As a result of the fragility of the thin film gold cathode it was replaced with a bulk copper cathode machined to the same dimensions as the convex lens originally used. For a material to be a suitable photocathode its work function must be less than the energy of the photons used for photo-emission. The work function depends strongly on the index of the crystallites exposed at the surface, its cleanliness and the grain size of the crystallites. For copper this value ranges from 4.4 eV to 4.9 eV [5–7]. The energy of the photons in the UV pulse is approximately 4.6 eV, corresponding
2.3 The Sample Chamber

The sample chamber (Fig. 2–4) is connected to the electron source chamber through a gate valve and a beam tube surrounded by a magnetic lens. The gate valve allows for samples to be cycled and optics aligned without breaking vacuum on the source chamber. The sample chamber is kept at a vacuum of $\sim 10^{-6}$ Torr with a

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**Figure 2–3:** Diagram of the current electron gun, capable of reaching 95 kV. The cathode geometry remains the same. Supporting the cathode are Macor rods (white), and stainless steel (hatched) shields are installed between the cathode and the Macor rods to block emitted electrons.

closely to the work function of copper. If the work function is significantly lower than the photon energy, the excess energy results in an increased electron kinetic energy, reducing the beam emittance.
2.3 The Sample Chamber

Figure 2–4: Overhead drawing of the sample chamber (left). The gate valve, turbo pump and camera locations are indicated. Although only five smaller ports can be seen here, there are four more; two above and two below the three shown at the top. A perspective drawing is shown to the right and the access port, where the samples are cycled and optics installed, is indicated at the top.

turbo pump. Opposite the port for the turbo pump are seven 2-3/4” ports which are used for various purposes including electrical feedthroughs, optical feedthroughs and pressure meters; two additional angled 2-3/4” ports are adjacent to the camera port. The bottom of the sample chamber is machined with 1/4-20 screw holes spaced 1” apart which are used to mount optics and linear stages to the bottom of the chamber. Sample positioning is accomplished using three vacuum compatible Micos MT-40 linear stages to provide motion in the $x$, $y$ and $z$ directions. These stages have a maximum travel range of 26 mm and a bi-directional repeatability of 2 $\mu$m. A 10” port on the top of the chamber has a hinged cover attached which seals with an O-ring. This allows for rapid cycling of samples and optical adjustments and the chamber will reach a pressure suitable for experiments ($\sim 10^{-5}$ Torr) after approximately 20 minutes, depending on the components in the chamber.
2.4 The CCD Camera

The CCD camera used in the diffractometer is a commercially available Gatan UltraScan 1000. The camera uses a phosphor film that is fibre-optically coupled to the CCD. This CCD is 2048 x 2048 pixels with the total dimensions 28.7 mm x 28.7 mm and a pixel width of 14 µm. It is cooled with a thermo-electric cooling module and retracts to keep the CCD under vacuum when the sample chamber is opened; this lessens the risk of contamination and condensation when opening the sample chamber. The number of counts generated on the CCD per electron is a function of energy and was calibrated using a faraday cup connected to a Keithley 6514 electrometer capable of measuring currents as low as 1 pA, and was found to be 0.186 counts/(electron kV) or 17 counts/electron at 95 kV. The dark counts present in an image were measured to be ±2 counts/pixel, significantly lower than the counts generated from a single electron. Upon installation, scattered pump light from the sample often caused saturation of parts of the CCD which made performing pump-probe measurements extremely difficult. To overcome this we removed the phosphor/fibre-optic module from the camera and sputtered 300 nm of aluminum onto the surface of the phosphor in an attempt to reflect away scattered laser light. After the coating was applied there were still certain pixels which would saturate due to pinholes in the aluminum film. The surface of the phosphor is quite rough making deposition of a truly continuous film difficult. Nevertheless, the amount of detected laser light was significantly reduced, enabling us to perform pump-probe measurements.

2.5 Electron Beam Properties

In order to perform time-resolved electron diffraction measurement we need the ability to control both the pulse duration and the transverse electron pulse size. In
the compact geometry the transverse beam properties are manipulated using a single magnetic lens. This magnetic lens has a solenoid design and is inside an iron housing which surrounds the electron beam tube. The lens is mounted immediately (7 cm) after the electron source and before the sample chamber. The focusing properties of a magnetic lens are similar to that of an optical lens but with a variable focal length controlled by the current through the lens [8]. The focusing properties of the magnetic lens for electron pulses containing 5000 electrons can be see in Fig. 2–5. These results were generated using the General Particle Tracer software, a software package which simulates charged particle dynamics in electromagnetic fields in three dimensions. In order to produce a diffraction pattern with narrow line widths using

![Diagram](image)

**Figure 2–5:** Simulation results displaying the electron beam diameter as a function of propagation distance for various magnetic lens currents (5000 electrons/pulse, 70 keV electrons). The current displayed is a current per area defined in the simulation, it scales linearly with the real current used in the diffractometer. Each electron pulse contains 5000 electrons. The positions of the magnetic lens, the sample and the detector are indicated.

a single magnetic lens, the electron beam waist needs to be located at the detector. This results in a transverse electron beam diameter of approximately 500 $\mu m$ - 1 mm at the sample, depending on the initial conditions of the electron pulse.
The pulse duration in the compact geometry is controlled by space-charge interactions in the pulse, which are determined primarily by the bunch charge and the source to sample distance. The evolution of the pulse duration as a function of propagation distance for various bunch charges as computed by GPT can be seen in Fig. 2–6. The initial measurements, presented in this chapter, were performed at a sample position of 26.8 cm, with ~500 electrons per pulse, resulting in a pulse length of ~200 fs.

**Figure 2–6**: Electron pulse duration as a function of propagation distance for various bunch charges.

### 2.6 An introduction to the theory of electron diffraction

Electron diffraction is a phenomena that results from the wave-like nature of the electron. The de Broglie wavelength of an electron is given by

$$\lambda = \frac{h}{p},$$  \hspace{1cm} (2.1)
where $h$ is Planck’s constant and $p$ is the electron momentum. Taking into account relativistic effects, an electron accelerated in a potential, $U$, will have a wavelength

$$\lambda = \frac{h}{\sqrt{2m_0eU}} \frac{1}{\sqrt{1 + \frac{eU}{2m_0c^2}}}$$

(2.2)

where $m_0$ is the rest mass of the electron, $e$ is the electron charge and $c$ is the speed of light. For the accelerating potentials used in our diffractometer, 50 kV - 95 kV, an electron wavelength of 5.4 pm - 3.8 pm is obtained, significantly smaller than the atomic length scales of interest which are on the order of 1 Å. By observing the constructive and destructive interferences that results from electrons interacting with a crystalline sample we can extract information about the potential energy distribution within the sample.

If we consider an electron source far from the sample, the incident electron wave function can be approximated as a plane wave (or sum of plane waves)

$$\Psi_i = e^{i(k_0 \cdot r' - \omega t)}$$

(2.3)

with an incident wavevector $k_0$ and a source-sample vector $r'$; the time dependence of the wave will be neglected as we are focusing on the spatial dependence of the diffracted wave although it can easily be recovered\(^1\). Any scatterer, e.g. electron or nucleus, which experiences this wave will radiate a spherical scattered wave

$$\Psi_s = f(k_0, k) e^{ik|r-r'|}$$

(2.4)

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\(^1\) The theory presented in this section is primarily derived from *Transmission Electron Microscopy and Diffractometry of Materials* by B. Fultz and J. M. Howe and a more thorough treatment of the theory of electron diffraction and the associated techniques can be found therein [8].
where $\mathbf{k}$ is the outgoing wavevector and $\mathbf{r}$ is the sample-detector vector. The function, $f$, is a scattering length which depends on the orientation of $\mathbf{k}_0$ and $\mathbf{k}$ and is obtained by solving the Schroedinger equation for the incident electron inside the scattering potential. If the assumption is made the the incident wave is undiminished by the scattering event and is only scattered once (this is known as the Born approximation), it can be shown that the scattering length of Eq. 2.4 depends only the difference of the incident and scattered wave vector, $\Delta \mathbf{k} = \mathbf{k} - \mathbf{k}_0$, and is given by

$$f(\Delta \mathbf{k}) = -\frac{m}{2\pi \hbar^2} \int V(\mathbf{r}) e^{i \Delta \mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{r},$$

(2.5)

where $V$ is the scattering potential (for electrons, the scattering potential is the electrostatic potential, for X-rays, it’s the electron density). The integral of Eq. 2.5 is easily recognizable as the Fourier transform of the scattering potential and illustrates the fact that the scattered wave amplitude is proportional to the Fourier transform of the scattering potential. This result is the basis for the interpretation of diffraction patterns in the limit of a single scattering event per electron, known as kinematical diffraction. If the scattering potential used in Eq. 2.5 is that of a single atom, the result is what is known as the atomic form factor for electrons, $f_{el}$, which are employed when solving the diffraction pattern of an ensemble of atoms. These atomic form factors can be found in many references [9,10].

### 2.6.1 The Crystal Lattice

As a result of the scattered wave amplitude being proportional to the Fourier transform of the scattering potential, it becomes clear that diffraction is a technique which naturally lends itself to samples with a periodic nature. Crystals are periodic arrays of atoms which have translational symmetry in three dimensions; this symmetry is defined by three unit cell vectors, $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$. The crystal is invariant under
any translation
\[
R = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c},
\]
where \( n_1, n_2 \) and \( n_3 \) are integers and this translational symmetry defines a lattice known as the Bravais lattice. The physical crystal is described by placing a basis set of atom(s) at each lattice site. The repeating unit, or unit cell, is then defined by the parallelepiped formed by the three unit cell vectors. If a crystalline sample is illuminated with a plane wave the resultant scattered waves will constructively and destructively interfere with each other. The condition for this constructive interference can be given by
\[
R \cdot \Delta \mathbf{k} = 2\pi m
\]
(2.7)
where \( m \) is an integer, or alternatively
\[
e^{i(\Delta \mathbf{k} \cdot R)} = 1,
\]
(2.8)
for all lattice vectors, \( \mathbf{R} \). This condition, known as the Laue equation, is satisfied by a set of wavevectors, \( \mathbf{G} \), which define a reciprocal lattice. Similar to the lattice defining the translational symmetry of a crystal, the reciprocal lattice can be defined as all vectors
\[
\mathbf{G} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*
\]
(2.9)
where \( h, k \) and \( l \) are integers, known as the Miller indices, and \( \mathbf{a}^*, \mathbf{b}^* \) and \( \mathbf{c}^* \) are the reciprocal lattice basis vectors. These reciprocal lattice vectors can be derived from the real space lattice vectors by
\[
\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}
\]
(2.10)
with \( \mathbf{b}^* \) and \( \mathbf{c}^* \) given by the cyclic permutations of Eq. 2.10.
This condition for constructive interference, that the change in wavevector must be a vector of the reciprocal lattice, leads naturally to a geometric construction which aids in visualizing the diffraction condition. For elastic scattering, the incident and scattered wavevectors are of the same magnitude and, as such, the scattered wavevectors describe a sphere in reciprocal space. The diffraction condition is satisfied for every reciprocal lattice point which lies on this sphere, the Ewald sphere. For X-rays, which have a relatively long wavelength (e.g. for Cu Kα, $\lambda = 1.54$ Å) the Ewald sphere radius is on the order of the reciprocal lattice vector length, whereas for electrons in the 100 keV energy range, the Ewald sphere is nearly planar on the length scale of the reciprocal lattice vectors (Fig. 2–7).

**Figure 2–7:** Ewald sphere construction for X-rays (long wavelength) and electrons (short wavelength).

Diffraction is also a useful technique for studying samples consisting of many, randomly oriented crystallites, as opposed to a single crystal. For these polycrystalline samples, if the number of crystallites is large, the diffraction condition for each reciprocal lattice point can be satisfied for a single incident probe direction. In this geometry the reciprocal lattice consists of a superposition of all possible crystal orientations. This results in each reciprocal lattice point mapping out a sphere, each
with a radius of $|\mathbf{G}|$. The diffraction condition is then satisfied where the spheri-
cal reciprocal lattice intersects the Ewald sphere resulting in a diffraction pattern
consisting of rings instead of points. The benefit of this method is that all diffrac-
tion conditions are satisfied simultaneously, although all three-dimensional (vectoral)
information about the reciprocal lattice is now lost.

2.6.2 The Structure Factor

If the potential of a crystal lattice, or any other periodic potential, is used in
Eq. 2.4, it can be shown that the the scattered wave will have an amplitude

$$F(\mathbf{G}) = \sum_j f_j(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}_j},$$

(2.11)

where the sum is over all atoms in the basis and $f_j(\mathbf{G})$ is the electron atomic form
factor for the corresponding atom; this quantity, $F(\mathbf{G})$, is the structure factor. The
intensities of the reflections in a diffraction pattern are proportional to the structure
factor squared, and thus, determining the structure factor is critical to extracting
the scattering potential from the acquired diffraction data. If the structure factors
are known it is simple to perform a Fourier transform and extract the form of the
scattering potential. The difficulty in determining the structure factors lies in the fact
that they can be complex and thus have an amplitude and a phase. Since a diffraction
pattern only contains information on the value of the square of the structure factor, all
phase information is lost. This causes the determination of the actual structure factor
to be difficult and leads to what is known as the phase problem in crystallography.
Various algorithms have been developed to circumvent this limitation and extract
meaningful information though [11], in addition convergent beam electron diffraction
allows for phase information to be preserved in the diffraction pattern [12].
2.6.3 Dynamical Diffraction Effects

The preceding kinematical description of electron diffraction relied on the assumption that each electron was scattered at most one time. Due to the strongly interacting nature of electrons this assumption is not valid in many situations. The parameters of relevance when considering dynamical scattering effects are the mean free path of the incident electrons in the sample and the sample thickness. If the mean free path is on the order of the sample thickness multiple scattering can be significant resulting in the redistribution of intensity amongst the Bragg reflections. In single crystalline samples the diffraction intensity for a given reflection becomes a function of the sample thickness and displays a non-monotonic oscillatory behaviour as the sample thickness is increased [13]. This increases the difficulty in extracting structural information from the diffraction pattern although there are many sophisticated methods available which crystallographers use to either minimize or model this effect [14–17]. For polycrystalline samples this effect is lessened and results in a monotonic decrease in peak intensity as a function of sample thickness and serves to redistribute counts from low scattering angle to high scattering angle. We performed measurements on VO$_2$, results from which will be presented in Chapter 5, and 70 nm samples were used. The elastic mean free path for VO$_2$ can be estimated using the relationship

$$L = \frac{1}{n\sigma},$$

(2.12)

where $n$ is the number density and $\sigma$ is the elastic scattering cross section. Using the elastic scattering cross sections for 95 keV electrons [18] gives an elastic mean free path of approximately 50 nm. Although this indicates the presence of dynamical effects in the diffraction pattern this should lead to negligible error in the calculated peak positions and the qualitative nature of the dynamics should remain unchanged.
2.6 An introduction to the theory of electron diffraction

[13, 19]. Generally, dynamical effects can be ignored in polycrystalline samples if the thickness is less than a few hundred nanometers [20]. If a complete reconstruction of the crystal potential was to be attempted though, dynamical effects would need to be considered.

2.6.4 The Radial Pair Distribution Function

The interpretation of diffraction patterns from polycrystalline samples can be difficult due to the inability to accurately determine the relative intensities of the many, often overlapping, reflections. One technique often employed in the analysis of polycrystalline diffraction patterns is the determination of the radial pair distribution function (PDF). As was described previously, the scattering amplitudes, $\Psi$, are the Fourier transform of the scattering potential. Similarly, the Fourier transform of the diffraction intensities provide an autocorrelation of the scattering potential, or alternatively, the pair distribution function.

To calculate the radial PDF, we first need to calculate the structure function (not to be confused with the structure factor),

$$S(Q) = 1 + \frac{I(Q) - \sum c_i |f_i(Q)|^2}{|\sum f_i(Q)|^2},$$  \hspace{1cm} (2.13)

where $I$ is the properly normalized scattered intensity, $f_i$ is the atomic form factor of the $i$-th atom and $Q = 4\pi \sin \theta/\lambda$ is the scattering vector. It should be noted that the proper normalization of the scattered intensity is non-trivial and requires knowledge of the incident flux through the sample in addition to factors such as the sample geometry, and Debye-Waller effects [21]. Fortunately, this normalization does not affect changes in the PDF, which is how this technique will be used primarily in this thesis. The radial PDF, $G(r)$, can be obtained from the structure function.
2.7 Initial Results

The completed electron diffractometer in the compact geometry can be seen in Fig. 2–8; visible in the photograph are the electron source chamber, the sample chamber with attached turbo pump and the CCD camera. The pump pulses enter the chamber through the optical feedthrough in the bottom right and both the BBO crystal and focusing lens can be seen. To ensure that all components of the diffractometer were functioning as expected an initial trial experiment using a single crystal gold sample was performed. This sample was purchased from SPI Supplies, its intended use is to calibrate standard TEMs. The thickness of this sample is unknown. A sample diffraction pattern obtained from the single crystal gold sample can be seen in Fig. 2–9.

