A new lab diffractometer for surface X-ray diffraction (SXRD)

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Abstract

We introduce the new lab diffractometer for surface X-ray diffraction (SXRD) mesurements which has been installed in the X-ray lab of the Division for Synchrotron Radiation Research at Lund University. The device is equipped with a molybdenum microfocus X-ray source and a 2D hybrid photon counting detector. The setup is inspired by high energy surface diffraction setups (HE-SXRD) found at synchrotrons. We discuss how this device performs for studying the 111 surface of Rh and Au single crystals and describe noise reduction measures which had to been taken to discriminate the weak singal of crystal truncation rods (CTRs) from random noise generated by diffuse scattering from air.

1 Introduction

Surface X-ray diffraction (SXRD) is a powerful technique to study surface structures on single crystals.[(Felici, 2012)] In order to be able to observe diffraction from a metallic single crystal surface it is necessary to prepare the crystal surface under suitable conditions in high or ultrahigh vacuum. [XYZ] This is done in specially designed high vacuum (HV) or ultrahigh vacuum (UHV) reaction chambers in which it is possible to prepare the surface and to perform gas adsorption or catalysis experiments. A surface diffractometer needs thus to support heavy and large reaction chambers like the flow reactor which was used in the diffraction experiments performed in the context of this work. [(van Rijn et al., 2010)] In traditional SXRD studies synchrotron radiation is used to measure the weak diffraction signal from the surface or a surface structure with a sufficiently high signal to to noise ratio on a reasonable timescale. This may be up to 60 min ??? for a rotational scan of 180°. Given that synchrotron beamtime is rare it is crucial to use it as efficiently as possible. Beeing able to perform preliminary experiments on a lab based diffractometer is an enormous advantage and makes it possible to narrow down experimental parameters in previous studies. Different types of diffractometers have been designed to study surfaces efficiently. These instruments have in common that they combine a sufficient amount of degrees of freedom for the alignment of a sample surface

parallel to the incident beam and make it possible to set a specific incidence angle. They can be divided in instruments in which the motion of the sample is coupled [[(Lohmeier & Vlieg, 1993)]] with the motion of the detector and devices where this motion is not coupled. [XYZ]. An overview of possible diffracometer types and their geometry has been given by Bunk et al. previously. [(Bunk & Nielsen, 2004)] These devices have been designed to perform surface diffraction experiments at low X-ray energies ($\tilde{2}$0keV). In order to cover a large portion of reciprocal space, it is necessary that the detector can be positioned on a sphere around the sample so that the necessary information can measured by specific scans through reciprocal space. With the development of high energy surface X-ray diffraction (HE SXRD) the instrument geometry to perform suitable surface diffraction experiments has become simpler. By using a 2D detector at X-ray energies between 50 and 70 keV it is possible to collect a large portion of reciprocal space in a single rotational scan.[(Gustafson et al., 2014)] Herein we introduce the X-ray diffraction lab which was built at the Division for Synchrotron Radiation Research at Lund University. The lab is equipped with a new type of surface diffraction setup which combines the simplified design of diffractometer for high energies with a lab based microfocus X-ray source with 17.6 keV. While a lab source has a much lower photon flux than a synchrotron beam, the ulimited availability of beamtime in combination with a noise free hybrid X-ray photon counting detector should make it possible to do preliminary surface diffraction experiments. The new diffractometer was designed and assembled by the German company Sirius XRS. We will present angle calculations for the new setup and compare its performance in measuring single crystal surfaces of the Rh(111) and Au(111). Furthermore we will discuss the required noise reduction measures and the resulting limitations of the current instrument configuration.

