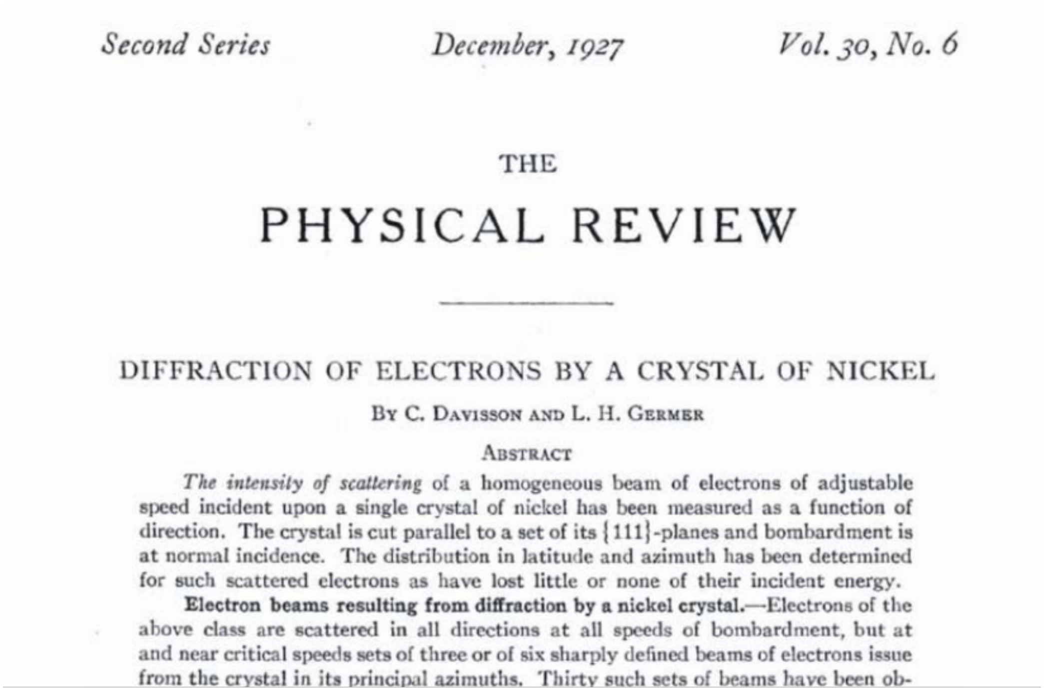
(LEED = Low Energy Electron Diffraction)



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PHYSICAL REVIEW

DIFFRACTION OF ELECTRONS BY A CRYSTAL OF NICKEL

By C. Davisson and L. H. Germer

Abstract

The intensity of scattering of a homogeneous beam of electrons of adjustable speed incident upon a single crystal of nickel has been measured as a function of direction. The crystal is cut parallel to a set of its {111}-planes and bombardment is at normal incidence. The distribution in latitude and azimuth has been determined for such scattered electrons as have lost little or none of their incident energy.

Electron beams resulting from diffraction by a nickel crystal.—Electrons of the above class are scattered in all directions at all speeds of bombardment, but at and near critical speeds sets of three or of six sharply defined beams of electrons issue from the crystal in its principal azimuths. Thirty such sets of beams have been ob-

The general aim of this experiment is to familiarize you with the operation of a low energy electron diffraction apparatus. Studying a simple example, you will learn how to use this method to determine the structure of surfaces. In addition, the experiment shows that electrons can actually behave like waves. Historical side note: In a corresponding experiment in 1927, Davisson and Germer first discovered the wave character of electrons. This initiated the development of the quantum mechanical description of matter (see the extract from the publication above).

1 Introduction

Inform yourself by means of books [1-3] or the web about the following terms (see also bibliography at the end):

Properties of free electrons, interaction of electrons with matter, Coulomb potential, De Broglie wavelength, work function, Fermi energy*, crystal surfaces, interference, diffraction by a lattice (lattice formula), Ewald construction*, real lattice, unit cell, basis, Miller indices, reciprocal lattice*, Bravais lattice, Fourier transformation*, Debye-Waller factor*, surface reconstruction*, surface adsorption, superstructures (commensurate / incommensurate)*, rotational, mirror and translational domains*, growth modes of films*.*

Generation of free electrons (thermionic emission), construction of electron guns, acceleration of electrons in electric and magnetic fields, generation and measurement of vacuum*, surface impact rate of a gas.*

* identifies terms for advanced issues which are developed and deepened in the module.