Upon excitation with an ultrashort laser pulse, electrons in a metal are excited and rapidly thermalize within approximately 500 fs [22,23]. Following this excitation, these hot electrons lose their energy to the crystal lattice through electron-phonon scattering on time scale of about a picosecond. This rapid heating of the sample results in a thermal stress which can launch coherent acoustic waves through the lattice [24] in addition to resulting in a thermal expansion of the crystal lattice. The coherent acoustic waves of interest would be propagating in a direction normal to the surface of the film with a period of \( dv \), where \( d \) is the sample thickness and

\[
G(r) = \frac{2}{\pi} \int_{Q_{\text{min}}}^{Q_{\text{max}}} Q [S(Q) - 1] \sin (Qr) dQ
\]

where \( r \) is the radial coordinate in real space [20]. The radial PDF is a useful method to interpret dynamical diffraction as it can be calculated directly from the scattered intensity and can provide a direct measure of the changes occurring to the scattering potential in real space.
2.7 Initial Results

Figure 2–8: Photograph of the ultrafast electron diffractometer in compact geometry. Shown is the electron gun chamber (left), the sample chamber (centre) and the phosphor-coupled CCD camera (right).

$v_s$ is the speed of sound in gold. In order for our measurements to be sensitive to these waves, a reciprocal lattice point with a component in the direction of the acoustic wave propagation needed to be observed. Thus, the sample was placed with the surface normal at $45^\circ$ with respect to the electron beam propagation direction; in this geometry the diffraction conditions for the (112) reflection were satisfied, as indicated in Fig. 2–9. The gold sample was then excited with a laser fluence of 3.3 mJ/cm$^2$ using 50 fs, 400 nm laser pulses, and probed with electron pulses after a variable delay. A repetition rate of 250 Hz was used in order to allow the sample to relax completely between excitation pulses. Approximately 500 electrons per pulse were used in these measurements which would result in a pulse duration of about 250 fs. The geometry of this experiment though results in a further decrease in time resolution. Since the thin film sample is placed at $45^\circ$, the electron pulse scatters from different areas of the sample at different times. To minimize this effect the electron
beam was reduced to 300 µm before the sample with an aperture, but an electron velocity of 0.43c for 55 keV electrons still resulted in an effective time resolution of ~2.1 ps.

The results of this measurement can be seen in Fig. 2–10; the radial position of the diffraction spot rapidly decreases as a result of the lattice expansion which is then followed by an oscillation about a new equilibrium position. The observed oscillation has an initial amplitude of 0.03%, corresponding to a lattice oscillation
of 1.2 mÅ. The time scale associated with this lattice expansion is 2.1 ps, although, this number should be considered as an upper limit as it is similar to our expected instrument response. A fast Fourier transform of the residual of this exponential fit exhibits a peak at 0.125 THz, or a period of 8 ps. Given the speed of sound in bulk gold of 3280 m/s [25], this oscillation is indicative of a film thickness of 26 nm.

![Figure 2–10](image)

**Figure 2–10:** Percent change in peak position relative to the electron beam focus as a function of time for the (112) reflection after being pumped with 400 nm laser pulse with a fluence of 3.3 mJ/cm². The exponential decay shown in red has time constant of 2.1 ps.

These results demonstrate the ability probe structural dynamics on the picosecond time scale. The primary limitation of operating in this geometry is, as previously mentioned, the requirement of low bunch charge in order to achieve the desired electron pulse durations. The implementation of radio-frequency compression techniques, described in Chapter 4, allows us to overcome this limitation, providing sub-500 fs time resolution with a dramatic increase in electron bunch charge.
Figure 2–11: Fast Fourier transform of the time resolved position measurements shown in Fig. 2–10 with the exponential decay subtracted. A peak can be seen at approximately 1.3 THz, which corresponds to a film thickness of 26 nm.
References


CHAPTER 3

Characterizing the evolution of ultrashort electron pulses

The goal of the pulse compression techniques discussed in the introduction is the manipulation of the electron pulse position-momentum distribution in order to create high brightness, short duration, electron pulses at the sample. The ability to accomplish this relies on our understanding of the space-charge dynamics present in these ultrashort electron pulses. Space-charge driven dynamics in femtosecond laser produced electron pulses are important in a number of applications in addition to the RF compression techniques presented in this thesis; from the pulsed relativistic electron beamlines in synchrotrons and free-electron lasers to the non-relativistic beams in dynamic transmission electron microscopy and femtosecond photoemission electron microscopy [1]. Given their importance, space-charge driven dynamics in pulsed electron beams have been actively explored, primarily through simulation and theory [2-4]. These studies have lead to a number of important insights such as the orders of magnitude on-specimen brightness advantages associated with compact electron sources for UED studies [5], the utility of spatially shaping the photocathode excitation pulse to generate well-behaved uniformly filled ellipsoidal bunches [6, 7],

43
and how the internal dynamics of space-charge dominated electron bunches result
in linear velocity-time correlations [2]. This work has been primarily guided by
simulation since the detailed characterization of non-relativistic, low bunch-charge
ultrashort electron pulses has been challenging due to the required time resolution.
Appropriate techniques exist for characterizing pulsed, relativistic electron beams
that provide the ability to measure relevant beam parameters from a single pulse [8,9],
but these techniques typically operate using electro-optic sampling that relies on
relativistic bunch-field enhancements making them unsuitable for characterizing the
relatively low charge, non-relativistic electron pulses used in UED experiments.

To date, the characterization of ultrashort electron pulses has been focused on
the determination of the electron pulse duration. The conventional approach has
been to employ streak-camera methods (discussed in Chapter 4) that use a beam
deflection system (either deflection plates or a deflector cavity) to map the temporal
information onto the spatial coordinate (i.e. in the deflection direction) at a suitable
detector [10, 11]. Deflection systems with time resolution (FWHM) approaching
100 fs have recently been demonstrated [7,12,13]. The measurements presented in
this chapter were performed using an alternative optical approach [14]. Here, cross-
correlation measurements are conducted which use the ponderomotive interaction
between a femtosecond laser pulse and the electrons in a pulse.

As a characterization tool for ultrashort electron pulses this method has a num-
ber of unique advantages. First, the time-resolution of this approach is fundamentally
determined by the laser spot size at the region where the electron and laser pulse
interact and the laser pulse duration; i.e. the time resolution is tunable based on the
laser beam properties and can readily be made below 100 fs for easily obtainable spot
sizes and pulse durations. Second, the interaction region in which the measurement
is performed is the size of the laser focus, which is much smaller than the typical interaction region in a beam deflector (deflection plates or cavity). Thus, the measurement provides information on the electron pulse at a precise point in the electron beamline, not an average over an extended interaction region. This is important in systems where the electron pulse properties vary rapidly with position like the UED system presented in this thesis. Third, the measurement operates in a pump-probe geometry similar to a UED experiment; the measurement is synchronized with the photocathode excitation pulse to within a few femtoseconds and is capable of directly determining any electron pulse arrival time jitter at the specimen position.

The measurements presented in this chapter focus on the exquisite sensitivity of the electron-laser pulse cross correlation approach to explore features of the space-charge driven dynamics beyond characterization of the electron pulse duration. The details of the electron pulse envelope dynamics were investigated by using the electron-laser cross correlation method to directly measure the spatio-temporal charge density inside femtosecond laser produced electron pulses at various stages of evolution and over a range of bunch charges. We also investigate the effects of magnetic focusing on the charge density in low aspect ratio electron pulses; i.e. the beam width is much larger than the pulse length. In addition, these measurements are compared with analytical predictions and simulations of space-charge driven dynamics in ultrashort electron pulses and find that the results are in excellent agreement. Many of the results shown in this chapter have been published in Morrison, V. R., Chatelain, R. P., Godbout, C., and Siwick, B. J. (2013). Direct optical measurements of the evolving spatio-temporal charge density in ultrashort electron pulses. Optics Express, 21(1), 21, and reproduced with permission.
3.1 Grating-Enhanced Ponderomotive Scattering

In instruments in which both the pump and the probe are laser pulses (i.e. ultrafast spectroscopy), auto-correlation and cross-correlation techniques are often used to characterize pulse lengths and determine the instrument response [15]. A similar approach, the cross-correlation of an electron pulse and a laser pulse, can be realized due to the nature of the interaction between a charged particle and an inhomogeneous, oscillating electromagnetic field, i.e. the ponderomotive interaction.

Charged particles interact with an electromagnetic field through the Lorentz force,

$$F_L = qE + v \times B,$$

where $E$ is the electric field, $B$ is the magnetic field and $v$ is the charge velocity. In order to describe the interaction between an electron and our laser pulse, we need to consider an oscillating electromagnetic field with a slowly varying pulse envelope;

$$E(r, t) = \frac{1}{2} \left( \tilde{E}(r, t)e^{i\omega t} + \tilde{E}^*(r, t)e^{-i\omega t} \right)$$

$$B(r, t) = \frac{1}{2} \left( \tilde{B}(r, t)e^{i\omega t} + \tilde{B}^*(r, t)e^{-i\omega t} \right).$$

$\tilde{E}(r, t)$ and $\tilde{B}(r, t)$ are assumed to be slowly varying envelope functions, in addition to the spatial oscillatory term, $e^{i\mathbf{k}\cdot\mathbf{r}}$. The assumption of two distinct time scales in the above fields naturally leads to describing electronic motion as the superposition of two different types of motion,

$$\mathbf{r}(t) = \mathbf{R}(t) + \mathbf{r}_o(t),$$

where $\mathbf{r}_o(t)$ is the fast, oscillatory motion of the electron and $\mathbf{R}(t)$ is the slower, drift component of the motion. On the time scale of a single oscillation the time-averaged value of the oscillatory motion, $\langle \mathbf{r}_o(t) \rangle$, is approximately zero whereas $\mathbf{R}(t)$
3.1 Grating-Enhanced Ponderomotive Scattering

is assumed to change only slightly over this time. Thus, on time scales long compared
to $1/\omega$, $\langle r(t) \rangle \simeq R(t)$. If we assume the intensity of the plane wave, $I = \frac{1}{2}c\epsilon_0|E_0|^2$, is low ($I < \sim 10^{18}$ W/cm$^2$), this will result in non-relativistic electron velocities, $v/c \ll 1$, and if the spatial variation of $\tilde{E}(r, t)$ is larger than $\lambda$, we can expand the electric field to

$$E(r(t), t) = E(R(t) + r_o(t), t) \simeq E(R(t), t) + (r_o(t) \cdot \nabla)E(R(t), t) \quad (3.4)$$

To lowest order, the equations of motion only describe the oscillatory motion of the electron;

$$m\ddot{r}_o = \frac{q}{2} \left( \tilde{E}(R, t)e^{i\omega t} + \tilde{E}^*(R, t)e^{-i\omega t} \right). \quad (3.5)$$

Under the assumption that $R$ is constant and that $\tilde{E}(R, t)$ is slowly varying in time (i.e. $\frac{d}{dt}\tilde{E}(R, t) \ll \omega \tilde{E}(R, t)$) we obtain

$$\dot{r}_o = -\frac{ie}{2m\omega} \left( \tilde{E}(R, t)e^{i\omega t} - \tilde{E}^*(R, t)e^{-i\omega t} \right)$$

$$r_o = -\frac{e}{2m\omega^2} \left( \tilde{E}(R, t)e^{i\omega t} + \tilde{E}^*(R, t)e^{-i\omega t} \right) \quad (3.6)$$

This purely sinusoidal motion is the same result one would obtain for an electron in an oscillating electric field with a constant amplitude. To determine the slower drift motion, we consider the higher order motion

$$m\ddot{R}(t) = e \left[ (r_o \cdot \nabla)E(R, t) + \dot{r}_o \times B(R, t) \right]. \quad (3.7)$$

Using Maxwell’s equations we know that $B(R, t) = i/\omega \nabla \times E(R, t)$ and inserting Eq. 3.6,

$$m\ddot{R}(t) = e \left[ -\frac{e}{4m\omega^2} \left( \tilde{E}(R, t)e^{-i\omega t} + \tilde{E}^*(R, t)e^{i\omega t} \right) \right] + \frac{e}{4m\omega^2} \left( (i\tilde{E}e^{-i\omega t} + i\tilde{E}^* e^{i\omega t}) \times \nabla \times (i\tilde{E}e^{-i\omega t} - i\tilde{E}^* e^{i\omega t}) \right). \quad (3.8)$$

(3.9)
We can discard terms which contain $2\omega$ as they will average to zero over the relevant timescales which leaves us with

$$m\ddot{\mathbf{R}}(t) = -\frac{e^2}{4m\omega^2} \left[ \mathbf{E} \cdot \nabla \mathbf{E}^* + \mathbf{E} \times \nabla \times \mathbf{E}^* + \text{c.c.} \right]. \quad (3.10)$$

The vector identity $\nabla (\mathbf{A} \cdot \mathbf{B}) = (\mathbf{A} \cdot \nabla)\mathbf{B} + (\mathbf{B} \cdot \nabla)\mathbf{A} + \mathbf{A} \times (\nabla \times \mathbf{B}) + \mathbf{B} \times (\nabla \times \mathbf{A})$ allows us to simplify this to

$$\mathbf{F}_P = -\frac{e^2}{4m\omega^2} \nabla \left| \mathbf{E}(\mathbf{R}, t) \right|^2 = -\frac{e^2\lambda^2}{8\pi^2 m\epsilon_0 c^3} \nabla I \quad (3.11)$$

This force, known as the ponderomotive force, is proportional to the intensity gradient of the field and causes charges to drift from regions of high field intensity to regions of low field intensity. Alternatively, we can define a ponderomotive potential,

$$\Phi(\mathbf{R}, t)_P = \frac{e^2}{8\pi^2 m\epsilon_0 c^3} I(\mathbf{R}, t), \quad (3.12)$$

such that the ponderomotive force is proportional to the negative gradient of the potential, $\mathbf{F}_P = -\nabla \Phi_P$. Thus, with a sufficient laser intensity gradient, electrons can be scattered from the electron pulse by the laser pulse, providing the ability to perform an electron-laser cross correlation measurement.

The ability to perform an electron-laser pulse cross correlation was first demonstrated by Hebeisen et al. [16] using a single, high intensity, laser pulse delayed with respect the electron pulse. Although these initial measurements demonstrated the feasibility of the ponderomotive scattering technique for electron pulse characterization, the pulse energies required, about 10 mJ, are larger than what is produced in most table top chirped-pulse amplification systems. This large pulse energy requirement makes performing such measurements unfeasible in many labs which attempt to employ ultrafast electron diffraction techniques. If we wish to increase the strength
of the ponderomotive interaction while maintaining a relatively low pulse energy, the gradient of the pulse envelope needs to be increased. One way this can be accomplished is by using two counter-propagating laser pulses, creating a standing wave in place of the initial single laser pulse [17]. In this scenario the intensity modulation is on the length scale of $\lambda/2$ as opposed to the pulse length, $l$, of the scattering pulse; for laser pulses with $\lambda/2 \ll l$, this results a dramatic increase in the strength of the ponderomotive interaction.

To understand the nature of the grating-enhanced ponderomotive force, we need to first consider two counter propagating electromagnetic plane waves, travelling in the $x$ direction, with the electric and magnetic fields given by

\begin{align}
    E_y &= \frac{1}{4} \tilde{E} \left( e^{i(\omega t - kr_x)} + c.c. \right) + \frac{1}{4} \tilde{E} \left( e^{i(\omega t + kr_x)} + c.c. \right) = \tilde{E} \cos \omega t \cos kr_x, \\
    B_z &= \frac{1}{4} \tilde{B} \left( e^{i(\omega t - kr_x)} + c.c. \right) - \frac{1}{4} \tilde{B} \left( e^{i(\omega t + kr_x)} + c.c. \right) = \tilde{B} \sin \omega t \sin kr_x,
\end{align}

where $\tilde{E}$ and $\tilde{B}$ are the real amplitudes of the electric and magnetic fields, polarized in the $\hat{y}$ and $\hat{z}$ directions respectively, $\omega$ is the angular frequency, and $k$ is the wave vector, $2\pi/\lambda$. The factor of $1/4$ is a result of splitting a plane wave (Eq. 3.2) into two counter propagating plane waves. These two counter propagating plane waves result in a standing wave in which the electric field is $90^\circ$ out of phase in space and time with respect to the magnetic field. Here we’ve chosen zero phase to occur at $t = 0$ and $r_x = 0$. An electron placed in these fields will undergo a quiver motion as
a result of the electric field, with the motion described by

\[ m\ddot{r}_y = eE_y = e|\vec{E}| \cos \omega t \cos kr_x \]  (3.15)

\[ \dot{r}_y = \frac{e|\vec{E}|}{\omega m} \cos kr_x \sin \omega t \]  (3.16)

This resulting electron velocity is in phase with the magnetic field and, as a result, the Lorentz force experienced by the charge does not average to zero over a single cycle;

\[ \mathbf{F}_m = e\mathbf{r} \times \mathbf{B} = e \begin{pmatrix} 0 \\ \dot{r}_y \\ 0 \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix} = \frac{\vec{E} B e^2}{\omega m} \cos kr_x \sin kr_x \sin^2 \omega t \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}. \]  (3.17)

Averaged over a single cycle of the electromagnetic field gives a spatially dependent force

\[ \mathbf{F}_P = \frac{E^2 e^2}{4\omega cm} \cos kr_x \sin kr_x \hat{x} = \frac{E^2 e^2}{4\omega cm} \sin 2kr_x \hat{x}. \]  (3.18)

This spatially dependant force is parallel to the direction of propagation of the electromagnetic wave and has a periodicity of half the wavelength of the initial fields. As with the case of a single propagating wave described previously, we can express this force as the gradient of a ponderomotive potential,

\[ \mathbf{F}_P = -\nabla U_P = \nabla \frac{e^2}{4m \omega^2} |\vec{E} \cos kr_x|^2. \]  (3.19)

We can see now the benefits gained by using this counter-propagating geometry; the intensity of the field increases from zero to its maximum value over a distance of λ/4 as opposed to w/2 in the case of a single laser pulse. As such, the gradient, and therefore the ponderomotive force, is dramatically larger in the counter-propagating
3.1 Grating-Enhanced Ponderomotive Scattering

geometry. The work of Smorenburg et al. provides a more thorough description of the interaction between a charged particle and a standing wave [18].