2 The surface diffraction setup

The new surface diffractometer was custom built for surface diffraction studies by SIRIUS XRS from commercially available components (Figure 2). It is designed to support a UHV reaction chamber which was designed to study surface diffraction during catalytic reactions. [XYZ] The diffractometer is located in an irradiation room and remotely operated withe commercially available control software SPEC which runs on a Unix computer. [XYZ] For the description of the instrument the same definitions are used to describe the laboratory framework as they are used by the SPEC software package. The direct beam is defined as y-axis, the sample normal as z-axis and the axis perpendicular to the direct beam as x-axis. The diffractometer (also referred to as goniometer in lab setups) has four rotations and three translations axis (x, y, z). With these degrees of freedom the reaction chamber with the single crystal sample inside can be properly aligned. The sample surface is aligned to be parallel to the indident beam with ϕ and χ, these rotations rotate the sample around the x-axis or y-axis depending on the position of the θ rotation stage. The incidence angle

between the sample surface and the incoming beam is set with the underlying μ rotation which rotates the sample around the x-axis. Surfaces are characterized by θ rotational scans around the z-axis. The focal distance of the X-ray optics is at 250 mm where the single crystal sample is positioned under high vacuum. The X-ray beam travels this distance through air. A frame was build around the setup from aluminium construction profiles, so that a beamstop and the primary shield can be installed easily.

2.1 The Pilatus3 R 300K CdTe

X-ray photons are detected with a Pilatus3 R 300K CdTe detector from Dectris. [XYZ] CdTe has a quantum efficiency $>$ 90 % for Mo radiation. The detector consists of three modules and has a total area of 83.8 x 106.6 mm. [XYZ] It has a readout time of 7 ms and a maximum frame rate of 20 Hz. The detector is mounted on a three translation axis. Both motions which are perpendicular to the incident beam along the x and z axis are automated and their motion can be controlled via SPEC. The travel range of both translation axis is 500 mm. A surface of 500x500 mm^2. The sample to detector distance can manually be adjusted and it can be placed at a maximum distance of 500 mm from the centre of rotation. In contrast to synchrotron radiation, radiation from the lab source is not polarized. The detector is mounted on two motorized translation stages with a travel range of 500 mm each. It thus covers an area 0.25 m^2 in total. This would be equivalent to a detector with 2906 x 2906 pixel (8.4 MP).

2.2 The Mo Microfocus X-ray source

The setup is equipped with a "GeniX 3D Mo High Flux ???" microfocus X-ray source from Xenocs. This source is a combination of a sealed tube with a Mo target and the FOX2D Mo 25INF??? collimating multilayer opticss a graded multilayer mirror.[("GeniX3D - Installation and operation manual", 20/06/2014)] The beam shape can be modified with a system of slits in front of the optics. With these slits it is possible to cut the beam symmetrically along the x and the z axis. In order to maximize the number of photons the slits the source has been operated with the slits fully open along both axis. The resulting size of the direct beam on the detector is about of 1000 x 500 μm (Fig. XYZ). A total of $6.3{\cdot}10^6$ photons is detected per second is detected. The energy bandwidth of the primary beam is reduced by the optics to the Kα doublet of Mo with an average energy of 17.6 keV. The focal point of the source is 250 mm away from the optics. The software SPEC requires a single wavelength on which all reciprocal space calculations are based on. Given that the Mo Kα doublet is used for the measurement an average wavelenght of 0.71 Åis used.

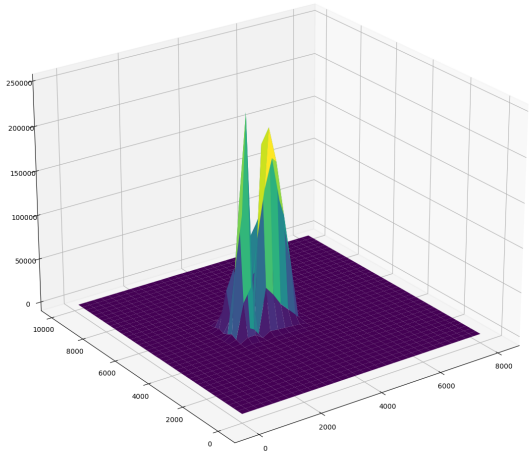

Figure 1: 3D representation of the direct beam each pixel has a length of 172 microns.

