Construction of a setup for Ultrafast Electron Diffraction
van Abswoude, Peter
Chapter 2 Experimental setup for Ultrafast Electron Diffraction

2.1 Introduction

A major part of this project consisted of building the experimental facility for Ultrafast Electron Diffraction (UED) at the Zernike Institute for Advanced Materials. This chapter describes the various components of the experimental setup, a photograph of which is shown in Figure 2.1 and a schematic overview is given in Figure 2.2.

Section 2.2 describes the laser system and the two parts of the beam path: the pump and the probe. This section also introduces the two different geometries that can be used for UED experiments and the technical difficulties that have been overcome. In Section 2.3 we discuss the electron beam path, including the electron lenses for transversal focusing and the compressor for temporal resolution. In Section 2.4 the streak camera is described that is used to determine the electron pulse duration. For the experiments, spatial and temporal overlap is of crucial importance; the method to achieve this is discussed in Section 2.5. Section 2.6 discusses the data collection procedure and in Section 2.7 we explain how the data is analysed. In Section 2.8, the Ultra High Vacuum (UHV) system is discussed. This chapter ends with Section 2.9, which discusses two commissioning experiments, one on CoO nanoparticles in transmission and the other on an Ag crystal in reflection geometry.
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2.2 Description of the laser beam line

2.2.1 Laser system

The laser system is the heart of the experimental setup and consists of two lasers: an oscillator and an amplifier. The oscillator is a KM Labs Halcyon Ti Sapphire laser. Its repetition rate is 75 MHz (the repetition rate can be tuned by changing the cavity length), the centre wavelength 780 nm, the pulse energy 1.3 nJ and the pulse duration 30 fs.

The beam of the oscillator is used as a seed for the amplifier, a KM Labs Wyvern. This is also a Ti Sapphire laser but with a cryo-cooled laser crystal, operating at 50 K. The principle of the laser is regenerative amplification, with a Pockels cell coupling in and out the pulses. The repetition rate is tuneable between 1 and 5 kHz; most of the experiments described in this thesis were carried out at either 2
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or 5 kHz. The pulse duration is 50 fs and the pulse energy is 0.4 mJ at 5 kHz and 0.8 mJ at 2 kHz.

Where the beam leaves the laser enclosure, a beam splitter splits it into a pump and a probe beam.

2.2.2 Pump beam
The first arm of the laser beam path is the pump beam. The central element of the pump beam path is the delay stage, a commercially available Thor Labs LTS300/M. Since the light travels twice the distance (forward and backward) at the delay stage, 1 mm at the delay stage corresponds to 6.67 ps delay. The span of the delay stage is 300 mm, leading to a maximum delay of 2 ns. The on-axis accuracy is 5.0 µm, corresponding to 33.5 fs. On the delay stage, a hollow retroreflector OW-10-1PG is mounted, commercially available from Laser Components, with a protective gold coating, 1 inch aperture, and 1.0” accuracy.

The final part of the pump beam path is set on a movable part on the optical table (breadboard), allowing to switch between reflection and transmission geometry by simply rotating the breadboard 180°.

For transmission geometry, the pump beam is reduced in size by a collimator, which is slightly misaligned in order to obtain a beam size at the sample of 500 µm to make sure to pump the complete probed volume of the sample. A mirror inside the vacuum chamber sends the beam to the sample, and the last two mirrors

Figure 2.2: Experimental scheme for ultrafast electron diffraction [11]
before the vacuum are used to steer it. The sample is rotated by 11° in order to compensate for the fact that the light is coming under an angle.

2.2.3 Beam tilting

In the reflection geometry, the sample can be illuminated in a perpendicular direction to have the sample pumped at once. However, the electrons in grazing incidence do not arrive at all places on the surface simultaneously as illustrated in Figure 2.3. This effect is enhanced by the fact that the electrons travel at a slower speed than the speed of light. This effect is as big as 10 ps per mm. In the case of an angle of incidence of 4.5° and an electron beam size of 400 μm, 2.5 mm of the sample is probed, resulting in a temporal broadening of 25 ps. To eliminate this problem, we introduced a beam front tilt in the reflection geometry, as described in ref. [1].