We can now formulate this with parameters specific to our electron diffractometer, i.e., with two counter-propagating laser pulses with Gaussian profiles in both space and time. The intensity of these two pulses is given by

\[ I(r, t) = \frac{I_0}{2} \left| \exp \left( \frac{i(-\omega t + kx) - (t - \frac{x}{c})^2}{2w_t^2} \right) + \exp \left( \frac{i(-\omega t - kx) - (t + \frac{x}{c})^2}{2w_t^2} \right) \right|^2 \exp \left( -\frac{y^2 + z^2}{2w_f^2} \right) \]

(3.20)

(3.21)

where \( I_0 \) is the peak pulse intensity (before the pulse is split), \( w_t \) is the temporal laser pulse length in seconds and \( w_f \) is the transverse focus size in meters. Fig. 3–1 shows the evolution of this intensity profile for various times as a function of \( x \) using 35 fs laser pulses. No standing wave can be see when the pulses are separated spatially \((t = -50 \text{ fs})\); when the pulses are completely overlapped, the intensity modulation is easily seen. We can now look at the behaviour of the ponderomotive force for the intensity given in Eq. 3.21.

The gradient of this intensity profile is predominately in the \( x \) direction, parallel to the propagation axis, since \( \lambda/2 \ll w_f \), for a wavelength of 800 nm and a transverse focus spot size of 15\( \mu \)m FWHM. Thus, we will only consider the ponderomotive force in this direction:

\[
F_x = -\frac{I_0 e^2 \lambda^2}{16\pi^2 m \epsilon_0 c^3} \exp \left( \frac{-y^2 + z^2}{2w_f^2} \right) \frac{\partial}{\partial x} \left[ \exp \left( -\frac{(t - \frac{x}{c})^2}{2w_t^2} \right) \right]
+ \exp \left( -\frac{(t + \frac{x}{c})^2}{2w_t^2} \right) + \exp \left( -\frac{t^2 + \frac{x}{c}}{2w_t^2} \right) \frac{\partial^2}{\partial x^2} \exp \left( \frac{-t^2 + \frac{x^2}{c}}{2w_t^2} \right) \frac{\partial}{\partial x} \left[ 2 \cos (2kx) \right].
\]

(3.22)

The first two terms in the derivative are the pulse envelopes of the two counter-propagating pulses and, as such, will be neglected as their derivative is much smaller.
than the last term, the standing wave term. Differentiating we obtain

\[
F_x(x, y, z, t) \approx \frac{I_0 e^2 \lambda^2}{16 \pi^2 m \varepsilon_0 c^3} \exp \left( -\frac{y^2 + z^2}{2 w_j^2} \right) \left[ \frac{8 \pi}{\lambda} \exp \left( -\frac{t^2 + \frac{y}{c}}{2 w_t^2} \right) \right. \\
\left. \sin (2kx) \right] \\
- \frac{4x}{w_t^2 c^2} \exp \left( -\frac{t^2 + \frac{z}{c}}{2 w_t^2} \right) \cos 2kx .
\]

(3.23)

Here we are left with a force which has a spatial envelope defined by the laser focus size and temporal pulse length, which oscillates with a spatial frequency of 2k.

**Figure 3-1:** Field intensity of two counter-propagating, 35 fs, laser pulses. At \( t = -50 \text{ fs} \) the pulses overlap minimally and no standing wave is present. At \( t = -25 \text{ fs} \) the pulses are partially overlapped and a relatively small standing wave can be seen. At \( t = 0 \text{ fs} \) the pulses are completely overlapped and the complete standing wave can be seen.
3.2 Experimental Methods

In terms of the intensity profile shown in Fig. 3–1, this force is pushing the electrons to the nearest node on the standing wave. As a result of this force, electrons present at the laser foci when both pulses arrive will either be deflected along the positive or negative $x$ direction, or will feel no force at all. This results in electrons being deflected out of the main electron beam in proportion to the electron density in the laser pulse overlap region.

The time resolution offered by an electron-laser pulse cross correlation measurement depends on the laser pulse length, the transverse width of the laser foci in the direction of the electron pulse propagation as well as the electron pulse velocity. The instrument response can be given by

$$
\tau_P^2 = \tau_l^2 + \left( \frac{w_f}{v_e} \right)^2,
$$

where $\tau_l$ is the laser pulse duration, $w_f$ is the size of the laser focus in the electron pulse propagation direction, and $v_e$ is the electron pulse velocity. For example, our 35 fs laser pulses focused to 80 µm and cross correlated with 75 kV electron pulses would give an instrument response time of 546 fs. The electron velocity here was calculated from

$$
v_e = \beta c = \sqrt{1 - \frac{m_e^2}{(T_e + m_e)^2 c^2}},
$$

where $T_e$ is the kinetic energy (75 keV) and the $m_e = 0.511$ MeV is the mass of the electron.

3.2 Experimental Methods

The electron optical configuration used in this experimental study of ultrashort electron pulse dynamics is shown in Fig. 3–2 along with the laser beam geometry used for the ponderomotive measurement. As described in Chapter 2, the electron source consists of a DC photoelectron accelerator and a single magnetic solenoid
lens was used to affect the transverse properties of the electron pulses. In these experiments the photocathode electrode is held at voltages ranging from $-50$ kV to $-95$ kV. Two motorized linear stages were used while performing ponderomotive measurements; the first to delay the arrival of both laser pulses relative to the electron pulse, and the second to delay one laser pulse with respect to the other. After the initial optical delay, which defines the pump-probe delay, $t$, the laser pulses are sent through a 50/50 beam splitter in order to create the two laser pulses required. One of these laser pulses is then sent through the second optical delay (referred to as the ponderomotive delay) which defines the laser-laser pulse delay, $\tau$. The appropriate ponderomotive delay is determined prior to the measurements and remains constant throughout, with $\tau = 0$ being defined where the spatial overlap of the two laser pulses intersects the trajectory of the electron pulses. A three mirror configuration was used for the second optical delay in order to reduce the pulse overlap errors as a result of laser pointing jitter. By having an even number of mirrors in both arms of the setup after the beam splitter, horizontal beam pointing errors result in both foci moving the same direction. If, in contrast, there was an odd number of mirrors in one arm, pointing errors would result in the foci moving in opposite direction, increasing the measurement noise.

In order to perform an electron-laser pulse cross correlation measurement the temporal and spatial overlap of all three pulses is required. The nature of the ponderomotive interaction, i.e., that near perfect alignment of all three pulses is required to produce an observable signal that only exists during the short interaction of all three pulses, means that the alignment of such a configuration is non-trivial. The algorithm used to achieve this will be presented.
In order obtain spatial overlap a pinhole placed at $45^\circ$ with respect to both the laser and electron propagation directions was required. As thickness is an issue for an aperture that will be used for two perpendicular directions, aluminum foil, which is approximately 100 $\mu$m thick, was used as the medium in which the aperture was made. This foil was placed as flat as possible on a one inch square metal frame which was mounted at $45^\circ$ on the linear stages in the sample chamber. Initially, the arm of the optical portion of the setup without a delay stage was aligned. The focusing lens, with a focal length of 75 cm, was positioned so that the focus was approximately intersecting the electron beam. A pinhole was made in the foil using the laser and then, beside the pinhole, a window was cut into the foil with the laser
that was approximately 1.5 mm x 1.5 mm. In vacuum, this pinhole was then centred on the electron beam. Now that the position of the electron beam was defined, the transverse size of the laser beam was determined by scanning the straight edge of the window across the laser. The transmitted light was detected using a power meter and this produced an error function as a function of stage position:

\[
\text{erf}(x) = \frac{2A}{\sqrt{\pi}} \int_{0}^{x} e^{-\frac{t-x_c}{w}} dt,
\]

where \( w \) is the width, \( A \) is the amplitude and \( x_c \) is the centre. The FWHM of the laser focus, where FWHM = \( 2\sqrt{\ln 2}w \), can then be extracted from the fit as shown in Fig. 3–3. This method was used in all subsequent beam size measurements presented in this thesis. Using this method, the position of the focusing lens was iterated until the laser focus was placed in the centre of the electron beam. The second arm of the optical configuration, which contains the optical delay stage, was then aligned to the pinhole. A similar procedure was used to place this second focus at the centre of the laser focus was placed in the centre of the electron beam. The second arm of the optical configuration, which contains the optical delay stage, was then aligned to the pinhole. A similar procedure was used to place this second focus at the centre of the

Figure 3–3: Error function obtained from scanning a straight edge past an 82 µm laser focus. The data is shown in red and the fit is shown in blue.
electron beam as well, with the exception being that instead of iterating the position of the focusing lens, the focus was moved in the $x$-direction using the optical delay line. This also provided rough temporal overlap of the two laser pulses due to the fact that the distance from the lens to both foci is the same.

Once spatial overlap between the two laser foci and the electron beam was achieved, the temporal overlap of all three pulses was required. Scanning both delay stages until ponderomotive scattering was observed was unfeasible due to the fact that the electron pulse path length was difficult to measure with much accuracy and small step sizes were required for the ponderomotive delay as the two laser pulses need to be overlapped in the small, $\sim 200 \, \mu\text{m}$, width of the electron beam after the pinhole. The approximate arrival time of both laser pulses with respect to the electron pulse can be determined to within a few picoseconds though by observing the distortion of the electron beam caused by a laser induced plasma on a copper TEM grid. This method of determining $t = 0$ has been used previously in UED experiments [5,19,20], and a similar effect, termed 'photoionization-induced lensing', has been used for UED measurements in the gas phase [10]. Fig. 3–4 illustrates the effect one of the ponderomotive laser pulses has on a copper TEM grid placed at the intersection of the electron and laser pulses. These images are created by illuminating the TEM grid with an unfocused electron beam, this creates a shadow of the grid on the detector. Before $t = 0$ no effect can be seen; at positive pump-probe delays the shadow of a small plasma cloud can be seen. $\tau$ can be set so that the onset of the plasma from both laser pulses is simultaneous. There is some error associated with the relative position of the copper grid and the alignment aperture due to the fact that the foil isn’t perfectly flat and the frame isn’t at exactly $45^\circ$ so it is still
Figure 3–4: Images of the shadow created by the pump induced plasma on a copper TEM grid with a 125 µm pitch. At negative pump-probe delays no plasma can be seen. Approximately 500 fs after the arrival of the pump pulse a small shadow can be seen while after 4 ps the shadow is much larger.

necessary to scan both \( \tau \) and \( t \) in order to search for an observable cross correlation signal.

After obtaining approximate spatial and temporal overlap of all three pulses using the aforementioned methods, ponderomotive scattered measurements could be attempted. Initially the measurements were attempted with the alignment aperture in place. This resulted in an excess of scattered laser light which saturated much of the CCD in addition to causing electron gun instabilities, most likely a result of ions being scattered from the edge of the aperture towards the electron gun due to the high field at the laser focus. To overcome these issues the aperture was moved towards the electron gun so that the laser pulses went through the large window and therefore had no interaction with the foil. The geometry of this configuration is shown in Fig. 3–5. In this geometry, the alignment aperture strips away all electrons outside of a \( \sim100 \) µm radius leaving only the centre core of the electron pulse which propagates towards the laser intersection. Thus, the cross correlation measurements performed in this geometry are only sensitive the local charge density in the centre of the electron pulses.
3.2 Experimental Methods

Figure 3–5: Geometry of the electron/laser interaction. A pinhole at 45° selects a small core from the center of the electron pulse for which the time-dependent charge density is determined by ponderomotive scattering as described in the text. Image data obtained with a) no overlap, b) partial overlap and c) complete overlap between the electron pulse and the laser pulses is shown in the three rightmost panels. The intensity of the scattered signal outside the main (unscattered) spot provides a relative measure of the local charge density.

In order to determine if the alignment procedures described provided the temporal and spatial overlap necessary for the cross-correlation measurements, a quantitative signal which represents the amount of ponderomotive scattering needs to be calculated. Using methods described by Hebeisen et al. [21], we define the signal to be

\[ S(t) = \int |X| D(X, Y, t) dX dY, \]  

(3.27)
where $X$ and $Y$ are the horizontal and vertical coordinates in the image relative to the electron beam centre and $D(X,Y,t)$ is the electron density at that coordinate (pixel) for a given time delay, $t$. Here, electrons which are farther from the centre of the pulse contribute more to the signal, thus, electrons which are scattered away from the centre of the pulse increase the signal. As the scattering potential is constant throughout the measurements the signal is linearly proportional to the number of electrons which experience this potential, i.e., linearly proportional to the electron density in the pulse overlap region.

The results of an initial scan of both $t$ and $\tau$ is shown in Fig. 3–6. The increasing background is a result of a slight misalignment in the ponderomotive optical delay line that resulted in scattered laser light being improperly subtracted from the images and varied as a function of the optical delay. As this delay is fixed in all of the cross-correlation measurements that were performed after the appropriate ponderomotive delay was determined, this misalignment had no effect on the results. As can be seen in figure Fig. 3–6, the location of the cross-correlation signal was within 2 ps in both $t$ and $\tau$ of where the search was centred.

After the temporal overlap of the two laser pulses has been determined, cross-correlation measurements can be performed. The electrons scattered as a result of the ponderomotive potential can be seen in Fig. 3–7; with no pump pulses the electron spot is circular, while with the appropriate spatial and temporal overlap of the laser pulses, electrons are scattered away from the centre of the electron beam. By subtracting the $t = 0$ image from a $t = -2$ ps image (Fig. 3–8) the resulting decrease of electrons in the beam centre and the electrons scattered in the $x$ direction can be seen.
3.2 Experimental Methods

Figure 3–6: Ponderomotive signal as a function of both pump-probe delay and ponderomotive delay while attempting to find the temporal overlap of both laser pulses and the electron pulse. Blue represents no scattering and red represents maximum scattering.

Figure 3–7: Images of the electron beam at various values of $t$. The logarithm of the pixel intensity is plotted in order to more clearly show the scattered electrons.
Figure 3–8: Image of the difference between pump on and pump off in a ponderomotive scattering measurement. Black represents a negative change and white represents a positive change. Electrons are scattered from the centre of the electron pulse in the direction of the laser propagation. The vertical integral of the image is shown below.
3.3 Simulation

We compare the cross-correlation measurements made with simulations of the diffractometer beam line, performed under various conditions. These simulations were performed using the General Particle Tracer (GPT) [22] software package which simulates charged particle dynamics in electromagnetic fields in three dimensions. In order to perform simulations which accurately reflect the electron pulse evolution of our electron diffractometer, field maps of both our electron gun and our magnetic lenses were calculated by Robert Chatelain using the Poisson Superfish software package and imported into GPT; the electron gun field map can be seen in Fig. 3–9.

![Scale diagram of the high voltage electron gun with equipotential lines shown in red.](image)

The simulation geometry consisted solely of the electron gun and a magnetic lens placed 7 cm away, consistent with the diffractometer. The relevant properties of the electron pulses were then initialized based on the conditions used in the electron-laser cross correlation measurements. The number of electrons, \( N_e \), and initial dimensions
of the electron pulse (FWHM radius and pulse length) were determined by the UV pulse properties. In these simulations, minor variations in the UV pulse length were negligible as the pulses were very short ($\tau = \sim 50$ fs), i.e. the photo-emitted electrons are effectively stationary over the 50 fs duration of the UV pulse ($v_e \tau \ll r$). Parameters specific to the diffractometer are the accelerating voltage, $V$, and the magnetic lens current, $I$. After these parameters are initialized, GPT calculates the trajectory of the electrons and the time at which each electron crosses the measurement position is output. In order to reflect the cross-correlation accurately, all electrons with a position outside the radius of the pinhole are discarded at the end of the simulation. Finally, all of the electrons are binned corresponding to their arrival time at the measurement position and this distribution is then convolved with a gaussian function with the same width as the cross-correlation instrument response. Here the temporal duration of the laser pulses are neglected as the instrument response is dominated by the laser focus size. As only a small number of macro-particles would exist within the pinhole radius, each simulation would be repeated many times in order to increase the signal to noise and produce a smooth pulse envelope.