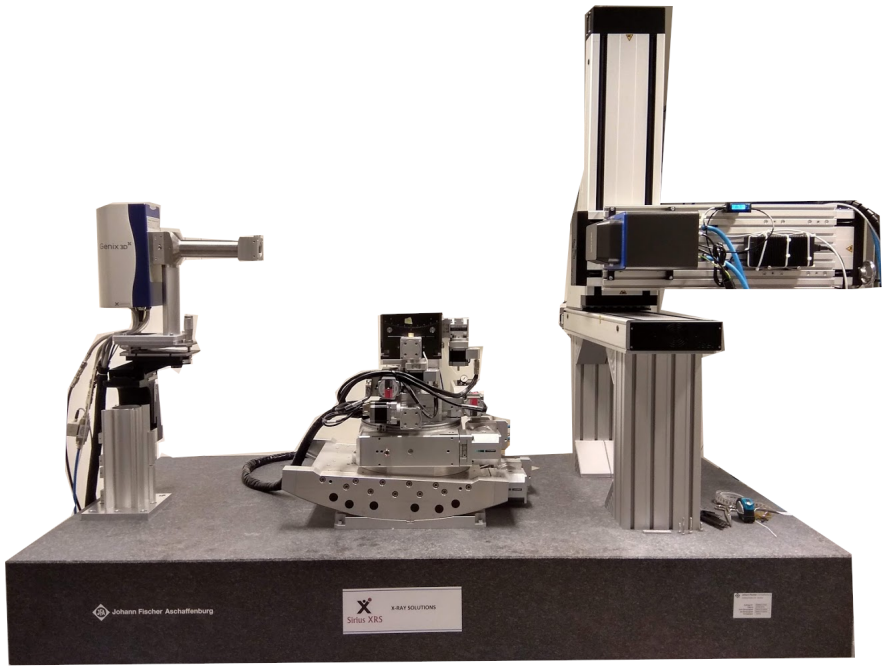

Figure 2: The surface diffractometer in the lab at the Division for Synchrotron Radiation Research at Lund University.

3 Angles Calculation

Angle calculations for diffractometers with a different number of circles and different instrument geometries have been presented earlier. An overview of this work has been given by Bunk et al. [(Bunk & Nielsen, 2004)]. The design of the new surface diffractometer is derived from high energy surface diffraction setups used at synchrotrons. In contrast to traditional surface diffractometer geometries there is no need to be able to position the detector on a circle around the sample. Thanks to the high energy X-rays used in HE-SXRD measurements, a sufficiently large fraction of reciprocal space is covered when a 2D Detector is used. After alignment of the sample surface parallel to the beam, the incidence angle μ with the direct beam is set and the changes on the surface are detected in θ rotational scans with the detector kept at the same position. The software SPEC which is used to operate the diffractometer is used in six-circle mode. In this mode the software assumes that the diffractometer μ circle which is used to set the incidence angle between the sample surface and the incidence beam is coupled with the out of plane motion of the detector. By setting an incidence angle μ the detector moves in z-direction to form the angle γ with the incident beam. (see Fig. 3). The aim of these angle calculations is to be able to index each point on the detector plane with its respective HKL coordinates. As a function of the θ circle with the incident beam. In order to be consistent with previous literature of this type of calculations we adopt the procedure from Lohmeier & Vlieg [(Lohmeier & Vlieg, 1993)].

The crystal lattice is spanned by the vectors $\mathbf{a}_i$ with the angles α_i betwen them (i = 1, 2, 3). The resulting reciprocal lattice vectors $\mathbf{b}_i$ is $|\mathbf{b}|$

4 Experimental

Surface diffraction was measured on the surface of Au(111) and Rh(111) single crystals. The surface has been prepared by 3 consecutive cycles of sputtering (Argon 2·10$^-$4mbar, 1.5 keV, 10 mA for 20 min) and annealing (5 min after carefully increasing the tempreature). The Au(111) crystal was annealed at XYZ °C, the Rh(111) crystal at XYZ°C

4.1 Data Collection Strategy

The surface diffractometer reported here was designed to perform surface diffraction measurements in similar way as it is done for high energy X-rays at the synchrotron ($<$ 60??? keV). While the intensity of synchrotron radiation makes it possible to record a 180 ° rotational scan within a couple of minutes and a good S/N ratio the same scan can take up to 24h with the lab source, even at a much coarser angular step size. Images of the shown hkl scans have been exposed for 250 or 300 seconds per point. In order to discriminate between the weak signal of the CTR and the background noise the S/N ratio is used in order to know to which extent the signal of CTRs can be measured with the