In the extreme case of the electrons in grazing incidence (0°) and the laser arriving perpendicular to the sample, the required tilt angle is simply

$$\alpha = 90° - \arctan \frac{v_{ei}}{c} = 71.7°$$

[1]

and as shown in [1] the value of the required tilt angle changes less than 0.5° for sample tilts up to 5°. Therefore we can use this value irrespective the tilt angle of the sample.

The implementation of this beam tilt follows the approach presented by Baum and Zewail [1]: a grating with 1800 grooves per mm (commercially available from Spectrogon, P/N 715.703.830 PC 1800 30x75x16 NIR) is used to obtain angular dispersion, given by:

$$\varepsilon(\lambda) = \arcsin \left( \frac{\lambda}{d} - \sin \Theta_{gr} \right)$$

[2]

where \(d\) is the groove distance and \(\Theta_{gr}\) is the angle of incidence at the grating.
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The corresponding beam tilt then follows from:

\[ \alpha = \arctan \left( \frac{d_{e}}{d_{i}} \lambda_{0} \right) \]  

Solving equations [2] and [3] for \( \alpha = 71.7^\circ \), \( \lambda = 780 \) nm and \( d = 1/1800 \) mm, we obtain \( \Theta_{gr} = 31.2^\circ \). The highest intensity reflection from the grating corresponds to the first negative order, the angle being 63° with respect to normal incidence in the direction of the incoming beam.

The beam at the grating is imaged one-to-one at the sample by a spherical mirror \((f = 200 \) mm\) in a \(2f-2f\) configuration. Since in grazing incidence a rather large part of the sample is probed, also a large part of the sample needs to be pumped. Therefore we use in the horizontal direction the beam size coming out of the laser \((4 \) mm\) and in vertical direction, we focus the beam down to about 0.4 mm using a cylindrical lens \((f = 500 \) mm\).

From geometrical analysis, it can be shown that for each 1 mm sample size that is indeed pumped and probed, a deviation of 1° in the tilt angle of the laser pulse
wave front leads to a timing error of 0.7 ps, so a good optimization of the beam tilting scheme is of crucial importance.

In Section 2.5.4 we discuss a way to characterize the effect of the wave front tilt and we show the results of this characterization.

2.2.4 Probe beam
One of the two arms of the laser beam path serves to generate the probe beam of electron pulses by photoemission from the photocathode in the electron gun. In order to overcome the work function of the photocathode (4.7 eV), the third harmonic of the fundamental 780 nm (1.6 eV) is generated (260 nm, 4.8 eV). Figure 2.4 shows the general setup for third harmonic generation (THG). In the first Beta Barium Borate (BBO) crystal, second harmonic generation (SHG) takes place, after which a group delay compensation plate is inserted to compensate for group delay from the first BBO crystal. A dual wave plate is used to align the polarization of the fundamental and the second harmonic. These two wavelengths are then mixed in the second BBO crystal. The whole set of the compensation plate, the dual wave plate and the two BBO crystals is obtained as a commercially available FemtoKit system from Eksma [2]. Before the THG setup, the beam size is reduced 3 times.

The maximum yield of the THG is 3 mW, or 1%. This is also used to optimize the settings of the compressor inside the Wyvern laser: maximizing the THG yield for a certain orientation of the wave plate corresponds to the shortest laser pulse. The intensity of the UV beam is tuned by misaligning the wave plate and thereby reducing the yield of the THG.

After THG the three wavelengths are present in the beam. After four laser line mirrors (266 nm) only the third harmonic is remaining, as measured by setting the wave plate to minimum THG yield and measuring < 0.5µW on the power meter.

The beam is first expanded a factor 2 by means of a telescope, to make the focus on the photocathode tighter. Furthermore it is cleaned up by an aperture of 150 µm at the focus of the first lens of the telescope. Inside the vacuum system the beam is guided to the photocathode by a mirror.
2.3 Description of the electron beam line

The electron beam line, “A Poor Man’s X-FEL”, was bought from AccTec, a spin-off company of the University of Eindhoven. It is designed in the group “Coherence and Quantum Technology” of Professor O.J. Luiten and described in a more extensive way in the PhD thesis by T. van Oudheusden [3]. A general schematic overview is given in Figure 2.5.