Initial simulations were performed using a fast, mesh-based routine which rapidly approximated the space charge fields within the pulse. This routine within GPT solves Poisson’s equation in 3D in the electron pulse rest frame, and scales with $O(N)$. The results of simulations using this space-charge algorithm can be seen in Fig. 3–10. Although these initial results seemed to reproduce the pulse lengths of our electron pulses reasonably well, features were present in the simulations which were not observed in the measurements. Sharp increases in the electron density at the leading and trailing edges of the pulses were observed depending on the focusing conditions and bunch charge used; this can be seen in Fig. 3–10. In an effort to
explain these features the space-charge model was changed from the mesh routine to a routine that models the relativistic point-to-point interactions of all particles in the simulation and scales as $\mathcal{O}(N^2)$. This resulted in a large increase in the computation time for the simulations and, as such, the simulations were performed using a smaller number of macro-particles, each with a charge, $Q = \frac{N}{N_m} q$, where $N_m$ is the number of macro-particles used. By using this new space-charge routine, the aforementioned artifacts were no longer present in the results.

![Space-charge artifacts](image)

**Figure 3–10:** Simulation results using 65 kV electron bunches, with varying bunch charge and a mesh-based 3D space-charge model. The artifacts on the leading edges of the pulses, which result from the failure of this model, are indicated in the figure.

Finally, the effect of macro-particle number on pulse duration was checked. Simulations were performed using electron bunches with 33 000 electrons, a 55 kV accelerating voltage and various values of $N_m$. The simulations were repeated so
that the total number of macro-particles simulated was the same for each value of $N_m$; the results can be seen in 3–1.

<table>
<thead>
<tr>
<th>$N_m$</th>
<th>Pulse Duration (ps)</th>
<th>Shots</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>5.31</td>
<td>3000</td>
</tr>
<tr>
<td>500</td>
<td>5.24</td>
<td>1500</td>
</tr>
<tr>
<td>1000</td>
<td>5.21</td>
<td>750</td>
</tr>
<tr>
<td>2500</td>
<td>5.42</td>
<td>300</td>
</tr>
<tr>
<td>5000</td>
<td>5.35</td>
<td>150</td>
</tr>
</tbody>
</table>

For all values of $N_m$, the corresponding pulse durations were within 4% of each other and no trend in pulse duration was noticed for increasing $N_m$. As there was no discernible benefit to increasing the number of macro-particles above this point, all simulations presented hereafter used 5000 macro-particles with the exception of bunches with less than 5000 electrons; here the number of macro-particles was equivalent to the number of electrons.

3.4 Results

The initial motivation for performing these cross-correlation measurements was to characterize the electron diffractometer in order to provide an accurate measure of the temporal instrument response. A full characterization of the electron diffractometer in the RF geometry will be presented in the next chapter. The cross-correlation geometry employed here though allows us to access more information; the small laser focus and short optical pulse length allow us to probe the local electron charge density within the electron pulses. In addition, by changing the accelerating voltage of the electron gun we effectively change the amount of time the pulse is allowed to propagate. This provides the ability to monitor the evolution
of the internal charge density of the electron pulses as a function of time. Fig. 3–11 shows the results of measurements performed on pulses containing $7.5\pm0.2\times10^4$ electrons ($N_e = 7.5 \pm 0.2\times10^4$) with energies, $E$, of 55 kV, 65 kV and 75 kV with a photocathode to measurement distance, $d$, of 26.8 cm, as well as the results of the corresponding simulations. The propagation times are 2.15 ns, 2.00 ns and 1.89 ns for the 55 kV, 65 kV and 75 kV accelerating voltages, respectively, and the increasing pulse length with increasing propagation time can be seen. The results of a cross-correlation measurement and GPT simulation of a 2300 electron pulse at 65 kV is shown as well and is a good representation of the impulse response of these cross-correlation measurements. These results clearly demonstrate that ultrashort electron pulses evolve to a relatively uniform charge density along the axis of propagation, in addition to broadening with time, and they are in excellent agreement with the GPT simulations performed. Fig. 3–12 shows the results of a simulation
in which no aperture was placed before the measurement position; here the flat top behaviour is no longer present and the shape of the entire pulse can be seen. This tendency towards a uniform charge density was observed in earlier simulations [2], and was predicted to be a robust feature of ultrashort electron pulses.

Figure 3–12: Simulation results (dashed line) from 65 kV electron pulses with $7.7 \times 10^4$ electrons. No aperture was used in the simulation and the difference in pulse shape from the cross-correlation measurement (circles) is clear.

An analytical model proposed by Reed [4] predicted similar behaviour, with a uniform charge density developing as the electron pulses propagate. This model predicts the behaviour of low-aspect ratio electron pulses, with the aspect ratio, $\alpha$, being the ratio of the spatial length of a pulse to its transverse diameter. It is a one-dimensional model which is solved analytically in Lagrangian coordinates. Although a complete description of this model is beyond the scope of this thesis, one of the significant results is that initially low aspect ratio pulses would develop a uniform charge density on time scales long compared to a characteristic time,

$$\tau \approx \sqrt{\frac{2mc_0}{e\rho_0(l)}},$$  \hspace{1cm} (3.28)
where \( l \) is the longitudinal coordinate at which the pulse charge density drops to 1/e of its maximum value and \( \rho_0(l) \) is the initial charge density at this point (i.e. all electrons within \( \pm l \) would have a characteristic time less than \( \tau \)). This can be interpreted as the high density regions of the electron pulses develop this asymptotic charge density relatively quickly, whereas the leading and trailing edges (i.e. low density regions) evolve at a much slower rate. For times \( t \gg \tau \), the pulses evolve towards a charge density,

\[
|\rho(t)| \approx \frac{2m\epsilon_0}{e\tau^2},
\]

which is independent of the initial charge density. Reed also addresses the two dimensional behaviour of ultrashort electron pulses which results in two characteristic time scales; one for the longitudinal expansion and one for the transverse expansion. These two time scales are coupled with low aspect ratio pulses being dominated by longitudinal dynamics and vice versa. Due to the one-dimensional nature of this model and the fact that we can’t extract absolute charge density from the cross-correlation measurements, we can’t quantitively compare our results with this model. We can, however, qualitatively compare our measurements if we minimize 2D effects and ensure that the pulse propagation time is large compared to the characteristic time. In order to minimize 2D effects and ensure low aspect ratio pulses the transverse electron beam size was constrained to be 2 mm at the measurement position. In order to ensure \( t \gg \tau \), a longer electron beam line (described in Ch. 4) was used with \( d = 80.3 \) cm. Fig. 3–13 shows both the measurement and simulation results for pulses with \( 7.5 \times 10^4 \) electrons per pulse accelerated to 75 kV. The large amount of noise in these measurements is primarily a result of a tighter laser focus (~15 \( \mu m \)) used in this extended geometry; since only a relatively small number of electrons are present in this focus the ponderomotive scattering signal is much weaker.
3.4 Results

Cross-correlation measurements were performed under these conditions with various energies while the on-axis charge density of the pulses and the propagation time was extracted from GPT simulations that are in quantitative agreement with the measurements. Table 3–2 shows the results of these measurements and simulations and it can be seen that, qualitatively, they support Eq. 3.29; although the charge density decreases as the pulses propagate, $|\rho| t^2$ remains constant. This trend was found to continue when the energy was held constant and the charge was varied. A four-fold increase in bunch charge resulted in only a slight increase (<10%) in

![Figure 3–13: Cross-correlation(circles) and simulation(dashed line) results for pulses with $7.5 \times 10^4$ electrons accelerated to 75 kV.](image)

| E(kV) | $N_e$ | $t$(ns) | $\rho$(electrons/mm$^3$) | $|\rho| t^2$ (s$^2$/m$^3$) |
|-------|-------|--------|---------------------------|-----------------------------|
| 95    | 75000 | 5.04   | 1.32±0.02x10$^4$         | 3.36±0.05 x 10$^{-4}$      |
| 85    | 75000 | 5.26   | 1.20±0.02x10$^4$         | 3.32±0.05 x 10$^{-4}$      |
| 75    | 75000 | 5.53   | 1.059±0.017x10$^4$       | 3.24±0.05 x 10$^{-4}$      |
| 75    | 37500 | 5.53   | 1.070±0.014x10$^4$       | 3.27±0.04 x 10$^{-4}$      |
| 75    | 150000| 5.53   | 1.134±0.008x10$^4$       | 3.49±0.03 x 10$^{-4}$      |
the local on-axis charge density at the interaction region. This demonstrates that for propagation times, \( t \ll \tau \), an increase in bunch charge simply translates into a proportional increase in the electron pulse duration since the local charge density tends towards a constant in this limit (Eq. 3.29) as predicted in [4].

Measurements and simulations were also performed in order to study the effect of magnetic focusing on the charge density distribution within the pulses. Focusing conditions were chosen which resulted in collimated to slightly divergent electron beams; this was done in order to maintain a low aspect ratio as well as to ensure that the pinhole selected a portion of the pulse representative of the local charge density. Figure Fig. 3–15 shows the results of cross-correlation measurements and GPT simulations performed on pulses with various bunch charges using a focusing current approximately 60% greater than the measurements shown in Fig. 3–11. The impulse response of the measurement can be seen in the short Gaussian traces from low bunch charge pulses which, in these measurements, is approximately 500 fs. The expected increase in pulse length with increasing bunch charge is apparent here, although the key feature to note is the increasing local charge density towards the leading edge of the pulses (positive delay) as a result of the increased focusing power. In order to provide a more complete picture of this effect, the charge density distribution of an entire pulse as a function of the radial distance from the pulse propagation axis, \( R \), and the longitudinal position, \( Z \), is compared in Fig. 3–14 in both a focused and an unfocused state. Here the redistribution of the charge density caused by the magnetic lens is apparent; the focusing causes an increase in the local charge density towards the leading edge of the pulse. This can be seen in the region of the pulse near \( R = 0 \). The portion of the pulse on which the cross correlation
measurements were performed is the section beneath the white dashed line and there is excellent agreement between the simulations and the measurements.

**Figure 3–14:** Simulations comparing the charge density distribution (increasing from blue to red) of a 37500 electron pulse without (a) and with (b) focusing. The increasing charge density towards the leading edge of the focused pulse can be seen near \( R = 0 \). The white dotted line demonstrates what portion of the pulse interacted with cross correlation measurements. Note the difference in the transverse size of the two pulses.
3.5 Discussion

Electron-laser cross-correlation measurements, mediated by the ponderomotive interaction, have been shown here to provide the ability to prove the spatio-temporal charge density distribution of non-relativistic ultrashort electron pulses with excellent sensitivity. Using this technique, electron pulse propagation dynamics were studied and compared with analytical and numerical models. The results show that the pulses develop a relatively uniform charge density as they propagate and are in excellent agreement with predictions. The effect of focusing on the charge density distribution of ultrashort electron pulses was also studied and simulations of the focusing induced charge density redistribution were presented. These results provide valuable insight into evolution of ultrashort electron pulses which could potentially be used to improve electron pulse compression techniques which depend sensitively
on the details of the electron charge density distribution. In addition, with only slight modifications to the techniques presented here, a measurement of the complete three dimensional charge density distribution of ultrashort electron pulses would be possible. This would require the ability to either control the transverse position of the electron bunches, or to translate the laser focus intersection in the plane parallel to the electron propagation direction. The optical alignment of this technique needs to be quite precise and, as such, translating the optics without causing any misalignment would be quite difficult. Scanning the the electron pulse in the transverse plane would be much easier to accomplish with the appropriate electron optics as long as the translation results in no distortion of the pulse shape.
References


CHAPTER 4

Radio-Frequency Electron Pulse Compression

Following the initial successes of UED in probing structural dynamics on ultrafast time scales, efforts were made to increase both the brightness and temporal resolution. The subsequent advancements in the field involved reducing space-charge effects, rather than manipulating them, and short source to sample distances and low bunch charges allowed for sub-500 fs time resolution [1,2]. However, these techniques offered no means to produce the high bunch charge pulses desired while maintaining sub-picosecond time resolution. The work presented in this chapter describes our efforts to take advantage of the linear position-momentum distribution which develops in propagating electron pulses and temporally focus them using a radio frequency cavity [3,4]. In order to fully describe the methods used to compress ultrashort electron pulses, a brief description of some electron pulse figures of merit will be discussed first. The measurements presented in this chapter were published in Chatelain, R. P., Morrison, V. R., Godbout, C., and Siwick, B. J. (2012), Ultrafast electron diffraction with radio-frequency compressed electron pulses, Applied Physics Letters, 101(8), 081901, in which I was a joint first author with Robert Chatelain.
My contribution was designing the cross-correlation measurement and making characterization measurements. All simulations presented in this chapter are courtesy of Robert Chatelain.

4.1 Electron Beam Properties

The performance of an electron beam, with regards its use in UED, can be evaluated using certain figures of merit, primarily emittance, brightness, and pulse duration. The emittance of an electron beam, which affects our ability to manipulate the beam and produce high quality diffraction pattern, is a parameter which depends on the beam’s width and divergence. This relates closely to the concept of the volume occupied by the pulse in the six-dimensional phase space of position \( \mathbf{r} \) and momentum \( \mathbf{p} \). Liouville’s theorem states that the volume of a phase-space distribution of non-interacting particles which experience no external forces will remain constant. In the physics of charged particle beams, the transverse normalized emittance \([3]\),

\[
\epsilon_x = \frac{1}{mc} \sqrt{\langle x^2 \rangle \langle p_x^2 \rangle - \langle xp_x \rangle^2},
\]

where \( x \) is the transverse position, \( p_x \) is the transverse momentum, \( m \) is the electron mass and \( c \) is the speed of light, is a quantity related to the phase space volume which is used as a measure of beam quality. The emittance of a beam is a conserved quantity in the absence of nonlinear forces. The only pulse shapes that will conserve emittance during propagation are uniformly filled ellipsoids, i.e., the internal self-fields of a uniformly filled ellipsoid are linear with respect to position \([5]\). Thus, these pulses will change size and shape as they propagate but remain ellipsoidal with linear self-fields. Standard electron optics (e.g., the solenoidal magnetic lenses used in our diffractometer) possess linear fields and also conserve emittance in the absence of aberrations. If one assumes that the position and momentum of the initial
electron distribution is uncorrelated [6], then the emittance at the cathode is given by

\[ \epsilon_x = \sigma_x \sigma_{px}, \]  

(4.2)

with \( \sigma_x \equiv \sqrt{\langle x^2 \rangle} \) and \( \sigma_{px} \equiv \sqrt{\frac{p^2}{mc}} \). Thus, in order to reduce the emittance we can reduce the size of the initial distribution and attempt to reduce the size of the initial momentum distribution.

For our diffractometer, the size of the initial position distribution is determined by the laser spot size on the cathode, typically about 100 \( \mu m \). In contrast, there are various contributions to the initial momentum distribution in our diffractometer; the thermal energy of the electrons \( (k_B T \approx 25 \text{ meV}) \), the bandwidth of the work function of copper \( (\approx 100 \text{ meV [7, 8]}) \) and the bandwidth and wavelength mismatch of our UV pulses with respect to the work function. A bandwidth of 10 nm, or wavelength mismatch of a similar amount would give an additional momentum distribution of \( \sim 100 \text{ meV} - 200 \text{ meV} \). For our electron gun, these contributions to the momentum distribution are generally not under our control although work is currently being performed using ultracold plasma sources to reduce the thermal emittance of the photoelectron source [9, 10].

The transverse normalized emittance relates to a quantity more directly relevant to the ability of an electron beam to produce a diffraction pattern, the transverse coherence length, \( L_c \). In order to produce a resolvable diffraction pattern, the coherence length must be larger than the distance between the repeating units in the crystal; if the coherence length is reduced to the length of the unit cell, the diffraction features will overlap and no longer be resolvable. The transverse coherence at a beam waist is given by [3]

\[ L_c = \frac{\hbar \sigma_x}{mc \epsilon_x}. \]  

(4.3)
4.1 Electron Beam Properties

For pulsed photo-emission from metal photocathodes, the initial emittances are typically \( \epsilon_{i,x} = 8 \times 10^{-4} \sigma_x \) [3]. Thus at a beam waist of 500 \( \mu \)m, and given initial transverse electron distribution size of \( \sim 100 \ \mu \)m, we can expect a transverse coherence length of \( \sim 2.5 \) nm. This quantity clearly varies depending on the parameters of the measurement being made, but given a unit cell length of less than 1 nm (such as the longest unit cell vector for monoclinic VO\(_2\) of 5.7 Å, discussed in Chapter 5), the coherence length of our electron beam is sufficient.

Eq. 4.1 indicates that if the transverse size of the electron pulses is reduced, such as with an aperture, then there will be a corresponding decrease in emittance. This is true, but it comes at the cost of a reduced number of scatterers. Any reduction in emittance is irrelevant if there aren’t sufficient electrons scattered to produce a well defined diffraction pattern. A more useful metric would be the beam current for a given emittance, or the brightness of the beam. The brightness of an electron pulse with an ellipsoidal distribution is given by

\[
B = \frac{2I}{\pi^2 \epsilon_x^2},
\]

for an electron beam current, \( I \) [11]. Ideally, we want to be able to increase our beam brightness without reducing our emittance.