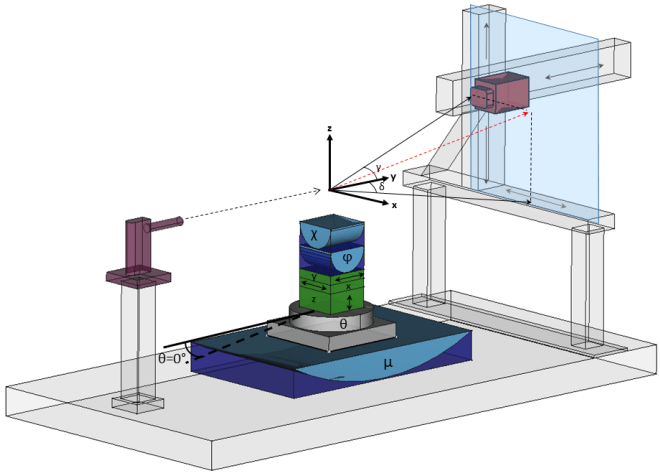

Figure 3: Schematic representation of the surface diffractometer with the four rotations μ, θ, χ and ϕ without the UHV chamber. The setup is shown a for $\theta = 0°$.

current experimental configuration. Given that the photon flux of the lab setup is much lower than the photon flux of synchrotron radiation experiments need to be adjusted. While it is possible to make up some of the

5 Noise and Noise Reduction Measures

As mentioned above the S/N ratio of CTRs is weak. Given that the photon flux of the X-ray source and the resulting number of scattered photons is fixed, the only way to improve this ratio is to decrease the noise on the detector. This means to eliminate the number of unwanted photons which result in unwanted counts on the detector on the timescale of an exposure of 600-1800 seconds. When exposing the detector in the dark (shutter closed) for 1800 seconds it becomes evident that there is a certain number of counts detected.

6 Results and Discussion

The photon flux of the synchrotron beam for the surface diffraction beamline ID03 at ESRF has been reported to be as high as $2{\cdot}10^{13}$ ph/s (Balmes et al., 2009) The primary beam thus contains approximately 3 million times more photons than provided by the lab source. While the Bragg diffraction spots cannot be measured on the detector at the same time as the CTRs with synchrotron radiation, this is not an issue with the currently used lab source. Bragg diffraction spots are magnitudes higher in intensity than the crystal truncation rods

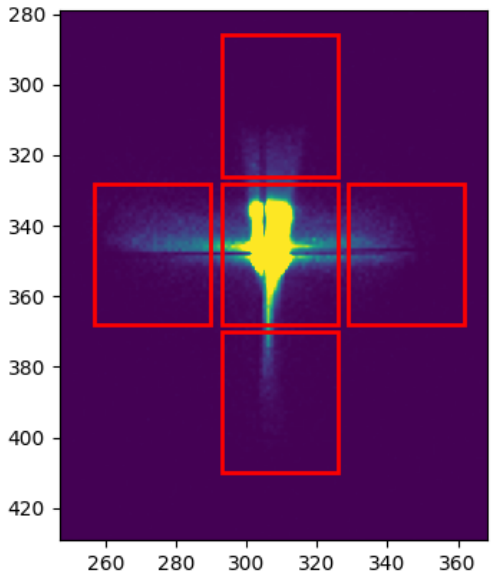

Figure 4: Image of of the direct beam with the ROI of the signal of interest (center rectangle). The four surounding regions of interest are used to extract the intensity of the background noise.

(CTRs) which are relevant for the determination of surface structures. The number of accumulated photons over the time span of 300 seconds for the 101 diffraction spot of the Au(111) crystal corresponds approximately $1.4 \cdot 10^6$ photons. The Bragg diffraction spot is quite broad compared to the CTR or the direct beam. As a consequence the region of interest to estimate the noise would need to be re defined to properly estimate the S/N ratio.