2 Preparatory tasks

2.1 Derive a general formula for the De Broglie wavelength of free mass particles with mass m and kinetic energy E.

Apply the formula to the special case of electrons.

Which wavelengths (in angstroms) are available at energies of 30 eV, 100 eV and 300 eV?

2.2 Consider which elastic and inelastic processes can occur in the scattering process of low energy electrons by solids. Why and how do the electrons interact for instance with a metal crystal?

2.3 Make a sketch of the ideal (unreconstructed) Au(111) surface and calculate the lattice constant of the surface unit cell and the density of the atoms on the surface (in cm^{-2}).

2.4 Use Figure 2 to comprehend the path of the electrons from the thermionic cathode to the LEED screen.

Explain the function of the individual components of the LEED optics!

What influence do the electric fields have on the electron beam?

Please also pay attention to the polarity of the individual voltages!

3 Experiment

Security note: You work partly in the dark. Therefore, behave cautiously. Your phone´s flashlight might be helpful.

3.1 General setup of the experiment

Let the supervisor explain the design of the experimental setup (see

Figure 1). In particular, the following facts are important:

- How is the vacuum of the apparatus generated?
- Which samples are available?
- How is the diffraction apparatus constructed?
- How is the preparation of the samples done?

Ask the supervisor to explain the following terms related to the diffraction experiment: *filament, Wehnelt, anode, acceleration voltage and effective electron energy, LEED screen, suppressor, horizontal and vertical deflection plates.*

Look at the pictures on the following pages.

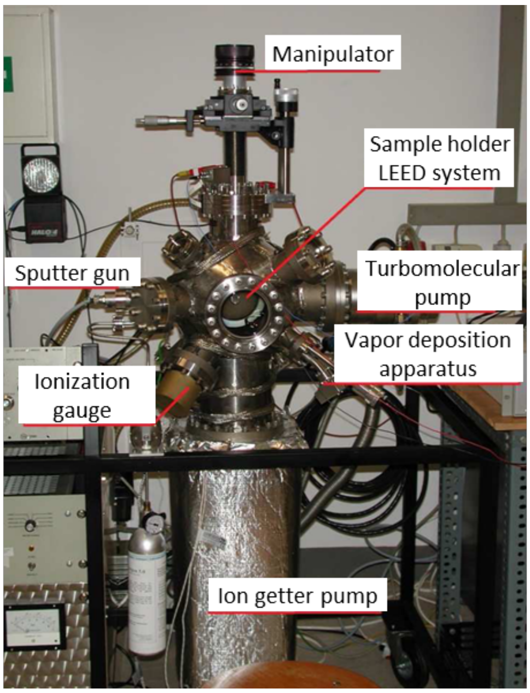

Figure 1: Overview of the vacuum apparatus.

3.2 Experimental setup for the diffraction of electrons

In this experiment, electrons are accelerated by an electron gun and directed by static electric fields onto the surface of a metal single crystal. Some of the electrons are elastically diffracted by the lattice of the surface atoms, i.e. reflected back from the surface at defined angles. These scattered electrons hit a fluorescent screen and generate a characteristic diffraction pattern. From this diffraction pattern, it is possible to deduce the geometric structure of the surface.

In order to generate and focus the electron beam, several components are necessary. These make up the so-called “LEED optics”. Figure 2 shows the schematic structure of the LEED optics used, consisting mainly of the electron gun in the center of the screen and the screen with several grids. The electron gun consists of several electrodes, e.g. the Wehnelt (cylinder) and the anode, which define special electric fields that are needed produce and to focus the electron beam onto the sample surface. Since the noted electrodes have an analogous function as an optical lens has for focusing a beam of light, the voltages applied to these electrodes will be referred to as ”lens voltages” in the following.