Finally, the pulse duration of our electron pulses must be sufficiently short if we are to be able to resolve sub-ps structural dynamics. Similar to the emittance described above, we can increase our pulse duration at the expense of lowering the number of electrons in our pulse. The goal of the pulse compression techniques, described in the next section, is to increase the brightness of our electron pulses while maintaining a low pulse duration and beam emittance.
4.2 Radio-Frequency Pulse Compression

The concept of electron pulse compression using a time dependent electric field is one that results from the observation that electron pulses develop a linear position-momentum correlation as a result of space-charge expansion. The simulation results from Siwick et al. [4], shown in Fig. 1–2, illustrate this fact. At the photo-cathode the position and velocity of the electrons are uncorrelated but rapidly develop a linear relationship as the pulse propagates, i.e., fast electrons are at the front of the pulse and the slow electrons are at the back.

For the previously described uniform ellipsoidal electron bunches, which can be generated using a ‘half-circle’ laser intensity distribution at the cathode, this linear correlation develops rapidly and the transverse emittance is conserved throughout the evolution of the pulses [5]. This represents an ideal scenario though and creating a uniform ellipsoidal distribution at the cathode can be challenging. Fortunately, the development of both a uniform ellipsoidal pulse shape and a linear position-momentum correlation are robust features of ultrashort electron pulses. Non-ellipsoidal pulses, generated from Gaussian and flat-top cathode illumination conditions for example, exhibit an increase in emittance over the first few mm of propagation but still develop the desired linear correlation [5]. In addition, the rate at which this linear correlation is achieved increases with the initial charge density, as was discussed in Chapter 3 [12]. The ‘half-circle’ distribution can by approximated reasonably well by a truncated Gaussian distribution, which is easy to achieve experimentally and offers electron pulse characteristics sufficient for radio-frequency pulse compression [3]

Similar to the CPA optical pulse amplification method, the longitudinal properties of the beam can be altered by manipulating this robust linear relationship which
develops in electron pulses. More specifically, if the position-momentum distribution of the pulses can be reversed, resulting in the fast electrons at the back and the slow electrons at the front, the electron pulse will compress ballistically as it propagates towards the sample. One method by which this can be accomplished is to expose the pulses to a time-dependent electric field; RF resonant cavities provide this ability.

The simplest RF cavity is one with a ‘pillbox’ design; a cylindrical shape with flat conducting faces normal to the electron beam axis. Analytical solutions for the electric and magnetic fields of such a cavity can be found in many textbooks on electrodynamics, and will not be described in detail in this thesis. The solution to Maxwell’s equation for such a cavity results in modes with oscillating electric fields in the longitudinal direction, resulting in the the longitudinal magnetic field being zero everywhere in the cavity. These are the transverse magnetic (TM) modes, described be three indices, $m, n$ and $p$, which indicate the azimuthal, radial and longitudinal periodicity of the mode. The lowest mode, TM$_{010}$, has no azimuthal and longitudinal periodicity and one node in the radial direction at the cavity wall. This mode offers purely longitudinal electric fields and is commonly used in RF cavities. Driving the cavity results in an electric field given by

$$E(r = 0, t) = E_0 \cos(\omega t + \phi) \hat{z}. \quad (4.5)$$

where $E_0$ is the electric field amplitude, $\omega$ is the angular frequency of the oscillating field and $\phi$ is a phase offset. In order for such a field to be used to in electron pulse compression, the resonant period must be long with respect to the electron pulse length so that the field is approximately linear in time. Fig. 4–1 illustrates the process by which such a cavity can compress an electron pulse. First, the electron pulse
is short and the electrons uncorrelated. After acceleration and a sufficient propagation time, the linear position-momentum correlation has developed. As the pulse enters the cavity, the electric field accelerates the leading electrons in the negative $z$ direction. As the pulse transits the cavity, the field switches direction, accelerating the trailing electrons in the positive $z$ direction. The pulse then compressesballistically as it propagates and at the temporal focus all kinetic energy (in the rest frame of the bunch) has been converted to potential energy.

After exiting the RF cavity, a momentum difference has been introduced between the leading and trailing electron, this difference is given by

$$
\Delta p_z \approx \frac{eE_0 \omega \tau d}{v_z} \cos \phi
$$

(4.6)

where $\tau$ is the duration of the electron pulse, $d$ is the cavity length, $\phi$ is the relative cavity phase and $v_z$ is the velocity of the electron bunch in along the propagation axis [3]. From this change in momentum, it can be shown that the RF cavity acts
as a temporal lens with a focusing power

\[ P_L \approx \frac{1}{f_L} = \frac{eE_0d\omega}{m\gamma^3v_z^3}\sin\phi \]  

where \( \gamma \) is the Lorentz factor calculated with \( v_z \) and \( f_L \) is the focal length of the RF cavity [13]. This results in a positive focal length over one half of the RF cycle (\( 0<\phi<\pi \)) and a negative focal length, which further stretches the pulse, over the other half. Similar to a solenoidal magnetic lens which has a focusing power which varies with the applied current, the RF cavity has a focusing power which can be varied with the electric field strength.

4.3 The RF Cavity

Although, in principle, the pillbox cavity previously described would function effectively as an RF compression cavity, power losses in such a cavity are very high. In order to effectively compress electron pulses, a pillbox cavity would require >10 kW of RF power, requiring the use of a klystron to drive the cavity which are large and expensive [14]. To reduce the cost associated with the driving the cavity, a more efficient cavity design was used with a resonant frequency of 2.99 GHz. This frequency was chosen as it is in the microwave S band, used for radar and communications satellites, and components compatible with the frequency are commercially available. The cavity design used in our electron diffractometer is shown in Fig. 4–2. It is a lobed design, symmetrical around the electron beam axis, and based on a design by the group of Prof. O. J. Luiten of the Technical University of Eindhoven [3]. This design can produce field strengths of 10 MV/m in the 6 mm gap at the centre of the cavity with less than 1 kW of input power; this allows for the use of a solid state microwave amplifier to drive the cavity in place of a klystron. At the lab temperature of 21 °C, the resonant frequency is 2.9983 GHz with linear temperature dependence.
of 0.5 MHz/°C. The cavity is machined out of copper with water channels to allow for cooling of the cavity. This provides the ability to temperature tune the resonant frequency of the cavity in order to effectively couple the input RF power.

4.3.1 RF Cavity Electronics

As the derivative of the electric field with respect to time is relatively constant at the zero crossing of the cavity cycle, small errors in the phase of the cavity should have an insignificant effect on the pulse duration. Unfortunately, these small phase changes will result in a net acceleration of the pulses which will change their arrival time. This arrival time jitter results in a lower effective time resolution for the measurements and, as such, proper synchronization of the cavity with the arrival of the electron pulses is critical. The change in arrival time at a distance, $L$, away
4.3 The RF Cavity

from the cavity can be shown to be [13],

\[ \Delta t \approx -L \frac{eE_0d}{m_e \gamma^3 v_z^3} \Delta \phi. \]  (4.8)

As to be expected, the arrival time error at the measurement position increases with the distance the pulse has to travel and with the electric field strength. To achieve the desired time resolution of the diffractometer, phase stability of the RF cavity on the order of 1 mrad is required.

In order to synchronize the phase of the RF cavity with the arrival time of the electron pulses a commercial phase locked loop (PLL) synchronizer, purchased from AccTec B. V. Eindhoven, was used. This unit provides an output 3 GHz RF signal, synchronized to a 75 MHz pulse train obtained from the laser oscillator. A detailed description of the synchronization can be found in reference [15]. The PLL operates at a central frequency of 2998.5 MHz, with operating range of ±1.5 MHz. Published work on the synchronizer demonstrates an 18 fs rms jitter [15].

A complete schematic of the cavity synchronization, the electron pulse generation optics, as well as the electron-laser cross correlation optics can be seen in Fig. 4–3. A small portion of the output of the mode-locked oscillator (~1%) is incident upon a fast photo-diode (ThorLabs FDS02 silicon photodiode, 47 ps rise time). This pulse train with a 75 MHz repetition rate is then sent to the PLL. The PLL then outputs a 3 GHz signal synchronized with the input 75 MHz pulse train. The PLL operates optimally when the 5th harmonic of the input 75 MHz is as close as possible to the 8th sub-harmonic of the 3 GHz output (375 MHz); this 375 MHz is the signal which is phase-locked in the PLL. The PLL can operate in a non-synchronized mode and the beat frequency between the the 75 MHz fifth harmonic and the PLL internal 375 MHz can be monitored on an oscilloscope. We minimize this beat frequency by
moving one of the laser cavity end mirrors, mounted on a linear delay stage, which adjusts the repetition rate of the oscillator. The output power of the PLL is typically 10 mW, much less than what is required to drive the RF cavity. As such, the PLL output is sent to a microwave amplifier in order to produce a synchronized RF pulse with the desired amplitude. The amplifier used is a Microwave Amplifiers Ltd. 3 GHz 1 kW High Power Amplifier. The output of this amplifier is then sent to the RF cavity through a variable attenuator, in order to control the electric field strength of the cavity. As the amplifier can operate at a maximum duty cycle of 10%, its operation is controlled by a TTL pulse synchronized to the 1 kHz output of the laser amplifier, this pulse enables the amplifier before (∼5 µs) the arrival of the RF pulse.

The completed electron diffractometer, with RF compression cavity, can be seen in Fig. 4–4.
Following the implementation of the RF cavity and the associated synchronization electronics, electron-laser cross correlation measurements were performed in a similar method to the results presented in Chapter 3. The instrument response of the measurements previously presented was \( \sim 500 \) fs due to the transverse laser focus size of \( \sim 80 \) \( \mu \)m. In order to provide the 100 fs instrument response desired to characterize the RF compressed pulses the single external 750 mm lens was replaced by two 50 mm lenses placed inside the sample chamber in order to reduce the transverse laser focus size. These lenses were in mounts which provided linear motion in three dimensions. The cross correlation measurements performed in this geometry used two 35 fs, 100 \( \mu J \), 800 nm pulses focused to a transverse spot size, \( d_t \), of 15 \( \mu \)m.
4.4 Pulse Compression Results

FWHM. This provides a measurement impulse response, \( t_m \), of

\[
t_m \approx \sqrt{\tau_l^2 + \left( \frac{d_l}{v_z} \right)^2} = 105 \text{ fs FWHM},
\]

where \( \tau_l \) is the laser pulse duration and \( v_z \) is the electron pulse velocity.

4.4 Pulse Compression Results

![Figure 4–5: Electron-laser cross correlation scans for various cavity field strengths with a bunch charge of 0.1 pC and 80 keV electrons. The IRF for a field strength of 1.57 MV/m (blue) is 334 ± 10 fs, the shortest IRF obtained.](image)

Fig. 4–5 demonstrates the temporal focusing properties of the RF cavity for various electric field strengths at the optimal cavity phase. These measurements were performed with 0.1 pC bunches of electrons accelerated to 80 keV. The pulses were generated by imaging a 100 \( \mu \)m pinhole on the photo-cathode, which provides a truncated Gaussian laser illumination distribution. The increasing electron charge density and decreasing instrument response is clearly visible as the optimal
4.4 Pulse Compression Results

electric field strength, 1.57 MV/m, is approached. Here, the minimum measured instrument response of 334±10 fs, after deconvolving the instrument response of the cross-correlation measurement, \( t_m \), is shown. This optimal result is a time-averaged measurement over approximately 45 minutes. Fig. 4–6 illustrates the same focusing properties of Fig. 4–5 with instrument response as a function of electric field strength shown. The dotted line is the theoretical pulse length, assuming zero arrival time jitter, calculated using GPT [16]. Our measured impulse response agrees well with the simulations except in the immediate vicinity of the optimal electric field strength; here our impulse response is larger than expected.

**Figure 4–6:** IRF as a function of cavity field strength for 0.1 pC electron pulses accelerated to 80 kV. The dashed line is a simulation result performed by Robert Chatelain [16]; the expected minimum IRF was not achieved due to synchronization issues between the RF cavity and the arrival of the electron pulses.
The focusing properties of the RF cavity can be modified with the cavity phase as well as the cavity field strength (Eq. 4.7). If the field strength is less than or equal to the optimal value ($\leq 1.57$ MV/m for the measurements presented here), then a single minimum exists as a function of phase. If, in contrast, the field strength is greater than the optimal value, the cavity is over focused and the temporal focus is located before the measurement position. In this scenario, the phase-pulse length relationship shows a double minimum as a deviation in phase in either direction will lower the focusing power of the cavity, and move the sub-optimal temporal focus back to towards the measurement position. This double minimum can be seen in

![Figure 4–7: IRF as a function of cavity phase with $E_0 = 1.66$ MV/m for 0.1 pC electron bunches accelerated to 80 kV. The cavity field strength is larger than the optimal value (1.57 MV/m) and as a result the expected double minimum is observed. The dotted line denotes the IRF predicted from GPT simulations.](image-url)
4.5 Cavity Synchronization Issues

Two issues were encountered when performing the characterization measurements of the focusing properties of the RF cavity; first, the arrival time of the electron pulses would drift on the minute to hour time scale, and secondly, our measured minimum impulse response was greater than the 150 fs impulse response expected. Fig. 4–8 shows an example of the aforementioned drift. By measuring the arrival time of the electron pulses as a function of phase an arrival time change of 63 ps/rad was found (for $\phi \ll 2\pi$). Alternatively, if we desire an arrival time stability of $<100$
fs, a phase stability of $<1.6$ mrad (or RF cycle synchronization of $<85$ fs) is required. From the perspective of the long term drift, temperature fluctuations are assumed to be the cause. After the mode-locked oscillator, the laser pulses travel a distance $>20$ m before generating the electron pulses. A path length change of only $90\mu m$ over this distance would result in an arrival time error at the measurement position of $350$ fs. Similarly, the synchronization signal from the photo diode travels through $>5$ m of cable before entering the PLL. Temperature changes in the cavity due to both the lab temperature and the recirculating chiller used will change the resonant frequency of the cavity and therefore the amount of RF power coupled to the cavity will change; this would also cause a change in the arrival time of the pulse. Efforts were made to reduce this drift through various means. The electrical cables for the synchronization signal were thermally insulated, and the initial cable which contained a teflon insulator, was replaced with a more temperature stable cable with a silicon-oxide insulator. The optical table was closed off to limit the effects of the air conditioning system which outputs cold air on one side of the lab. In addition, some correlation was found between the repetition rate of the oscillator and the arrival time drift. This was addressed by actively controlling the end mirror of the oscillator to keep the repetition rate at $\pm 1$Hz from the initial value. The degree to which these changes affected the drift of the cavity is unknown due to the fact that the drift behaviour was not consistent. Long periods of relative stability were present in our characterization (the 334 fs measurement taken over 45 minutes is one example), in addition to periods with large arrival time changes (up to 10 ps arrival time change). Fortunately, the effect of this slow scale drift can usually be removed in post-processing of the data (as will be shown in Chapter 5), and measurements taken during periods of abnormally high drift our discarded.
With regards to arrival time jitter, we were unable to make the single shot measurements which would provide the information required to determine if our pulses are as long the measured impulse response, or if arrival time jitter is broadening the impulse response.

### 4.6 Streak Camera

Due to the instability of the pulse compression techniques presented, we require the means to verify the time resolution of the diffractometer prior to performing time resolved measurements. This necessitates a reliable and simple means to verify the time resolution on a day to day basis. Unfortunately, the electron laser pulse cross correlation measurement is quite elaborate, requires sensitive alignment and interferes with pump-probe measurements. In place of the ponderomotive measurements we use a streak camera provided by the Schwoerer group of the University of Stellenbosch in South Africa. This compact streak camera was developed specifically for ultrashort electron pulses, a complete description of which can be found in Kassier et al., 2010 [17].

A streak camera operates by exposing the electron pulse to a time dependent electric field. It operates on a similar principle to the RF cavity except the the electric field is perpendicular to the electron pulse propagation axis (Fig. 4–9). This time dependent electric field projects the temporal distribution of the pulses onto a spatial coordinate. The streak camera consists of a pair of 3 mm x 3 mm streak plates with a separation of 0.5 mm. These streak plates are held at 1 kV and are in electrical contact with each other through a GaAs photo-switch. Upon excitation of the photo-switch with a 800 nm laser pulse the streak plates discharge, displaying a damped oscillation with a frequency of 5.2 GHz [17]. In front of the streaking plates is a 50 μm aperture. The streak camera operates by first discharging the plates
4.6 Streak Camera

Figure 4–9: Schematic diagram of the streak camera. The streak plates are held at 1 kV with a power source (not shown) and are discharged by illuminating the GaAs photo-switch with a 35 fs, 800 nm pulse. The electron pulse (blue) enters the streak camera as the time dependent electric field, $E(t)$, is switching direction, projecting the temporal duration of the pulse onto the transverse spatial coordinate. The width of the streaked electron pulse, $\sigma_s$, is larger than the reference spot width, $\sigma_p$, on the detector.