2.3.1 Electron gun

The core element of the electron gun is a solid copper photocathode, which is front-illuminated by the UV laser pulses of the probe beam. The photocathode is mounted on an aluminium cylinder at negative high voltage, whereas the anode is grounded. A technical drawing of the electron gun is shown in Figure 2.6.

The gun is designed for use at acceleration voltages up to 100 kV; in our experimental setup it is used at 30 kV in order to have an electron wave length which allows for as many diffraction orders as possible to be captured by the detection system, even in reflection geometry. Since the wavelength of the electrons scales inversely with the square root of the electron energy, a lower electron energy is more suitable for this aim. The speed of the electrons with a kinetic energy of 30 keV is \(0.98 \cdot 10^8\) m/s, or 0.33c, where \(c\) is the speed of light and the corresponding wave length can be easily calculated from the relativistic De Broglie formula, giving \(\lambda = 7\) pm.

Figure 2.4: Scheme for Third Harmonic Generation (THG) [2].

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A positive side effect of using a gun that is designed for higher energies is that the chance of electrostatic breakthroughs is lower and therefore the gun could be used as delivered by the company; no additional conditioning of the gun was required.

### 2.3.2 Electron optics

Since electrons are like all charged objects subject to Coulombic repulsion, the electron beam tends to expand in all directions. In the lateral direction, this is compensated by DC solenoids, which act as magnetic lenses as described in e.g. [4]. In our setup, two solenoids are used; a first one to collimate the beam and a second one to focus the beam onto the detector. The first solenoid contains 360 windings and carries a current of 5.3 A; the second solenoid contains 935 windings and carries a current typically between 0.5 A and 0.6 A, depending on the use of the RF compressing cavity (see next sub-section). The UV beam is aligned on the photocathode such that the position of the electron beam at the detector does not move when the current through the first solenoid is changed; the second solenoid is aligned and mounted such that changing the current does not move the electron beam.
For the use of the RF compressor cavity it is of crucial importance that the electron beam goes straight through the centre of the cavity. Since the electron beam line can never be perfectly straight, corrections need to be made by means of deflecting magnets. For each direction (x and y) there are two coils, both carrying the same current and having the same number of windings. Between the coils, the external magnetic fields add up to give a homogeneous magnetic field. The electrons are deflected by the Lorentz force of this magnetic field.

2.3.3 RF compressing cavity
Space charge not only leads to an expansion of the electron bunches in the lateral direction but also in the propagation direction. This is not easily resolved by static electron optics. Straightforward solutions for this problem include low bunch charges and compact gun design [5]; these solutions reduce the number of interacting particles or the time that the electrons can interact. However, they come at a price, namely very long experimental times or very strict constraints on the vacuum chamber design.

The solution adopted in our experimental setup does not have these disadvantages. It is a way to actively compensate for the effects of Coulomb repulsion: the electrons that are the fastest are decelerated, whereas the slowest electrons are accelerated in order to achieve the smallest possible electron bunch.
dimensions at the sample position. This is done by a RF standing wave in a cavity, described more extensively in the before mentioned PhD thesis by Thijs van Oudheusden [3]. The principle is shown schematically in Figure 2.7.

Crucial for this system to work in practice is the synchronization of the oscillating electric field with the laser pulses. For this reason, the frequency of the RF field is locked to be exactly 40 times the repetition rate of the laser oscillator by a Phase Locked Loop (PLL) circuit [6], yielding an RF signal with a frequency of 40-75 MHz = 3 GHz. Small variations in the repetition rate of the oscillator, typically of the order of 200 Hz (2.7 ppm), are compensated for by the PLL circuit. The signal coming out of this is then attenuated with the AV/AF97 Attenuator from Advanced Technical Materials, Inc. This is a variable attenuation and serves as a way to tune the power sent into the RF cavity, since afterwards it is amplified by a constant factor of $10^5$ with the Microwave Amplifiers AM84-3S2-50-60R Amplifier. This signal is sent into the RF cavity, which is designed to be resonant at this frequency. Since the resonance frequency is highly dependent on the temperature, the cavity temperature is kept constant with mK precision.