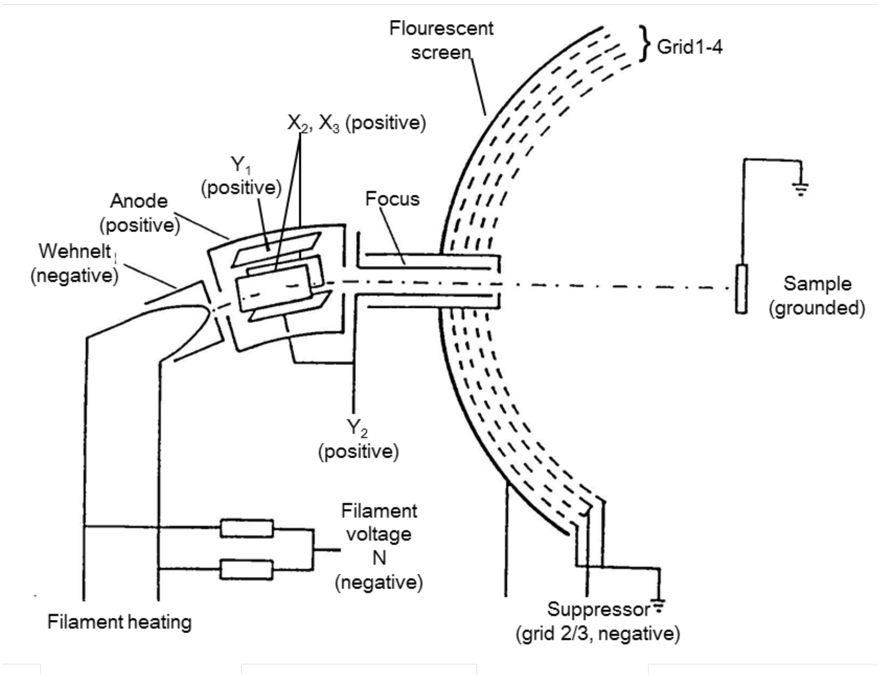

Figure 2: Scheme (cross section) of the LEED optics and the individual voltages for creating, deflecting, and focusing the electron beam. The so-called ”lens voltages” (filament voltage, Wehnelt, anode, Y1, X2, X3, Y2) and the voltage of the suppressor are digitally controlled via a LEED power supply using the desktop computer.

The kinetic energy of the electrons, and thus their wavelength, is determined by the voltage on the filament with respect to the sample. In the following, this voltage is simply referred to as N. All other lens voltages must be varied with respect to N in order to maintain the focussing of the gun. In a preceding test, the appropriate functional dependencies have already been determined: For each filament voltage N, there is a set of lens voltages (anode, Wehnelt, ...), for which a sharp diffraction pattern is obtained.

The functional dependencies are stored in a program that is executed on a desktop computer. The computer is connected via a digital interface to a LEED power supply, which produces and supplies all voltages (N, Anode, Wehnelt, ...) to the LEED optics. This setup is illustrated schematically in Figure 3.