With an ultrashort laser pulse with a delay appropriate so that the electron pulse enters the streak camera as the electric field switches direction. This results in no net deflection of the electron pulse, but a deflection of the front of the pulse with respect to the back of the pulse which increases with pulse length.

The impulse response of the streak camera is given by

$$\sigma_{\text{imp}} = \frac{\sigma_\theta}{\omega_s} \approx \frac{\sigma_p}{\omega_p},$$

(4.10)

where $\sigma_\theta$ is the angular spread of the beam and $\omega_s$ is the angular streak velocity in mrad/ps [17]. The angular deflections by the streak camera are very small, so it’s easier to work with distances given in pixels on the CCD rather than angles, with the transverse electron spot size in pixels, $\sigma_p$, and the streak velocity given in pixels/ps, $\omega_p$. For the reference electron spot shown in Fig. 4–10, the spot has a FWHM of 4.8 pixels. Fig. 4–11 shows a calibration measurement with streak velocity of 11 pixels/ps for a streak plate voltage of 1 kV and a 95 kV electron pulse acceleration voltage; this gives us an impulse response of $\sim$435 fs FWHM. The resulting electron pulse length can then be extracted from the known the streaked spot width and the
known impulse response. The electron pulse length is then given by
\[
\tau = \sqrt{(\sigma_s/\omega_p)^2 - (\sigma_p/\omega_p)^2},
\]
where \( \sigma_s \) is the streak pulse width in pixels. For the 5.0 pixel FWHM streaked pulse shown in Fig. 4–10-B, this provides a pulse length of 455 fs FWHM. Using this streak camera we are able to quickly and easily find the cavity amplitude and phase which provides the optimal pulse compression.
Figure 4–11: Electron pulse deflection in pixels as a function of pump delay (ps). A streak velocity of 11 pixels/ps was obtained with a streak camera voltage of 1 kV and an electron pulse accelerating voltage of 95 kV.
References


CHAPTER 5

On the contribution of Mott and Peierls instabilities to the semiconductor-metal transition in VO$_2$

Vanadium dioxide (VO$_2$) undergoes a first-order phase transition from a low temperature semiconducting phase to a high temperature metallic phase at $\sim$343 K. This semiconductor to metal transition (SMT), first discovered by Morin in 1959 [1], results in a dramatic change in conductivity by as much five orders of magnitude and is associated with a change in crystal structure [2]. Early studies by Goodenough, based on molecular orbital considerations, attributed the SMT to the Peierls-like distortion present in the lattice in the low temperature phase [3]. In contrast, experimental evidence indicating that the structural distortion was incapable of opening an insulating gap prompted Mott and Zylbersztejn to propose an alternative mechanism attributing the semiconducting nature of the low temperature phase to electron-electron interactions [4,5]. To date, the relative contributions of both electron-lattice interactions and electron-electron interactions to the phase transition remain controversial. UED is a technique which is sensitive to both the crystal structure and
charge distribution on ultrafast time scales and is able to provide valuable insight into nature of this much debated phase transition. In this chapter I present the results of UED measurements made on VO$_2$ using RF compressed electron pulses as well as ultrafast IR transmittance measurements. Pump-probe measurements performed over a range of excitation fluences are used to identify distinct structural and electronic phase transitions, the first measurement of its kind using UED.

5.1 The structure of VO$_2$

The high temperature phase of VO$_2$ is metallic with a simple rutile crystal structure (R) and space group P4$_2$/mnm (Fig. 5–1). In this phase, the rutile unit cell vectors, $a_R$ and $b_R$ both have a length of 4.55 Å and $c_R = 2.85$ Å [6]. The vanadium atoms are each located at the centre of an oxygen octahedra with slight Jahn-Teller distortion and an average V-O distance of 1.9 Å. These octahedra form 1D edge-sharing chains along $c_R$ with the vanadium atoms being equally spaced. The vanadium atoms are located at the Wyckoff positions (2$a$) with coordinates $(0,0,0)$ and $(1/2,1/2,1/2)$ while the oxygen atoms are located at the Wyckoff positions (4$f$) with coordinates $\pm (x,x,0)$ and $\pm (x+1/2,x+1/2,1/2)$ with $x =0.30$ [6].

The transition from rutile to monoclinic VO$_2$ results in a lowering of symmetry of the crystal lattice with the vanadium atoms forming dimers (a Peierls-like distortion). These dimers are rotated slightly with respect to $c_R$, giving a shortest V-O distance of 1.76 Å [7]. The low temperature phase of VO$_2$ is insulating with a monoclinic (M1) crystal structure and space group P2$_1$/c (Fig. 5–2). This unit cell has volume twice that of the rutile unit cell with the monoclinic unit cell vectors given by $a_M = 2c_R$, $b_M = a_R$ and $c_M = b_R - c_R$. All atoms in this phase occupy the $(4e)$ Wyckoff positions $(x,y,z)$, $(\bar{x},y+1/2,\bar{z}+1/2),(\bar{x},\bar{y},\bar{z})$ and $(x,\bar{y}+1/2,z+1/2)$, for the coordinates given in Table 5–1. With this pairing and tilting of the V atoms there
5.1 The structure of VO$_2$

![Crystal structure of rutile (R) VO$_2$](image)

**Figure 5–1:** Crystal structure of rutile (R) VO$_2$. The vanadium atoms are indicated in blue, the oxygen atoms are indicated in green and the rutile unit cell in indicated with the dashed lines (note: two unit cells are depicted).

**Table 5–1:** Atomic coordinates for the monoclinic unit cell of VO$_2$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.242</td>
<td>0.975</td>
<td>0.025</td>
</tr>
<tr>
<td>O1</td>
<td>0.1</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>O2</td>
<td>0.39</td>
<td>0.69</td>
<td>0.29</td>
</tr>
</tbody>
</table>

are now two distinct V-V separations along $c_R$; the shorter, dimer separation of 2.61 Å and the longer separation of 3.16 Å.
5.2 Peierls or Mott-Hubbard? Previous work on the mechanism of the SMT in VO$_2$

Early work suggested that the SMT could be explained completely in terms of electron-lattice interactions and the change in crystal structure [2,8]. This distortion of the lattice was thought to result in a modification of the band structure, opening a gap at the Fermi-level. This idea was formalized by Goodenough who presented an ionic model based on crystal field splitting [3]. Here, the vanadium 3$d$ orbitals are split into two sets, $e_g$ and $t_{2g}$, due to the crystal field of the surrounding oxygen.
5.2 Peierls or Mott-Hubbard? Previous work on the mechanism of the SMT in VO$_2$

The two $e_g$ orbitals, $d_{3z^2-r^2}$ and $d_{x^2-y^2}$, are directed towards the oxygen atoms which results in strongly $\sigma$-(anti)bonding V3$d$-O2$p$ molecular orbitals. The otherwise degenerate $t_{2g}$ orbitals are split by the tetragonal lattice contribution. The $d_{xy}$ ($d_{4}$) orbital is oriented along $c_R$ and is positioned to mediate $\sigma$-type overlap with the adjacent vanadium but is nominally non-bonding in the rutile phase (Fig. 5–3).

In contrast, the $d_{xz}$ and $d_{yz}$ orbitals are oriented such that they are involved in $\pi$-type overlap with the O-2$p$ orbitals of surrounding oxygen atoms forming bonding ($\pi$) and anti-bonding ($\pi^*$) combinations. These notations refer to a local coordinate system ($z \parallel [110]$) for a given vanadium atom. In this ionic model the orbital occupation is determined by the effective ionic charges, V$^{4+}$ and O$^{2-}$. Of the five valence electrons

![Diagram](image.png)

**Figure 5–3**: An illustration of the V-3$d$ states that form the $t_{2g}$ molecular orbitals in VO$_2$. The $d_{xz}$ and $d_{yz}$ V-3$d$ states mix with O-2$p$ states through $\pi$-type overlap, forming orbitals of bonding ($\pi$) and anti-bonding ($\pi^*$) character.
from vanadium, four occupy π states of primarily O-2p character with the remaining valence electron occupying $d_{\parallel}$ or $\pi^*$ states, i.e., a 3$d^1$ electronic configuration. In the rutile phase, the energies of both the $\pi^*$ and $d_{\parallel}$ band are located at the Fermi level, resulting in metallic behaviour (Fig. 5–4). There are two effects on the energy diagram upon transitioning to the low temperature phase. First, the dimerization of the vanadium atoms results in increased overlap of the $d_{\parallel}$ orbitals; this splits the band into bonding ($d_{\parallel}$) and anti-bonding ($d_{\parallel}^*$) states with the latter above the Fermi level. Secondly, the vanadium displacement perpendicular to $c_R$ increases the $\pi$ overlap of the $t_{2g}$ and O$-2p$ states and is thought to increase the energy of the $\pi^*$ band. Goodenough attributes the opening of the insulating gap to this combination of the $d_{\parallel}$ splitting and $\pi^*$ upshift. The single $d$ electron occupies the bonding $d_{\parallel}$ states and the gap is formed between this and the bottom of the $\pi^*$ band; $d_{\parallel}^*$ remains unoccupied and its energy above the bottom of the $\pi^*$ band (Fig. 5–4).
Experimental evidence was soon found that contradicted the Goodenough picture. Studies on chromium doped VO$_2$ (V$_{1-x}$Cr$_x$O$_2$) observed that the addition of small amounts of chromium (0.0035 < $x$ < 0.025) resulted in a second monoclinic phase of VO$_2$ (M2) [4]. In this M2 phase half the vanadium chains along $c_R$ are paired, with no tilting, whereas the other half were tilted with no pairing. Despite the lack of a Peierls type distortion in half of the chains, the insulating behaviour remained. In addition, this M2 phase was found to exist in pure VO$_2$ under uniaxial strain along the [110]$_R$ crystal axis [9]. These observations led Zylbersztejn and Mott to propose an alternative to the Goodenough model in which electron-electron correlations in the $d_{\parallel}$ states were the primary mechanism for the insulating properties of the M1 phase [5]. This Mott picture includes the competition between electron localization and itinerancy (or delocalization) in minimizing the electronic energy when local electron-electron Coulomb interactions are considered. If the reduction of Coulombic potential energy associated with localizing the electrons to avoid the energetic cost of V-site double occupancy outweighs the decrease in kinetic energy from electron delocalization the system exhibits insulating behaviour. If this is the case, a gap in the corresponding band is opened resulting in an occupied lower Hubbard band (LHB) and an unoccupied upper Hubbard band (UHB). In the proposed Zylbersztejn model, the uncorrelated $\pi^*$ states effectively screen the electrons in the $d_{\parallel}$ states, resulting in the metallic properties of the rutile phase. The energetic upshift of the $\pi^*$ states and splitting of the $d_{\parallel}$ states that occurs as a result of the SPT results in the removal of screening in the the now filled lower $d_{\parallel}$ states, opening a Mott-Hubbard gap. The debate surrounding the nature of the transition in VO$_2$ has focused primarily on the relative contributions of the electron-lattice interactions and electron-electron interactions.
5.2.1 Computational studies on VO$_2$

Calculations attempting to identify the nature of the phase transition in VO$_2$ have taken a variety of approaches. Wentzcovitch et al. employed density functional theory (DFT) within the local density approximation (LDA) and suggested that VO$_2$ is more bandlike than correlated [10]. Although their calculations qualitatively supported key aspects of the picture put forward by Goodenough, primarily the splitting of the $d_{\parallel}$ states and the energetic upshift of the $\pi^*$ states, they failed to observe the opening of an insulating gap [11], and instead found a band overlap of -0.04 eV. Additional DFT calculations found similar results, with an exaggeration of the lattice distortion required if a band gap was to be formed [6,12]. This failure of DFT-LDA to predict an insulating gap also applies to the M2 phase [6]. Nevertheless, these studies concluded the insulating state to be due primarily from the Peierls-like lattice instability. The inability to open an insulating gap was attributed to known imperfections in the LDA. However, DFT studies using LDA+U, where U is the Coulomb repulsion parameter, also failed to produce consistent results as they predicted the M1, M2, and R phases all to be anti-ferromagnetic insulators, in contrast with the observed non-magnetic M1 and paramagnetic, metallic R properties [13–15]. Subsequent calculations using DFT+GW did manage to open an insulating gap [12], although the gap was much smaller than the measured value.

More recently, dynamical mean field theory (DMFT) has been used in conjunction with DFT in to order model electronic correlations more accurately. A cluster-DMFT model in combination with DFT-LDA, implemented by Biermann et al., found that the M1 phase was insulating with $E_g \sim 0.6$ eV [16]. These authors found that correlations led to the two $d$ electrons of the V-V dimer forming localized singlet states which resulted in the opening of the insulating gap. In addition, they
found that the transition resulted in a strong redistribution of the occupation of the sub-shells of V-3$d$ character near the Fermi level. The rutile phase was found to have an almost isotropic occupancy, with the occupancy of the $d_{∥}$, and both $\pi^*$ states being 0.42 and 0.29 respectively. In contrast, the occupancy in the insulating phase was found to switch almost completely to the $d_{∥}$ states. This study however assumes a key aspect of the ionic picture; only a single 3$d$ electron per vanadium atom, consistent with the 3$d^1$ ionic picture put forward by Goodenough. This ionic picture is in contrast with results from x-ray absorption spectroscopy measurements which suggest that the states of VO$_2$ cannot be accurately described with a single $d$ electron [17].

The work of Weber et al. addressed this using cellular cluster DMFT with DFT on large supercells containing hundreds of atoms, while adopting an iterative approach that allowed the electron occupation of the V-3$d$ and O-2$p$ states to vary [18]. They found an insulating state which the authors describe as “based on an orbital selective Mott transition, assisted by the Peierls distortion”, where bonds of the $d_{xy}$ and $d_{xz}$ states form along $c_R$ with one electron in each for a total occupancy of the $d$ states of two. The Mott instability is then generated in these states. Experimental evidence for this type of orbital selective transition will be discussed and is relevant to our experimental results.

The Biermann and Weber pictures are distinguished by the hierarchy of the roles played by electron-electron and electron-lattice interactions. The Biermann work considers VO$_2$ to be Mott assisted Peierls insulator. Here, the bandgap opens due to the lattice distortion and correlations shift it downwards to centre on the Fermi level; this results in the observed insulating behaviour [16]. In the picture put forward by Weber, VO$_2$ is a Peierls assisted Mott insulator. The role of the lattice
5.2 Peierls or Mott-Hubbard? Previous work on the mechanism of the SMT in VO$_2$

distortion is to enable the strong electronic correlations, which are responsible for opening the gap [18].

5.2.2 Experimental Findings

Determining the electronic and structural properties of the phase transition in VO$_2$ has been the focus of many measurements. Photoemission spectroscopy (PES) measurements have identified the 0.6 eV bandgap between the occupied $d_{\parallel}$ states and the unoccupied $\pi^*$ states [11]. In transitioning from the metallic phase to the semiconducting phase, the high spectral intensity at the Fermi level is observed to shift to lower energy, opening the insulating gap, while no change is observed in the O2$p$ states. Similar photoemission measurements from Koethe et al. identify a previously unobserved satellite peak in the photoemission spectra of metallic VO$_2$ at an energy of -1.3 eV, in addition to the high spectral weight at the Fermi level [19]. These observations are in agreement with the CDMFT measurements of Biermann et al., and the authors suggest the role of another degree of freedom in the SMT, that of a switch in orbital occupation which leaves the system more susceptible to a Peirels transition.

X-ray absorption spectroscopy (XAS) measurements have also been used to study the electronic structure of VO$_2$. Initial work by Abbate et al. identified a splitting of more than 2 eV in $d_{\parallel}$ in the low temperature phase [20]. Polarization dependent XAS measurements, performed by Haverkort et al., provided evidence of a change in orbital occupancy through the phase transition, i.e., a dramatic, qualitative change in the occupation of the subshells [17]. These measurements found that the occupation of the V-3$d$ subshells near the Fermi level in the high temperature phase is almost isotropic. Upon entering the low temperature phase, however, the electronic structure becomes almost 1D along $c_R$, in agreement with CDMFT studies [16, 18].
The 1D nature of the monoclinic electronic structure leaves it more susceptible to the Peierls transition. They conclude that the transition demonstrates many features of a Peierls transition, but that the strong orbital switching indicates that the system must be close to the Mott regime. Thus, the authors call the SMT in VO$_2$ an “orbital-assisted Mott-Peierls transition”. Similar results using XAS were found by Koethe et al., i.e. a strong 1D electronic structure in the low-temperature phase, supporting their conclusion that the V-3$d$ orbital switching is key to opening the band gap [19].