The RF amplifier is designed to work at a duty cycle of around 1 %. For that reason, the PLL circuit and the RF amplifier receive a TTL signal to be switched on and off around the arrival time of the electron bunches. A small portion of the amplified light directed onto a photodiode is split off and this signal is delivered to a Digital Delay Generator (Sapphire 9212, Quantum Composers). Since the cavity has to be powered a few μs before the electrons arrive (this corresponds to a distance of the order of km travelled by the light), the electronics is triggered on
the pulse preceding the pulse to be compressed. The same signal is used for the
gating of the camera (see next sub-section).

The overall performance of the electron bunch compression was tested using a
streak camera; the results are presented in Section 0.

2.3.4 Detection system
After passing the sample, the (diffracted) electron bunch is captured by a
detection system (Princeton Instruments PI-MAX), equipped with a phosphor
screen for electron detection. When the electrons hit the phosphor screen, it
emits photons that are captured by a photocathode. The generated electrons are
subsequently multiplied by a Multi-Channel Plate (MCP). This multiplies the
intensity by generation of an avalanche of secondary electrons, which then fall
again on a fluorescent screen, from which the light is sent through a fiberoptic
bundle to a CCD chip. The advantage of this on first sight redundant imaging
system is that by gating the MCP (it is on for only 50 μs for each electron bunch)
the noise is reduced by a factor of 10 (based on a repetition rate of 2 kHz). The
gating time and the number of gates per read-out of the CCD chip (gates per
exposure or gpe) can be set in the software of the detection system (WinView).
The gate time can be set as low as 1 ns, but in our case the response time of the
phosphorescent screen is limiting and 50 μs turned out to be a good value. The
gpe-value can be seen as an analogue of the exposure time of the CCD chip.

2.4 Streak camera
2.4.1 Concept
The electron bunch duration in our experiment can be measured by a streak
camera. This is a device capable of transforming the temporal dimension into a
spatial dimension by applying a temporally varying electric field perpendicular to
the propagation direction of the electrons. Different designs of streak cameras
have been proposed: some are streaking cavities comparable to the compressing
cavity described above [7]; others are based on photoswitches like ours [5].

The streaked electron bunch can be used to determine the electron bunch
duration at the position of the sample and can be therefore used in our setup to
optimize the settings of the compressor cavity.
2.4.2 Design

Our streak camera was developed in the group of Professor Heinrich Schwoerer at the University of Stellenbosch and is described in [5]. The design and a picture of the streak camera are shown in Figure 2.8. The key component of the streak camera is a GaAs photo switch, which is triggered by the pump laser. A constant voltage is applied between two streaking plates and upon activation of the photo switch a damped oscillation of the electric field between the plates takes place as shown in Figure 2.9 (left part). Making use of the first slope of this oscillation, the electron bunch is streaked.

For the calibration of the streak camera the arrival time of the activating laser light with respect to the arrival time of the electrons is being varied by changing the position of the delay stage in the pump beam path. This leads to a movement of the electron streak. This calibration process is illustrated in the right pane of Figure 2.9. After this calibration, the length of the streak can be converted into an electron bunch duration.
2.4.3 Characterization of the RF compressor using the streak camera

The bunch duration was measured in the described way for different settings of phase and power of the compressing RF cavity. For each power value, the phase was adjusted such that the centre of the streak did not move when switching the compressor on and off. The results for the optimization of the power at a repetition rate of 5 kHz are shown in Figure 2.10; for a repetition rate of 2 kHz a similar behaviour was found, leading to an optimally compressed beam at 31 W compressor power (equilibrated). The found calibration of the streak camera was

\[
\frac{(t_2-t_1)_{ps}}{d_{pixels}} \ [5].
\]

Figure 2.9: Left panel: Typical behaviour of the oscillation after photo-excitation of the switch of the streak camera. Right panel: The calibration of the streak camera: the change of position at the delay stage can be converted to a time change and related to a deflection of the centre of the streak. In this example, the outcome of the calibration was \(\frac{(t_2-t_1)_{ps}}{d_{pixels}}\) [5].