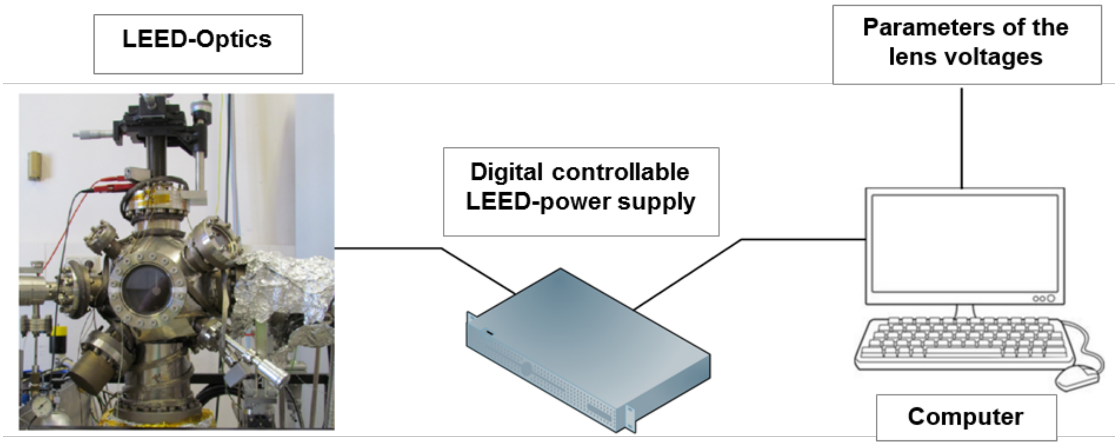

Figure 3: Block diagram showing the power supply and control computer of the LEED optics.

As a consequence, upon a change of the kinetic energy only the filament voltage N needs to be adjusted; the other lens voltages are automatically readjusted by the program on the computer, and thus a sharp diffraction pattern for all energies is continuously provided. As noted, the functional dependencies for the lens voltages were determined from optimizing the resolution and brightness of the diffraction spots in test experiments.

3.3 Experimental procedure

3.3.1 Sample cleaning

Together with your supervisor, clean the sample (Au(111) crystal) by ion etching (sputtering) and annealing. Use the following conditions for sputtering: energy of the ions 1 keV, $p_{Ar} = 1 \times 10^{-5}$ mbar, T_{sample} = room temperature (RT). Temperature during the subsequent annealing: 973 K. Annealing time in total approx. 90 min.

6.5Manipulator settings: x = 5.0; y = 15.5; z = 0.0; Θ = 161°.

Important: Switch off the ion getter pump before dosing the argon gas. Do not forget to switch it back on, after having finished sputtering and after the argon has been pumped off the chamber by the turbo pump!

3.3.2 Adjustment of the sample

Position (together with the supervisor) the sample in the center of the LEED apparatus using the following manipulator settings: x = 22.0; y = 15.0; z = 0.0; Θ = 276.5°.

3.3.3 Activation of the LEED power supply and digital control

Switch on the power supply for the LEED screen and turn the potentiometer to 500 scale divisions (500 ScD).

Now switch on the digitally controllable LEED power supply. On this device there is a rotary knob for controlling the filament heating and a rotary knob for adjusting the filament voltage N (energy). Set the filament heating to 120 ScD and the filament voltage N to 300 ScD. This corresponds to a heating current of 3.1 A and a filament voltage of 60 V.

Now turn on the computer and log in using the password "digileed" on the user account "Abt. Sokolowski".

Open the file "Linsenspannungen für Au(111)" from the desktop. Two windows will appear: The window in the front is called "Frontplatte" and allows to set the individual lens voltages such as anode or Wehnelt. The window "Schaltplan" in the back visualizes the calculation of the lens voltages by means of the control program ProfiLab 4.0. Decisive for you is only the window "Frontplatte".

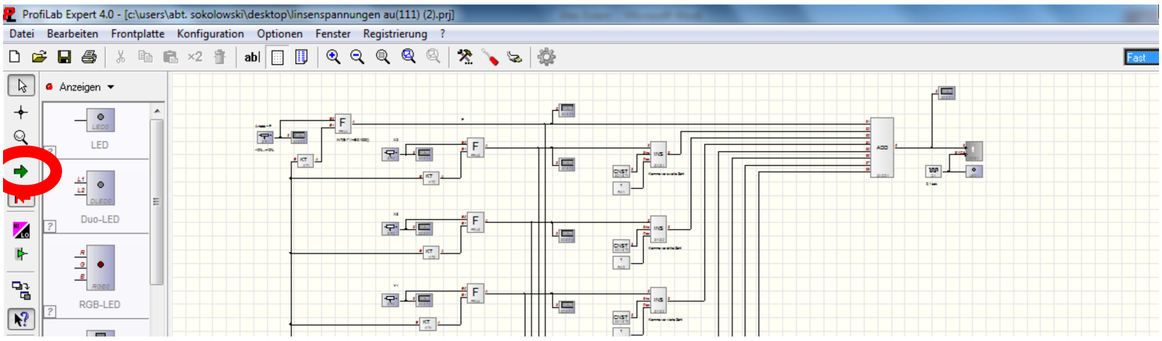

Figure 4: Screenshot of the program with the circuit diagram of the individual lens voltages. The red circle marks the button for starting the program.