Evidence that the SMT can be decoupled from the SPT has been demonstrated in some recent measurements. Infrared nanoscale imaging by Quazilbash et al., in addition to providing the first direct evidence of the percolative nature of the phase transition, also saw evidence for an intermediate metallic state which displayed optical properties which differed from the high temperature state [21]. In these measurements, nanoscale, mid-infrared imaging allowed them to observe changes in the conductivity of individual crystallites. The formation of intermediate, nanometre scale, metallic “puddles” were observed which displayed an optical conductivity consistent with a strongly correlated metallic state. These metallic regions coexist with both insulating regions and metallic regions with optical conductivities consistent with the high temperature phase; these metallic puddles then coalesce to form the bulk metallic high temperature phase as the temperature is increased. These measurements were followed by nanoscale mid-IR imaging and nanoscale x-ray diffraction measurements on the same sample which allowed them to monitor both conductivity and structure (albeit not at the same sample location). The transition from semiconductor to metal was found to be monotonic with increasing temperature whereas the SPT was not. Some crystallites which underwent the SPT would revert to the
monoclinic form, further supporting the position that the SMT and SPT are decoupled [22].

Nag et al. provided further evidence of this decoupling by observing that the hysteresis curve for the SPT, determined through XRD, was wider than the hysteresis curve for the SMT, determined using IR transmissivity measurements for thin film epitaxially grown VO_2 [23]. Likewise, XRD measurements by Kim et al. in concert with electrical transport measurements found that the SMT preceded the SPT [24]; in these measurements the sample was in a two-terminal device and the transition was initiated by increasing the current.

Finally, structural measurements have been employed to determine if there is an intermediate phase to the SPT. Corr et al., using PDF analysis on synchrotron XRD measurements, found that although there is a coexistence regime of both the M1 and R structures, there is no evidence for a significant phase-fraction of an intermediate structure in the thermally induced phase transition [25].

5.2.3 The Ultrafast SMT in VO_2

In addition to being thermally initiated, the phase transition can also be initiated with ultrashort laser pulses which allows the transition to be probed on ultrafast time scales [26, 27]. Ultrafast transmission and absorption measurements at 800 nm performed by Becker et al. remarkably found an upper limit on the transition time of approximately 500 fs which was limited by their instrument response [26]. Subsequent ultrafast transmission and reflections measurements were conducted by Cavelleri et al. which, by reducing the excitation pulse duration to as low as 15 fs, observed a bottleneck in the electronic phase transition time of about 75 fs [27]. This bottleneck was attributed to the electronic transition resulting from coherently driven structural motion, evidence that the structural transition is a prerequisite
for the electronic transition. Cavalleri also performed the first ultrafast diffraction measurements on VO$_2$ using plasma generated ultrafast xray pulses. This work demonstrated that the structural phase transition in VO$_2$ occurs on a time scale on the order of a few hundred femtoseconds [28] and provided evidence in favour of a structurally driven SMT.

In contrast with these results, ultrafast terahertz (THz) spectroscopy measurements [29, 30] have found instrumentally limited timescales for the electronic transition as low as 60 fs, in addition to demonstrating that the threshold excitation fluence required to initiate the SMT decreases as the phase transition temperature is approached [31]. Kubler et al. found that below a critical excitation fluence of 3.5 mJ/cm$^2$ at 320 K, the initial increase in conductivity rapidly decays in approximately 400 fs [29]. This behaviour has been attributed to carrier excitation across the band gap, but with insufficient density to screen the electron-electron interactions. The following rapid decrease in conductivity has been ascribed to the structural deformation shifting the excited dimer energy below a mobility edge, similar to exciton self-trapping. Above this critical fluence, the initial rise in conductivity displays a single oscillation in phase with coherent lattice motion before settling into a long lived metallic state. They conclude that this long lived metallic state is decoupled from the continuing coherent lattice motion and is a consequence of the strongly correlated low temperature phase [29,30].

Further evidence of this decoupling of the SMT and SPT has been found in other ultrafast measurements. Temperature dependent ultrafast THz spectroscopy measurements by Cocker et al. have indicated the formation of a metallic state apparently without lattice relaxation [32]. This was found to occur in samples with a temperature below 200 K and fluences between $\sim$5-8 mJ/cm$^2$, as evidenced by the
absence of the 6 THz phonons which are characteristic of the SPT. They conclude that there are critical thresholds for both the number of excited carriers required to screen the electron-electron interactions and for the number of transition phonons (phonons with a frequency of 6 THz which map the M1 phase onto the R phase) required to trigger the structural transition.

Finally, in contrast with the structural measurements on the thermally induced phase transition, UED measurements by Baum et al. in a reflection geometry identified two timescales (307 fs and 9.2 ps), which they attribute to a two step SPT. They identified the initial fast dynamics as the lengthening of the V-V dimers along the dimer axis followed by a slower motion perpendicular to \( c_R \) which brings the vanadium atoms into their high symmetry positions. These results will be further addressed in the discussion of this chapter.

5.3 The SMT in VO\(_2\) studied using UED

In this section, the techniques used to perform time-resolved UED measurements on VO\(_2\) using RF compressed electron pulses will be presented [33]. The sample preparation and characteristics will be outlined, followed by the data acquisition and data processing methods.

5.3.1 Sample Preparation

As described in Chapter 2, thin samples are required in order to minimize the effect of multiple scattering in electron diffraction measurements. The VO\(_2\) samples used in our measurements are 70 nm, polycrystalline thin films deposited on 50 nm thick silicon nitride membranes. The sample preparation was performed by Dr. Ali Hendaoui of INRS-EMT in Varennes, QC, Canada [34,35]. The thin VO\(_2\) layer was
deposited using reactive pulsed laser deposition from a pure (99.95%) vanadium target with a KrF excimer laser and wavelength of 248 nm. This was done under an oxygen pressure of 15 mTorr with a substrate temperature of 500°C. Using surface profilometry measurements and cross-sectional scanning electron microscopy of VO$_2$ deposited on silicon substrates, deposition rates were determined. This allowed for the determination of the deposition time for 70 nm thick films on the 50 nm thick silicon nitride membranes. The silicon nitride membranes are suspended across square silicon windows; two sizes, 250 $\mu$m$^2$ and 500 $\mu$m$^2$, were used. Fig. 5–5 shows a TEM image of one of the VO$_2$ samples used and a large distribution of crystallite sizes can be seen. The samples also display a hysteresis curve (10 °C), characteristic of the

![Figure 5–5: TEM image of a 70 nm thick, polycrystalline VO$_2$ film on supporting silicon nitride membranes. A) Polycrystalline structure of the as grown film. B) High resolution TEM image showing the lattice structure of a VO$_2$ single crystal.](image)

SMT in VO$_2$ (Fig. 5–6). The measured absorbed fluence at 800 nm was measured to be 60±10% of of the incident fluence.
5.3 The SMT in VO$_2$ studied using UED

**Figure 5–6:** Resistivity as a function of temperature for both heating (red) and cooling (blue) of the VO$_2$ samples used. The typical hysteresis curve of VO$_2$ with a width of 10 °C can be clearly seen.

### 5.3.2 Data Acquisition

The UED measurements performed on VO$_2$ were conducted with the diffractometer in the RF geometry and with a pump-probe geometry similar to that used for the initial measurements performed on single crystal gold (Fig. 5–7) [33]. Diffraction patterns obtained from the VO$_2$ samples in both the high and low temperature phases can be seen in Fig. 5–8. The polycrystalline nature of the samples is evidenced by the diffraction rings, as opposed to the spots observed in the single crystal gold samples. Although it is difficult to see in the images, certain weak reflections present in the low temperature phase are not present in the high temperature phase. The shadow visible in the centre of the image is a beam block which was used to prevent the unscattered electron beam from saturating the camera.

The initial pump-probe measurements were performed using a repetition rate of 1 kHz, with the unpumped sample held at approximately room temperature, i.e., in equilibrium in the M1, semiconducting phase. No strong time resolved signal could
be found in these initial measurements. It was concluded that the high repetition rate of the pump pulses was resulting in a steady state in which the average sample temperature being raised above the transition temperature before the arrival of the pump pulse. As these measurements were performed in vacuum, the heat conduction from the thin films was slow which prevented relaxation back to the monoclinic structure between laser shots. Thus, no evidence of the structural transition could be found. In order to allow the samples to completely relax to the low temperature phase, a pump repetition rate of 50 Hz was required. In an effort to increase the number of scattered electrons per pulse, we attempted to use the larger 500 \( \mu \text{m}^2 \) samples. Unfortunately, these large samples would not completely relax to the low temperature phase in the 20 ms between pulses due to poor heat conduction. Therefore, we were required to use the 250 \( \mu \text{m}^2 \) samples which did completely relax between excitations. This gave the best average signal levels and represents a compromise between the thermal relaxation time and the number of scattered electrons.

Figure 5–7: Schematic diagram of the ultrafast electron diffractometer in the RF geometry with a pump-probe optical setup. A mirror on a flip mount allows for streak camera measurements to be made without opening the sample chamber or changing the alignment in the pump line.
5.3 The SMT in VO$_2$ studied using UED

Figure 5–8: Diffraction patterns of low temperature (A) and high temperature (B) phases of VO$_2$. The red arrows indicate the disappearance of diffraction features which are present in M1, but not allowed by symmetry in the R phase.

per pulse. The electron pulses used contained on average 500 000 electrons per pulse, although this quantity varied with the performance of the laser. The majority of the measurements were performed with an accelerating voltage of 95 kV, with some measurements performed with an accelerating voltage of 85 kV. In order to produce well defined diffraction features, each UED measurement used a 15 sec exposure (750 electron pulses) at each time delay, and this was repeated on average 50 times for a given pump fluence. This resulted in an acquisition time of approximately one day for each pump fluence.

5.3.3 Data Processing

Upon acquiring the time resolved electron diffraction data, the first step was to subtract off the scattered laser light picked up by the detector. This was done by first acquiring images without an electron beam but with the pump laser prior to
the measurements; these were subtracted from the raw diffraction patterns. After background subtraction the images were normalized by the number of counts in the image and then azimuthally integrated in order to produce one dimensional diffraction patterns with electron counts as a function of scattering vector. The resulting azimuthally integrated, time resolved data can be seen in Fig. 5–9.

![Azimuthally integrated time-resolved diffraction pattern from VO$_2$ with an excitation fluence of 20 mJ/cm$^2$. All time delays are shown in this plot ranging from -5 ps (blue) to 600 ps (red). Inset: Enlarged view of the small $s$ region of the diffraction pattern in which the time dependent diffuse background can be clearly seen.](image)

**Figure 5–9:** Azimuthally integrated time-resolved diffraction pattern from VO$_2$ with an excitation fluence of 20 mJ/cm$^2$. All time delays are shown in this plot ranging from -5 ps (blue) to 600 ps (red). Inset: Enlarged view of the small $s$ region of the diffraction pattern in which the time dependent diffuse background can be clearly seen.

After the image processing, all of the experimental runs for a given pump fluence needed to be averaged in order to produce a single diffraction pattern at each pump-probe delay. The drift associated with the RF compression cavity resulted in the need for a dynamical correction to the arrival time of the electron pulse in order to accomplish this. To track the arrival time of the pulse, the largest diffraction feature, located at $s \approx 0.3$ Å$^{-1}$, was fit with a pseudo-Voigt profile and the amplitude of the reflection was determined as a function of both pump-probe delay and run; this is
shown in Fig. 5–10 (left). The Voigt profile is often used when fitting reflections in

![Diffraction pattern](image)

**Figure 5–10:** Amplitude of the 220 reflection as a function of pump-probe delay and scan number for an excitation fluence of 20 mJ/cm² (left). Blue represents no change and red represents an increase in amplitude. The white line denotes a pump-probe delay of zero as determined by an exponential decay fit to each scan. The arrival time of the electron pulses drifted by about 4 ps over the course of the 20 hour acquisition time. The same amplitude measurements are shown on the right, with the electron arrival time drift removed.

a diffraction pattern and is the convolution of a Gaussian and a Lorentzian profile. The pseudo-Voigt profile, given by

$$f(x) = A \left( \epsilon \frac{(w/2)^2}{(x-x_c)^2 + (w/2)^2} + (1-\epsilon) \exp \frac{-(x-x_c)^2}{2 \frac{w}{2\sqrt{2 \log 2}}} \right),$$  \hspace{1cm} (5.1)

is a linear combination of a Gaussian profile and Lorentzian profile, with a weighting factor, \( \epsilon \), full width half max (FWHM), \( w \), and profile centre, \( x_c \), and is often used in place of a true Voigt profile due to its relative simplicity. This reflection had sufficient intensity to allow for an exponential decay to be fit to each delay scan. The time-zero offset due to drift in the RF cavity can then be extracted from each scan and subtracted from the pump-probe delay in order to obtain a consistent pump-probe time-zero for all scans. The result of this subtraction can be seen in Fig. 5–10 (right).
In addition to the laser background, the diffraction data sits on a large diffuse background. Part of this background is a result of the amorphous silicon nitride thin film on which the VO$_2$ sits. This was removed by first acquiring diffraction images from silicon nitride windows without a VO$_2$ sample, these were then subtracted from the VO$_2$ diffraction patterns. The remaining diffuse background results from a combination of thermal diffuse background, and inelastic scattering events. This background is normally fit with a polynomial and subtracted before analyzing diffraction data. The difficulty in subtracting the diffuse background from the diffraction patterns presented here results from both the overlapping nature of the reflections, which masks the shape of the background, and its dynamical nature. The changing diffuse background as a function of time can be seen in the inset of Fig. 5–9.

The method in which this dynamical diffuse background was removed involved two steps. First, the time dependence of the background was determined by integrating the region of the diffraction pattern where $s < 0.15 \text{ Å}^{-1}$. The change in diffuse background was bi-exponential in form and can be seen in Fig. 5–11. Secondly, the shape of the diffuse background was determined both before time zero and at the time of its maximum change. This was accomplished by fitting pseudo-Voigt profiles on a linear background to reflections in small overlapping regions of $s$. The average value of these linear backgrounds was taken at each value of $s$, and then smoothed to give the calculated diffuse backgrounds shown in Fig. 5–12. This diffuse background subtraction procedure was applied to all UED measurements present in this chapter. The resulting background subtracted diffraction data for a single fluence can be seen in Fig. 5–13.
Figure 5–11: Temporal evolution of the change in diffuse scattering background for an excitation fluence of 20 mJ/cm². This was obtained by integrating the region of the diffraction pattern where $s < 0.15 \, \text{Å}$.

Figure 5–12: Diffraction data from $t = -5$ ps (blue) and $t = 5$ ps (red). The calculated diffuse background for each delay is shown with the dashed lines.
5.3.4 Modelling the polycrystalline diffraction pattern

Proper interpretation of the measurements requires that the Miller indices of the many reflections be identified. In contrast to most crystallographic studies, we are assuming that the initial structure of VO$_2$, the monoclinic phase, is known. As such, we can calculate the structure factors of all of the allowed reflections as a starting point. Ideally we would extract the intensity of each of the individual reflections in our measurements in order to compare, but the overlapping nature of the reflections in our data and our inability to determine the exact form of the diffuse background prevents this. If we use Eq. 2.11, we can calculate the structure factors for all allowed reflections. In the space group P2$_1$/c, the reflection conditions are [36]

\[ h0l : l = 2n \]
\[ 0k0 : k = 2n \]
\[ 00l : l = 2n. \]
Using the pseudo-Voigt parameters described earlier, we can place a diffraction peak for each reciprocal lattice point with the amplitude defined by the calculated structure factor, which results in the simulated diffraction pattern shown in Fig. 5–14. Although the simulated diffraction pattern is qualitatively similar to the measured one, a few diffraction features are significantly weaker in our measured pattern. In addition, three reflections in our measured pattern are extremely weak in the simulated pattern. These three weak reflections are important to our interpretation of the measurements and will be addressed shortly. One expects such discrepancies in thin film samples with a ‘texture’ or some preferred orientation. We know that our sample doesn’t have a single, well defined orientation since small angular deviations
Figure 5–15: Diagram illustrating the reciprocal lattice resulting from a Gaussian crystallite distribution with an angular width, \( \chi \). Each reciprocal lattice site takes the form of a spherical cap, instead of a point.

don’t result in the characteristic arc pattern that forms from strongly oriented polycrystalline sample [37]. As such, in the approach outlined here we give the crystallites a uniform gaussian distribution about a single orientation vector and calculate the resulting diffraction pattern; this is done for all possible orientations. The reciprocal lattice of a distribution of crystallites with a gaussian distribution with angular width, \( \chi \), is shown in Fig. 5–15. Each reciprocal lattice point is now replaced with a spherical “cap”. If the gaussian distribution is replaced with a uniform distribution, we would then retrieve the spherical shells which would result from a perfectly random crystallite distribution. Each distribution orientation is defined by a polar, \( \theta \), and azimuthal \( \phi \), angle. The intensity of each reflection in the simulated diffraction pattern is scaled by the intersection of the Ewald sphere, with the new reciprocal lattice distribution.

For each \( \theta \) and \( \phi \), we can calculate a diffraction pattern. Then, employing a minimization routine in Matlab, we minimize the difference between the simulated and real diffraction pattern by varying the weights of each orientation. The resulting diffraction pattern from such a minimization can be seen in Fig. 5–16. This suggests that the crystallites in our sample are primarily oriented with the \([2 3 0]_R\) crystal axes normal to the sample surface with a distribution width of \( \sim 25^\circ \), although
Figure 5-16: Calculated diffraction pattern (blue) compared with the measured diffraction pattern (red) for the monoclinic crystal structure. The inset shows the crystallite distribution used to produce the simulated pattern. The colour indicates the relative amount of crystallites for a given orientation increasing from blue (zero) to red.