Figure 2.10: Streaked electron bunches for different powers of the RF compressing cavity. For each power value, the phase was adjusted such that the centre of the streak does not move with respect to the uncompressed electron bunch. The repetition rate of the experiment was 5 kHz; the DC voltage between the streaking plates was 500V.
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0.4 ps/pixel. Since the width of the electron beam at the detector is 5 pixels, the resolution of the streak camera was 2 ps. Therefore, the conclusion of the experiment was that the streak length is limited by the streak camera resolution and the deducted value for the duration of the compressed bunch is less than 2 ps.

2.5 Spatial and temporal overlap
2.5.1 Photoelectric effect on a metal object
We define time zero \( T_0 \) as the position of the delay stage for which the laser pulse and the electron pulse arrive simultaneously at the sample. The knowledge of \( T_0 \) is of crucial importance for the interpretation of the data collected in real experiments since all time constants will be determined making use of this position. In addition, we need to make sure that the pumped and probed regions overlap in space.

A typical approach to ensure this spatial overlap and to determine time zero makes use of the photoelectric effect [8,9]. In such an experiment, an object (e.g. a TEM grid or a needle) is placed in the path of the electrons and the electron beam is focused in front of the object, or behind the detector, thereby creating a shadow image of the object (see Figure 2.11 (left)). The pump beam is also directed to the object, generating photoelectrons that produce a local and short-lived space-charge field. This field causes the electrons of the probe beam to be deflected if they arrive shortly after the pump beam, thereby blurring the shadow image of the object, as shown in Figure 2.11 (right). This effect can be used to optimize spatial overlap of the electron and laser beam, as well as to determine time zero, as explained in the next two sub-sections.

2.5.2 Spatial overlap
To optimize the spatial overlap of the pump and the probe beam at the sample, the experiment described before is carried out on a TEM grid and the delay stage is positioned such that the effect is very strong and visible by eye. Subsequently, the electron beam is slowly brought from overfocused to focused. Meanwhile, exact track is being kept of the position of the focused electron beam on the grid, i.e. which part of the grid is the last being visible before the electron beam is completely focused and no shadow image is visible anymore. An example of such an overfocused shadow image near the focus is shown in Figure 2.12. Now that
the part of the grid that is being probed at focus is known, the electron beam is over- or underfocused again and the laser beam is moved to make the centre of the effect overlapping with this area. Once spatial overlap is achieved in this way, it is valid for samples that are placed in the sample holder straight above or below this grid. Because of the tilt of the sample, the spatial overlap is only valid as long as the sample and the electron beam are not moved laterally (x) or in the propagation direction of the electrons (z).

2.5.3 Temporal overlap – finding time zero

To determine the delay stage position that corresponds to time zero, a shadow image of a TEM grid is created and the delay stage is moved to the position where the effect just starts to appear, as identified by eye. Now the delay stage is scanned for a region of time (typically 100 ps) around this position and images are recorded for each position at the delay stage. The effect can be made quantitative.
by summing the squared differences in pixel intensities between the image with and without the pump beam for a region of pixels where the effect takes place, as identified by eye.

A typical result of such a scan (both with the compressor and without the compressor) is shown in Figure 2.13, where the horizontal axis shows the time delay with respect to an arbitrary zero and the vertical axis represents the sum of squared differences of a certain area (which is explained more extensively in Section 2.7). Before time zero the effect is non-zero but this is due to normal fluctuations of pixel intensities and it is therefore a measure of the noise of the experiment. As can be seen, the effect is far from instantaneous, which is due to the low kinetic energy of the photoelectrons as also reported in [8]. However from the sharp edge in the case of the compressed electron bunches (red in Figure 2.13) it can be concluded that the electron bunch is short and time zero can be used for the experiments, as long as the sample is straight above or below the grid on which the determination of time zero was conducted.