From the initially $6.3 \cdot 10^6$ ph/s of the direct beam only 0.07 ph/s can be detected from the interaction of the primary beam with Au(111) surface at the weakest point (l=1.5 of the 110 - 113 CTR). At this point of the CTR the accumulated number of photons in the ROI of the CTR is approximately 20 photons higher than the signal in the ROI for the noise which has a total of XYZ photons.

–> With these low signals it is probably necessary to take into account air-scattering from the diffracted beam and air-absorption –> Why is this not a problem at higher X-ray energies (Diffuse scattering by air as a function of X-ray energy)

The S/N ratio at the wekest point of the 110 –> 112 CTR on Cu(100) is 1.61 at an exposure time of 1s (measured at Diamond, P07). The roi of the CTR contains approximately 200 counts, rois left an right about 110 counts.

–> Mention Differences between Synchrotron and the lab e.g. Polarization, Intensity

6.1 Crystal truncations rods of Au(111) and Rh(111)

In order to determine the limitations of the current setup configuration we have performed measurements on the 111-surface of Au (Z = 79) and Rh (Z = 45) crystals which are in different rows of the perodic table.

6.2 Au(111) surface

By running subsequent θ rotational scans at different detector positions it is possible to assemble an image which covers a large part of reciprocal space. Similar as it can be recorded at the synchrotron. The surface of the Au(111) crystal was investigated by applying this procedure. 16 θ-rotational scans of the Au(111) surface have been recorded and assembled into one image (Figure 11)

7 Conclusion

A new lab based surface diffractometer was built at Lund University which is designed to perform surface diffraction measurements. Comparing diffraction measurements on the 111 surface of Au (Z = 79) and Rh (Z = 45) single crystals has shown that the current setup configuration limits surface diffraction experiments to single crystals with an atomic number in the range of 79 or higher. With the microfocus X-ray source SXRD studies on atomic monolayers are currently restricted to high Z metals like Au or Pt (Z = 78). S/N ratios above