Other orientations needed to be included. This orientation in no way compromises the sensitivity of the diffraction pattern to changes along all three unit cell vectors. We now have the ability to identify the various reflections present in the diffraction pattern in addition to determining the effect atomic motion will have. It should be noted that this simple model isn’t used quantitatively in the analysis, but rather to help identify the various signatures we encounter in the dynamic diffraction data.

5.4 Results

The resulting time-resolved diffraction data (-0.5 ps to 20 ps) for an intermediate fluence of 20 mJ/cm$^2$ can be seen in Fig. 5-17-A. A variety of changes over a large range of scattering vector can be seen. The difference, relative to $t = -0.5$ ps, can be seen in figure Fig. 5-17-B; here the changes in the diffraction pattern are more apparent. Before attempting to interpret these dramatic dynamical changes to the diffraction pattern, the temporal evolution of key reflections (Fig. 5-18) will provide some insight. Here we see that, in the first 20 ps, there are two characteristic time
5.4 Results

Figure 5–17: Temporal dependence of the diffraction signal. A) Raw, background subtracted, diffraction data from 0-20 ps. Red vertical lines indicate several peaks allowed in the M1 phase due to the PLD but not in the R-phase. Blue lines indicate several peaks present in both equilibrium phases. The dashed lines indicate peaks for which $hM = 0$. B) Overall diffraction difference spectrum. The change in diffracted intensity from -0.5 to 20 ps, C) Diffraction difference spectrum for the fast dynamics. The change in diffracted intensity from -0.5 ps to 1.5 ps and D) Diffraction difference spectrum for the slow dynamics. The change in diffracted intensity from 2 ps to 10 ps (referenced to 2 ps) is shown.
5.4 Results

Figure 5–18: Time resolved diffraction peak intensity showing fast (310 ± 160 fs) and slow (1.6 ± 0.2 ps) dynamics respectively for peaks indicated by red and blue vertical lines in the diffraction spectra (Fig. 5–17). The dashed line demarks a delay of 1.5 ps and acts as guide to the eye.

Scales present in time-resolved diffraction data. After photo-excitation with a fluence of 20 mJ/cm², there is a fast 310 ± 160 fs reduction in the 302 reflection, followed by a slower 1.6 ± 0.2 ps increase in the 220 reflection. These two time scales are the only two time scales present in the first 10 ps after photo-excitation and the slow dynamics start ~1.5 ps after the fast dynamics as indicated by the dashed line in Fig. 5–18. These two characteristic time scales allow us to separate the evolution of the transition into two distinct parts by choosing suitable time points.

Fig. 5–17-C shows the change in diffracted intensity from $t = -0.5$ ps to 1.5 ps referenced to $t = -0.5$ ps, i.e. before the slow dynamics have begun. The nature of this transition can be deduced by looking at the reduction that occurs in the 302, 122 and 313 reflections, indicated in red. These three weak reflections are all forbidden reflections in the R phase and the decay in their intensity is indicative of the optically
induced SPT at this fluence. This is in agreement with previous ultrafast structural measurements which identified sub 500 fs timescales associated with the SPT [28,38]. The slow changes can be seen in Fig. 5–17-D, here the differences are referenced to $t = 1.5$ ps. Unlike the fast dynamics, which consist of many positive and negative going feature over the entire range of scattering vector, the slow dynamics are localized in the region $s \lesssim 0.45 \, \text{Å}^{-1}$ and consist of only positive going features. These changes occur in a region where electron diffraction is known to be particularly sensitive to the distribution of valence electrons [39, 40] and indicate other important changes to the Fourier components of the crystal potential. It is important to note these slow dynamics are absent for reflections with reciprocal lattice vectors perpendicular to $c_R$ ($h_M = 0$). This identifies definitively that the change in electron structure factor only occurs in reflections with components along $c_R$, i.e., the slow dynamics represent a 1D change in electrostatic crystal potential along the V-V dimer axis.

Both of these diffraction signatures scale with fluence, although they display different threshold fluences and scaling. Fig. 5–19 shows the relative change in intensity of the 220 and 302 reflections as a function of excitation fluence. The initial fast dynamics, associated with the SPT from M1 to R, have a threshold fluence of 9 mJ/cm$^2$ after which they scale linearly. The slow dynamics have a threshold fluence of 2 mJ/cm$^2$, scaling linearly with all excitation fluences $\leq 20$ mJ/cm$^2$. At fluences below $\sim 9$ mJ/cm$^2$, no change associated with the SPT is observed, only the slow dynamics remain.

To provide more insight into these two unique diffraction signatures, changes to the radial pair correlation function (PDF) were calculated. The PDF for the low temperature phase can be seen in Fig. 5–20. The peaks indicate prevalent interatomic separations in the VO$_2$ unit cell. The curves shown in Fig. 5–21, computed from the
Figure 5–19: Fluence dependence of the fast and slow signal amplitudes as measured for the (302) and (220) peaks shown in Fig. 5–18. The shaded region indicates fluences for which no fast, optically induced conversion to the R-phase is observed; there is no fast suppression of the M1 specific peaks (indicated with red lines in Fig. 5–17).

Change in diffracted intensity, are the pump induced differences in the radial PDF and represent the time-dependent difference in the radial autocorrelation function of the crystal potential following photo-excitation. The reference times and colour scheme correspond to those used in Fig. 5–17 C and Fig. 5–17 D. The nature of both the fast and the slow dynamics is more evident here. The positive going feature which grows in in Fig. 5–21A corresponds to an increased correlation at the R phase V-V separation along cR, 2.85 Å, while the adjacent negative going features represent a reduction at both M1 phase V-V separations, 2.62 Å and 2.85 Å. Thus, the fast dynamics represent a lattice structure reorganization best understood as breaking a fluence dependent fraction of the dimers on a time scale equal to or less than 310±160 fs. Fluences below 9 mJ/cm² result in no change in crystal symmetry, leaving the M1 crystal structure, and all dimers, intact.
5.4 Results

**Figure 5–20:** Calculated PDF for the low temperature phase, before photo-excitation. The labeled peak indicate I) the V-O separation, II) the V-V separation along $c_R$, III) the next nearest neighbour V-O and IV) the V-V separation along either $a_R$ or $b_R$. Note: In the monoclinic phase, due to the lowered symmetry, each of these peaks consists of more than one overlapping peak which we cannot resolve.

In contrast, the slower dynamics do not correspond to a change in lattice structure, i.e., no atomic movement of either the vanadium or oxygen atoms leads to an increase in the intensity of reflections shown in Fig. 5–17 D. The first prominent negative going feature is located at position of $\sim 1.3$ Å which corresponds to half of the dimer separation, $2.62$ Å. Similarly, the negative going feature at $\sim 4.4$ Å corresponds to the half dimer separation plus the undimerized V-V distance of $3.1$ Å. Positive going features are observed at $\sim 1.9$ Å, the average V-O separation and $\lesssim 0.8$ Å. These observations are consistent with a collective reorganization of valence charge density that preserves the M1 lattice structure. This reorganization increases the electron density in the vanadium dimer bond while decreasing the electrostatic potential on primarily the oxygen atoms; an effective modification of the atomic scattering factors. This observation will be interpreted in the discussion below.
Figure 5–21: Difference pair distribution functions for the two observed characteristic time scales. A) Difference PDF from -0.5 ps to 1.5 ps referenced to -0.5 ps. B) Difference PDF from 2 ps to 10 ps, referenced to 2 ps. The roman numerals correspond to the distances labeled in panel C with the exception of II) the R phase V-V separation along c_R and V) the average V-O separation.

If we look past the first 20 ps we see a continuing drop in the forbidden R phase reflections (Fig. 5–22). This indicates a continued transition to the rutile structure, however, at a much slower rate than the initial 300 fs response above the threshold fluence for the SPT. In contrast, positive going features (Fig. 5–17 D) reverse direction. At low fluences, these recover to a long lived value higher than the t = 0 value, which remains flat on the nanosecond time scale(Fig. 5–23). At higher fluences, these features continue to decrease over a longer time scale.
5.4 Results

Figure 5–22: Time dependence of the (30\(\bar{2}\)) reflection intensity over 500 ps for various fluences.

Figure 5–23: Time dependence of the (220) reflection intensity over 500 ps for various fluences.

5.4.1 Infrared Transmittance Measurements

In addition to the UED measurements performed on VO\(_2\), IR transmittance measurements were also performed under nearly identical conditions on the same samples in our lab. The details of the IR spectroscopy capabilities of our lab is beyond the scope of this thesis, but the measurement parameters will be presented.
Ultrashort IR pulses (centre wavelength of 5 µm, 0.25 eV) were generated in a Coherent OPerA Solo optical parametric amplifier (OPA) through the use of difference frequency generation of the OPA signal and idler [41]. Using a similar pump-probe geometry and pump conditions, the same VO₂ sample was excited using excitation fluences below the threshold for the SPT (9 mJ/cm²) and the transmitted IR pulses were detected on a 64 element mercury cadmium telluride array. During the IR transmittance measurements, the samples were held at atmospheric pressure as opposed to the 10⁻⁷ Torr at which the UED measurements were conducted.

Fig. 5–24 shows the results of the IR transmittance measurements. At lower fluences, we see a sharp drop in transmittance on the sub-500 fs timescale, which then recovers in less than 1 ps to a long lived transmittance lower than the initial, \( t = 0 \), value. At a fluence of only 3.4 mJ/cm², the transmittance decreases rapidly to less than 1% without recovering. Thus, at excitation fluences below the critical threshold to initial the SPT, VO₂ enters into a long lived metal-like state with a
5.5 Discussion

The most significant feature of the results described above is the observation of a long-lived photoinduced state that is metal-like from the perspective of mid-IR transmissivity, but with a lattice structure identical to the insulating M1 phase. We have shown that this state differs from the equilibrium insulator by a 1D reorganization of charge density, and from the equilibrium metal in that the induced electronic state is not isotropic. We interpret these results in the context of the recent cluster DMFT computations by Weber et al.

The negative going features at 1.3 Å and 4.4 Å in Fig. 5–21 suggests an increase in the filling of the $d_{xy}$ subshell that involved in V-V dimer bonds as this feature coincides with the half of the dimer distance (1.31 Å). The positive going features at 0.8 Å and 1.9 Å suggest reduced filling of the $d_{xz}$ subshell, which reduces charge density on the V and O atoms in the octahedral chains. The filling of $d_{yz}$ states oriented orthogonal to $c_R$, which are understood to be unoccupied in semiconducting VO$_2$ [18, 19], remain unchanged as demonstrated by the absence of diffraction intensity changes to the (021) reflection (Fig. 5–17). Thus, we suggest that optical excitation with fluences $<9$ mJ/cm$^2$ drives a 1D redistribution of occupancy in the $d_{xy}$ and $d_{xz}$ subshells, not a transformation to the isotropic state of the equilibrium
5.5 Discussion

metal. Suppression of a correlation induced splitting into upper and lower Hubbard bands, either preferentially in the $d_{xz}$ band (Fig. 5–25-A iv) or in both $d_{xz}$ and $d_{xy}$ subshells (Fig. 5–25-A ii), could lead to such a reorganization. The first case represents an optically induced orbital selective phase transition with a mixture of localized ($d_{xy}$) and itinerant ($d_{xz}$) behaviour [43]. The picosecond timescale of this transformation and its long-lived nature suggests that vibrational excitation of the lattice is a key factor in initiating and sustaining the reorganization, rather than the nonequilibrium population of excited carriers which relax in $\sim 1$ ps in thin pulsed laser deposition grown VO$_2$ films [18, 19]. Here a connection can be made to the work of Qazilbash et al. and their identification of the emergence of nanoscale correlated metallic domains with electronic properties unlike those of the rutile metal near the transition temperature [21, 22]. The lattice structure of these puddles was not identified, and we make a tentative connection between the correlated metallic state observed in the thermally activated phase transition and the M1 phase metastable metal accessed optically in this work.

In addition these observations, our measurements also provide insight into the SPT. Previous UED measurements by Baum et al. in a reflection geometry identified the structural transition as a two step process. The first step, the lengthening of a fluence dependent fraction of the V-V dimer, occurs with a 300 fs time constant, followed by the translation of the vanadium atoms perpendicular to $c_R$ to their R-phase coordinates with a time constant of 9.2 ps. In agreement with their measurements and those of Cavalleri et al. [28], we find an initial fast ($310\pm160$ fs) component to the structural change, however, the 9.2 ps time constant identified by Baum as the
**Figure 5–25**: Effective band diagrams of VO$_2$ and illustrations of the associated molecular orbitals. A-i) Band diagram for the rutile, metallic phase. A-ii) Modified band diagram as a result of the PLD. A-iii) The effect of el-el correlations as described by Weber et al [18]. A-iv) The band diagram resulting from the partial Mott melting of the $d_{xz}$ band. B) Illustrations of the molecular orbitals of primarily V-$3d$ character that form bands near the Fermi level in rutile VO$_2$. The oxygen atoms involved in the hybridized orbitals are indicated with colour.
second step of the SPT is absent from our measurements. Further analysis concerning the nature of the SPT and the long time scale dynamics of the SMT in VO$_2$ is ongoing.

The results presented here have several important consequences for our understanding of the hierarchy of roles for electron-lattice and electron-electron interactions in this controversial transition in VO$_2$. First, the profound decoupling of the SMT and the SPT induced through optical excitation demonstrates conclusively that the semiconducting properties of VO$_2$ in the M1 phase do not result exclusively from a Peierls mechanism. The SMT in VO$_2$ involves a mixed Peierls/Mott mechanism [16, 18]. Second, the large threshold excitation fluence for the SPT compared to that for the observed electronic reorganization demonstrates that the latent heat of the first order phase transition at $\sim$340K is dominated by the SPT rather than the electronic transition. Finally, from the perspective of the dramatic change in electronic properties, the principle role of the SPT is to alter the accessibility of the band formed by states of $d_{xy}$ symmetry [3]. In the monoclinic structure these states are depopulated, and the highest energy occupied bands have a 1D character and are susceptible to a Mott transition. The isotropic electronic character of the equilibrium rutile metal cannot be realized in the monoclinic structure [17].


Conclusion and Outlook

In summary, the design and implementation of an ultrafast electron diffractometer with RF cavity based pulse compression capabilities has been demonstrated. The temporal impulse response of the diffractometer is 334±10 fs with approximately $10^6$ electron per pulse [1]. This is a dramatic increase in instrument performance (approximately $10^2$-$10^3$ times more electrons per pulse for a sub 500 fs pulse duration) over the previous generation of ultrafast electron diffractometers without pulse compression capabilities [2,3].

Electron-laser cross correlation measurements were performed in order to measure the evolving spatio-temporal charge density of ultrashort electron pulses [4]. These measurements were compared with simulation and theory and were in excellent agreement. Similar electron-laser cross correlation measurements were also conducted to characterize the RF compression methods and demonstrate the short duration, high bunch charge electron pulses we are now capable of producing [1].

Finally, the semiconductor to metal transition is in VO$_2$ was studied using a combination of RF compressed electron pulses and time resolved IR transmittance measurements. Here, a phase transition to a metal-like state in the absence of a structural phase transition was identified. These measurements have offered unique
insight into the longstanding question of the nature of the SMT and the roles of electron-electron and electron-lattice interactions.

6.1 Outlook

The work presented in this thesis demonstrates significant improvement over the previous generation of ultrafast electron diffractometers but there is considerable room for improvement. The future goals remain similar, i.e., to produce higher brightness pulses with a shorter temporal duration. The current geometry of our diffractometer, with a large magnetic lens to camera distance, limits how small we can make the electron spot size at the sample; this results in many electrons being lost due to small sample sizes. A new sample chamber with a short lens to camera distance has been designed which, when implemented, should provide spot sizes under 500 \( \mu \)m at the sample. The temporal resolution of the diffractometer is also larger than expected and studies are being conducted to isolate the cause. A phase comparator (Analog Devices RF/IF Gain and Phase detector) is currently being used to identify which components in the RF synchronization system may be contributing to phase jitter.

The discussion of our measurements on the SMT in \( \text{VO}_2 \) has focused on the two distinct diffraction signatures that occur in the first 20 ps after photo-excitation. We are currently working to provide an interpretation of the measurements for the long time scale dynamics that occur on the \(~100\) ps time scale. In addition, future measurements will be performed on tungsten doped \( \text{VO}_2 \) samples. Doping with tungsten has been shown to strongly affect the temperature at which the SMT occurs and UED measurements will allow us to observe the effect this has on the photo-induced SMT [5]. Finally, the measurements presented on the SMT in \( \text{VO}_2 \), while providing valuable insight, would yield more information if performed on single crystals; this
would allow for a complete three dimensional reconstruction of the crystal potential. This type of crystallographic reconstruction requires extremely precise measurements of the structure factors which can’t be accomplished using a single sample orientation. Therefore, we are currently implementing the ability to precisely control the tip and tilt of our samples in order to make more accurate structural measurements.
References