2.5.4 Optimization of the wave front tilt
A similar approach can be used to optimize the beam tilting geometry for reflection experiments as described in sub-section 2.2.3 and to determine time zero in this geometry. To do this, a needle was attached to the sample holder, straight below the sample. Time zero was determined for different positions of the needle in the direction of the propagation of the electron bunches. Without beam tilting, the shift of time zero is expected to be 10 ps per mm movement. This is confirmed by an experiment with two different positions separated by 2.0 mm; the results are shown in Figure 2.14, upper panel. The experiment was repeated for a tilted pulse wave front, and these results are shown in the lower panel. From this experiment it is clear that the change in time zero is significantly reduced by tilting the wave front; for two positions that are 1.2 mm apart in space, the shift of time zero is reduced to below 5 ps, corresponding to 3 ps/mm. Due to a reduced fluence in the tilted pulse wave front geometry (not all intensity goes into the first diffractive order of the grating and the beam size is increased), it was not possible to make the effect as strong as in the non-tilted case and this limited our determination of the change in time zero.
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Figure 2.13: Determination of time zero by means of the photoelectric effect on a TEM mesh. In the analysis, the sum of squared differences is taken for an area of six pixels.

Figure 2.14: Determination of time zero for different positions of the needle. Upper pane: without beam tilt. Lower pane: with beam tilt the difference in time zero is reduced.
Data acquisition software 2.6

The data discussed in this thesis were acquired with the help of a LabView code summarized in Figure 2.15. The software is able to communicate with the delay stage to move a chosen distance and with the camera to acquire and save an image with settings that are established before in the WinView software. The starting position of the delay stage is set by the user in LabView, as well as the time window, the time step and the number of scans. The region of interest of the CCD chip and the number of MCP-gates per exposure (gpe) are set in WinView. The software operates the pneumatically driven shutter by changing the status of an RS232 port, which is connected via a relais to a pneumatic valve and cylinder. For each time step of a scan, two images are acquired and saved: one with the shutter of the pump beam open (pumped) and one with the shutter of the pump beam closed (unpumped). In this way, each pumped image has its own unpumped reference image. This is done in order to compensate for any long-term drift in intensity, e.g. due to a long-term drift in the laser output power. When the desired time series is finished, another scan will start from the same starting position of the delay stage until the specified number of scans is reached. Each file is given a name by the LabView program; the name of the experiment, the parameters of the experiment, and some identifiers for the time step and the scan in which it was taken are all encoded in the file name.

Data analysis software 2.7

A Matlab code was used to extract a transient signal from the recorded diffraction patterns. All WinView files are loaded to Matlab and added to a matrix.
Depending on the type of information that we were looking for, the subsequent analysis described in the following subsections was done. For each time step, the outcome for the unpumped image was subtracted from the outcome for the pumped image. These outcomes were averaged over the runs of the experiment and plotted as a function of delay between the pump and the probe pulse.

2.7.1 Data analysis for determination of temporal overlap
In the case of a determination of temporal overlap (“finding time zero”) we just looked for any change in pixel intensities: when the image gets blurred, the intensity of the pixels in the shadow of the bars of the TEM mesh increases, whereas the intensity of the pixels which are in the holes, decreases. The quantitative measure for all these changes is the sum of squared differences (SSD) for a small region of interest around the centre of the effect.

2.7.2 Data analysis for polycrystalline diffraction patterns
For the extraction of a signal from a polycrystalline, ring-shaped diffraction pattern, a radial average needs to be calculated. To do this, for each pixel that is not in the region of the beam block, the distance to the centre of the undiffracted beam is calculated and rounded. Subsequently, the value of the pixel is added to the sum of values for that particular integer distance and the number of pixels with that distance is increased by one. In the end, the average value is calculated. An example of such a radially averaged image is shown in the left panel of Figure 2.16 (left panel, red points).

To subtract the background of inelastically scattered electrons as well as the remainder of the unscattered central beam (the part that is not blocked by the beam block), the regions of the graph where there is no signal are extrapolated to the regions where there is a signal (Figure 2.16, left panel, black line) and this is subtracted from the graph, leading to a graph with only the peaks (Figure 2.16, right panel).

As soon as this information is retrieved, the difference between pumped and unpumped image is taken and divided by the unpumped image and this value is the relative change of diffraction intensity. This can be plotted in different ways as a trace graph for a specific value of the scattering vector. An example of the result of this analysis is given in Section 2.9 where the first test experiment is discussed.
2.7.3 Data analysis for single-crystalline diffraction patterns

For single crystals, the background subtraction procedure is different from the one used for polycrystalline diffraction patterns. In this case, instead of interpolation of the background between the diffraction peaks the approach is to ignore the diffraction spots when calculating the background.