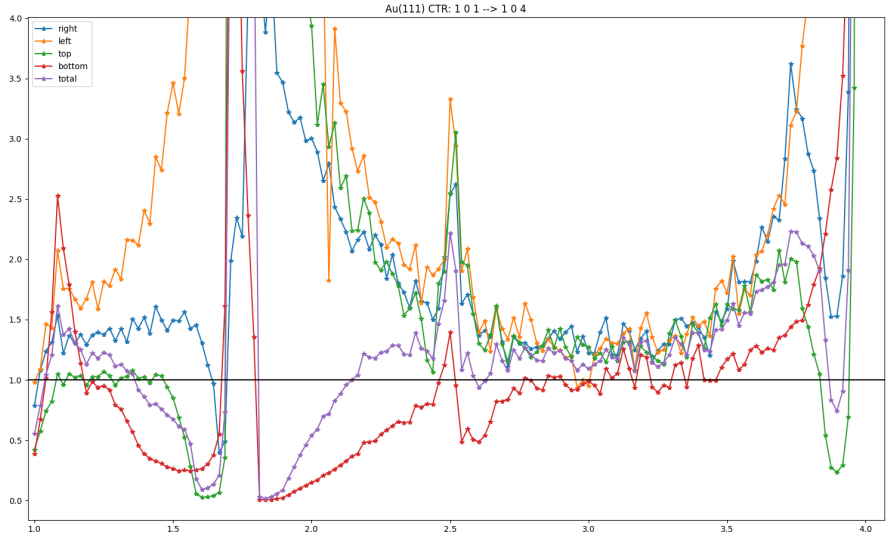

Figure 5: S/N Ratio of the CTR: Au(111) 1 0 1 - 1 0 4

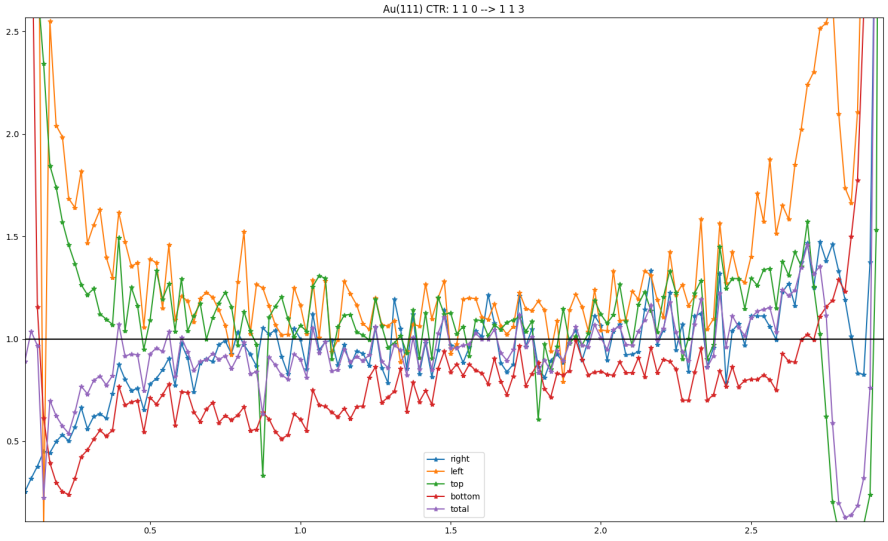

Figure 6: S/N Ration of the CTR: Au(111) 1 1 0 - 1 1 3

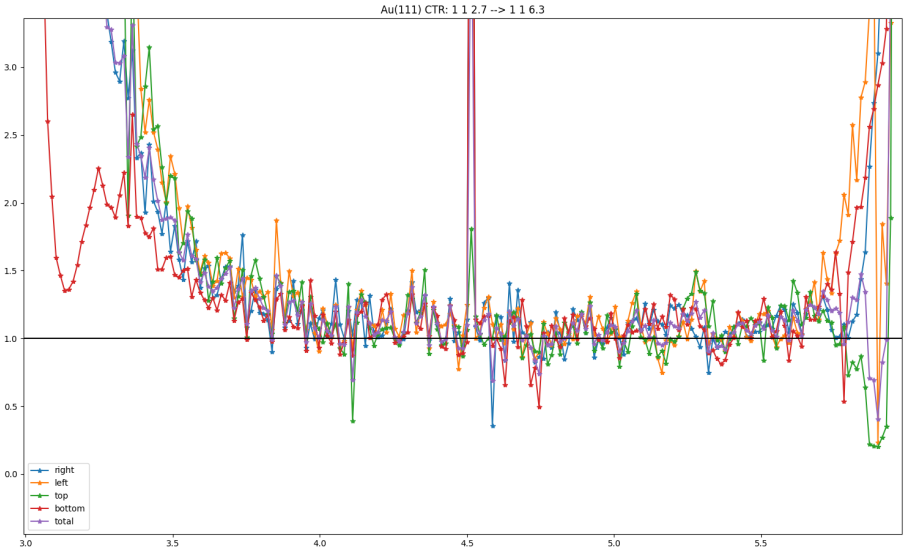

Figure 7: S/N Ration of the CTR: Au(111) 1 1 2.7 - 1 1 6.3

Figure 8: S/N Ration of the CTR: Rh(111) 1 0 1 - 1 0 4

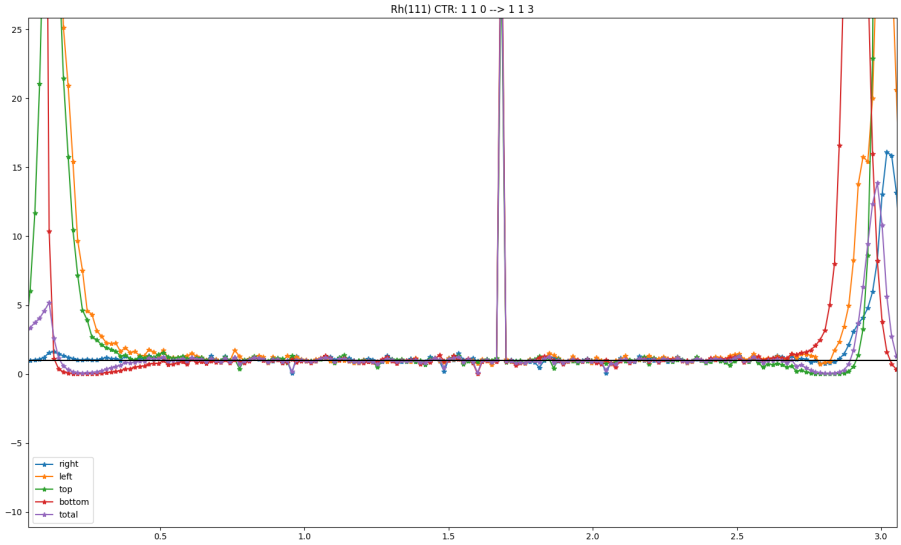

Figure 9: S/N Ration of the CTR: Rh(111) 1 1 0 - 1 1 3

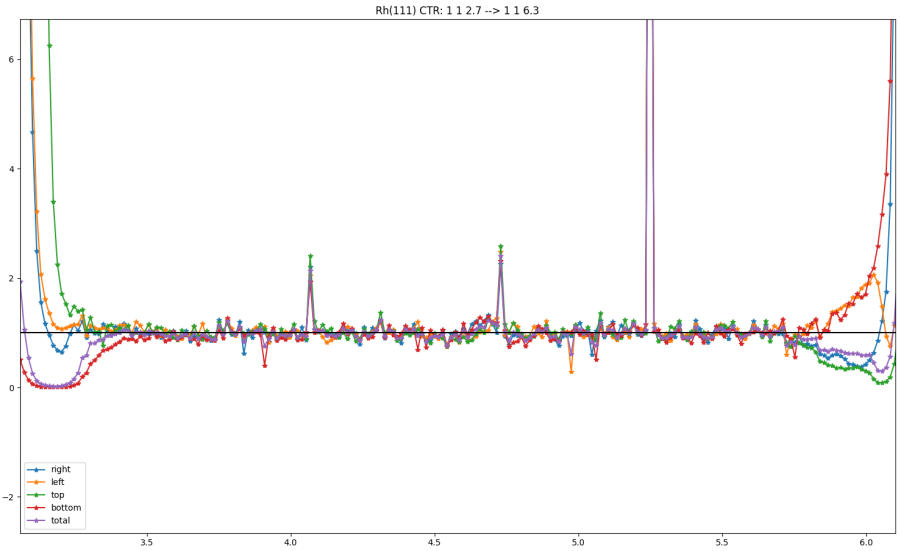

Figure 10: S/N Ration of the CTR: Rh(111) 1 1 2.7 - 1 1 6.3

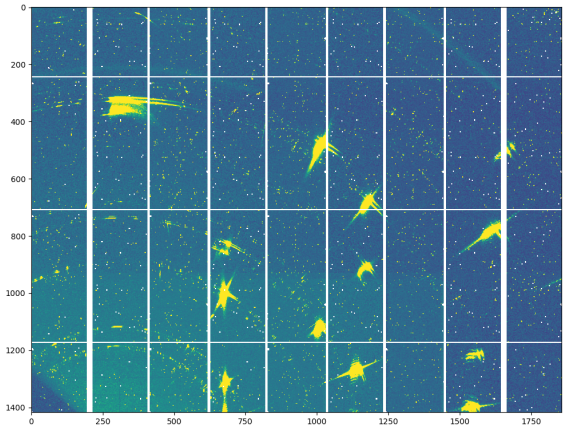

Figure 11: θ-rotational on a clean Au(111) surface covering a θ-range of 90°

1 can be observed for high Z metals only when measures are taken to prevent random photons from diffuse air scattering reaching the detector.

This is however not the case for experiments where multilayered oxides are studied or when studying the bulk crystal. The new surface diffractometer makes it possible to perform preliminary experiments prior to beamtimes in order to narrow down experimental of the catalysis experiments With the help of the new surface diffractometer it possible to demonstrate the basic principles of X-ray diffraction very well. It

8 Acknowledgements

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