3.3.4 The interface for varying the lens voltages: The "Frontplatte"

First click on the green arrow on the left in the schematic window to start the program.

The window of the "Frontplatte" automatically activates, and a green dot flashes on the bottom right coner. This starts the transmission of the lens voltage settings selected on the "Frontplatte" to the LEED optics.

On the "Frontplatte" you can vary the respective lens voltages in a range of +10% to -10% from the preset values by sliders, and thus examine their effect on the LEED pattern. This fine control allows an additional optimization of the diffraction pattern. You should use this fine control only at selected energies.

On the "Frontplatte", the absolute value of a lens voltage is displayed in the box on the left-hand side of the sliders. The box on the right-hand side shows the percental deviation of the selected voltage from the preset value. It should be noted that **all values** read in the program must be **divided by 10** to obtain the real output values in volts. When the "Frontplatte" is activated, all sliders are in the middle and the percental deviations from the default values are 0.

The previously mentioned preset values of the lens voltages are implemented in this program and are automatically reset for any variation of the filament voltage N. Thus, for a variation of the filament voltage N, all other lens voltages change simultaneously. If the sliders are *not* set to 0, the lens voltages for all values of N are corrected by the set percentage of the stored starting values. As a result, the absolute deviations scale with the starting values.

To adjust the electron energy, the filament voltage N can be operated by the slider on the front panel or the rotary knob on the LEED power supply. The switch circled in red in Figure 5 can be used to select between these two control elements.

To change the lens voltages, the program does not need to be stopped, but can be operated continuously. The selected lens voltages are transmitted to the LEED optics