An example of the procedure is illustrated in Figure 2.17, where the original diffraction pattern is shown in the first panel. First of all, the positions of the Bragg spots are indicated in the Matlab software. A circular region around each Bragg spot is excluded from the calculation of the radial average by setting the pixels to zero as indicated in the second panel. Now the radial average is calculated over the remaining pixels, as described before for the polycrystalline case. This radial average is plotted in the third panel. The last step is subtracting for each pixel in the image (including the Bragg spots) the value of the radial average from the original value. The diffraction pattern after background subtraction is shown in the last panel of Figure 2.17. Then the intensity of each Bragg spot is calculated as the sum of the pixels in a circle with a radius of 5 pixels around the centre of the spot.

2.7.4 Data analysis for satellite intensities

In chapter 4 the UED experiments performed to study the phase transition of a Heusler alloy with composition Ni$_{50}$Mn$_{30.5}$Ga$_{19.5}$ will be presented. For that sample one phase is characterized by satellite spots around the main Bragg spots, which are absent in the other phase (for details see chapter 4). We therefore had to develop a similar approach as explained for the background subtraction of the Bragg spots for extracting the intensity of these satellites. The environment of
each Bragg spot is considered individually. The first panel of Figure 2.18 shows such an area. The first step is again to exclude the regions of the satellites, as illustrated in the second panel. Subsequently the radial average is calculated (third panel) and subtracted (result in the fourth panel). After background subtraction, the intensity of each satellite peak is determined as the sum of the pixel values in a circle of 3 pixels around the centre of the satellite.

After calculating the background-subtracted values for both the Bragg spots and satellites, the relative difference is determined in the usual manner: the value without pump beam is subtracted from the value with the pump beam and the difference is divided by the value without the pump beam.

Figure 2.17: Example of the radial background subtraction for single-crystalline diffraction patterns. The upper left panel shows the original diffraction pattern; the upper right panel presents the diffraction pattern where all Bragg spot areas are excluded; the lower left panel represents the radial averaged intensity as a function of the distance to the centre; and the lower right panel shows the diffraction pattern after background subtraction.
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Ultrahigh vacuum system

Vacuum conditions are required for electron diffraction experiments to have a large enough mean free path for the electrons and no electrical breakthrough at the position of the photocathode. However in the case of our experimental setup where surface science experiments are planned, a much better, ultrahigh vacuum (UHV) environment is of crucial importance.

Our vacuum system consists of three vacuum chambers that can all be closed separately by valves. The first chamber is the electron gun chamber. Because of construction reasons the vacuum of this chamber is not UHV but the pressure is of

Figure 2.18: Example of the extraction of the intensity for satellite data. Roughly the same procedure as for the Bragg spots is followed: the upper left panel shows a Bragg spot and the satellites in its environment; the upper right panel displays the exclusion of the satellite positions; the lower left panel represents the radial average of the background intensity and the lower right panel shows the corrected image of the diffraction intensities of the satellite peaks.
the order of $10^{-7}$ mbar. This is not ideal but acceptable because the connection to the experimental chamber is narrow and therefore has a low pumping speed. Furthermore, at the position of the incoupling module of the UV light, there is additional pumping. The original high voltage feedthrough is replaced by a UHV compatible feedthrough to improve the vacuum.

The second chamber is the experimental chamber, which is pumped by an ion pump with a titanium sublimation pump. The typical pressure reached in this chamber is in the order of $10^{-10}$ mbar. The design of this chamber is such that the distance between the centre of the compressor and the position of the sample is as short as possible (11 cm).

The third chamber is the sample preparation chamber, which is pumped by a turbomolecular pump. The typical pressure reached in this chamber is in the order of $10^{-10}$ mbar. This chamber is equipped with a Knudsen cell and an e-beam evaporator for the preparation of metallic films, a sputter gun for cleaning single crystalline surfaces and an X-ray Photoelectron Spectroscopy (XPS) system for in-situ characterization of prepared samples. Furthermore there is a manipulator for x, y, z, θ motion and a cryostat for sample cooling. For room temperature diffraction experiments in transmission, the sample holder is very simple: a copper block with holes over which a TEM mesh or a disk with an aperture can be positioned and fixed with silver paint. However, the sample holder for low temperature reflection experiments is more sophisticated; a photograph is shown in Figure 2.19. The hole in the front is to mount the crystal. Behind the sample there are boroelectric resistive sample heating plates for annealing of the sample up to about 1050 K. A type K thermocouple can be mounted in or next to the crystal for precise measurement of high temperatures. For the measurements of low temperatures, a silicon diode (Lakeshore DT-670) is mounted in the copper frame.

2.9 Test experiments

2.9.1 Transmission geometry: CoO nanoparticles

A first experiment to test the performance of the experimental setup in transmission geometry was carried out on CoO nanoparticles with an organic ligand shell. The preparation of these nanoparticles is discussed in [10]; their size distribution was between 5 and 10 nm. The nanoparticles were dropcast onto a
TEM grid covered with holey carbon on lacy carbon (S1000 from SPI supplies) from a toluene solution. An optical microscope image and a Scanning Electron Microscope (SEM) image of this sample are shown in Figure 2.21, left panel.

The grid was fixed to the transmission sample holder with silver paint and a time-resolved electron diffraction experiment was carried out with a 250 fs step size, a window of 100 ps and 10 scans. For each time step, an unpumped and a pumped diffraction pattern were recorded with 10000 gates per exposure, corresponding to 5 seconds of acquisition time (the repetition rate was 2 kHz).

The diffraction pattern is shown in Figure 2.21, right side. The analysis described in sub-section 2.7 was performed and the results are shown in Figure 2.20. A transient graph is made for the centre of the (110) diffraction ring as well as for the (220) ring. The effect induced by the laser light on the diffraction pattern is fast: the maximum intensity change is obtained within 4 ps and the edge of the onset of the effect is sharp, indicating an over-all time resolution that is much

Figure 2.19: Sample holder for reflection experiments. On the copper block, the sample can be mounted in the circle on the right; on the left there is a diode for low temperature measurements and there is also a thermocouple to be connected to the sample for high temperature measurements. On the back of the sample holder, borolectric heating plates are mounted.
better than 1 ps. The time constant of the process is estimated to be 1.3 ps, which is well in accordance with a simulation similar to the one discussed in Chapter 3. The fast behaviour can be explained by considering the fact that the nanoparticles
are isolated so they do not interact and the time scale of the effect is not influenced by any diffusion process.

The size of the effect is several percent; especially in the data for the (111) diffraction ring the good signal to noise of the data is demonstrated. Since some scattered laser light hits the detector and creates counts on the CCD camera the relative intensity change before \textit{time zero} is not exactly zero. In later experiments the average of the data before time zero will be deducted to better show the size of the time resolved changes obtained; however in this chapter on the commissioning of the setup we found it useful to leave it in the data to show that an offset from zero exists and discuss it.

2.9.2 Reflection geometry: Ag single crystal

A second test experiment for the setup was performed on an Ag single crystal, mounted on the reflection sample holder as shown in Figure 2.22, left panel (where the laser beam is also visible on the sample). The crystal was cleaned by two cycles of Ar sputtering (2 kV ions with a sputter current of 4 μA), followed by thermal annealing at 125°C for 20 minutes.

The diffraction pattern in reflection geometry is shown in Figure 2.22, right panel. A time-resolved diffraction experiment was performed with the beam tilting scheme, as discussed in Sections 2.2.3 and 2.5.4. The laser power of the pump
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beam was 1100 mW (resulting in a fluence of about 11 mJ/cm$^2$, but the fluence is not well-known because of the issues also addressed in Section 2.5.4); the step size was 1 ps and the time window 180 ps.

The results of the experiment for the (111) reflection are shown in Figure 2.23, together with a simulation, which will be more thoroughly discussed in Chapter 3. Clearly, the value of the time constant from the simulation is much smaller than the one observed in the experimental data; most probably this is due to the wave front tilt geometry not being optimal.

References