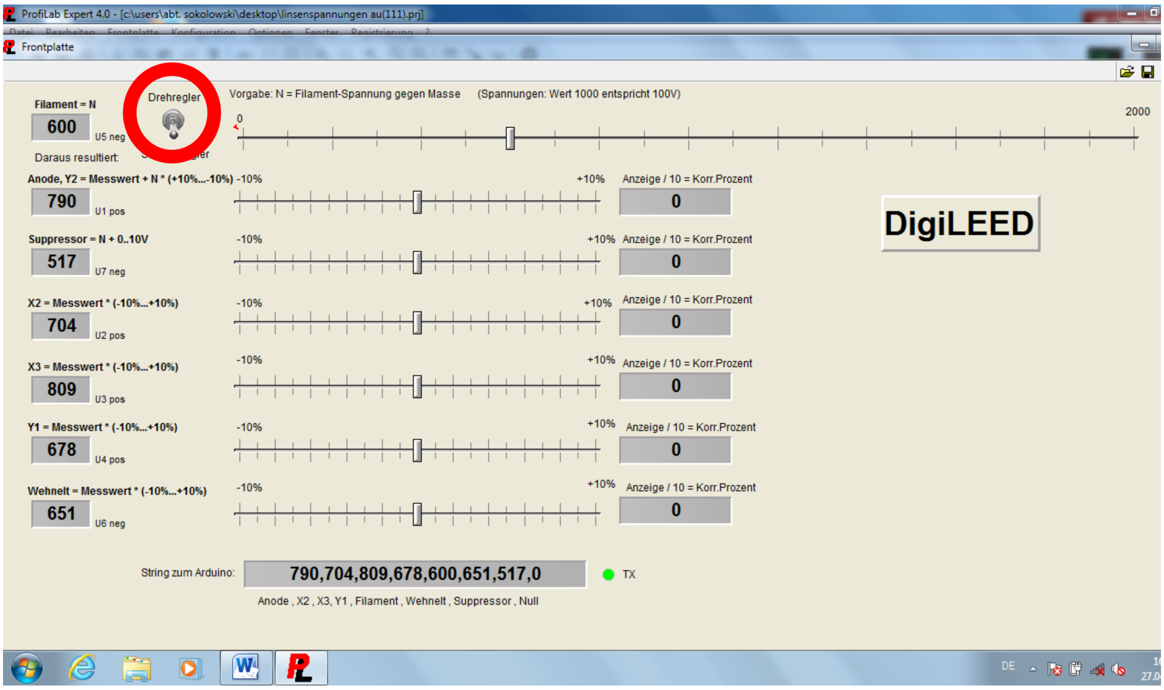

Figure 5: Screenshot of the "Frontplatte". The sliders in the middle can be used to adjust the individual lens voltages. The red circle marks a switch by which you can choose either to set the filament voltage N via the slider on the "Frontplatte" or via a rotary knob on the LEED power supply.

just as they are being adjusted so that a gradual change in the diffraction pattern can be observed.

3.3.5 Camera settings

To take photos of the LEED images, the following settings are suitable for the ”Canon PowerShot SX30 IS” camera (located in the practical course room):

- Focus 4,5
- 2 sec. Self-timer
- Zoom 30cm
- Close object recording
- ISO and Exposure time: see Table 1 .

These settings are also stored in the preset program C1.

Table 1: Overview of the setting parameters of the digital camera.

Energy (N)	**10 eV**	**15 eV**	**25 eV**
ISO	1600/800	800/400	400
Exposure time	15 sec.	15/13 sec.	13 sec. to 1 sec.

3.3.6 Introductory tasks

- Select an electron energy between 80 and 120 eV and observe the image on the LEED screen.
- Center the diffraction pattern on the screen by varying the rotation angle of the manipulator.
- Change the suppressor voltage (voltage at grids 2 and 3, see Figure 2) and observe its impact on the LEED image. Can you explain the effect?

Change the electron energy. Observe the change of the LEED image. Why is the LEED pattern changing as it does? Explain your findings using the Ewald construction (see Figure 6, below).

> (If the diffraction pattern is very blurred or too dark, you may try to focus or optimize the image by varying the lens voltages.)

3.3.7 Change of the angle of incidence

- Position the sample as accurate as possible in the center of the hemispherical LEED screen using the initial settings x = 22.0; y = 5.5; z = 0; and = 276.5°. Fine-tune the crystal orientation by varying the rotation angle on the manipulator to the *normal* orientation. There, the reflected electron beam, i.e. the (0,0)-spot, falls exactly onto the axis of the electron gun. Note that, of course, the (0,0)-spot is not visible then.
- Rotate the sample by 5° out of this position so that the (0,0)-spot can be observed on the screen again. Change the energy and check its impact on the position of the (0,0)-spot on the screen. It may be that the spot moves. What could be the reason for this?
- Rotate the manipulator by angles of by 5°, 10°, 15°, and 20° out of the normal orientation and take photos of the respective diffraction patterns. Determine the opening angle of the LEED screen.
- Rotate the crystal back to its normal orientation, where the (0,0)-spot falls exactly onto the axis of the electron gun. Up to which energy can you see the first order spots on the LEED screen? Which diffraction angle corresponds to the screen edge, where the LEED spots vanish?

3.3.8 Determination of the surface lattice constant

- Select an energy for which the *first* and *second* order LEED spots are visible. Make a sketch of the LEED image in the lab book. Mark the reciprocal unit cell of the surface and label all LEED spots by the corresponding indices (h, k).
- Take three photos at different energies. One photo should also show the spots of the third order. You will need these photos later on to determine the lattice constant of the surface.
- Illuminate the LEED screen by the external LED lamp and take a photo of it for reference purpose. Important: Use the same zoom settings on the camera as before.

3.3.9 Symmetry of the LEED image, variation of intensities

- Consider the intensities of the six *first* order spots as a function of energy. Are all intensities of the same magnitude? This is usually not the case, why is that? Consider the symmetry of the fcc-(111)-surface.

- Find energies at which the intensities of the first order spots exhibit minima and maxima. Make a hand sketch of the intensity as a function of the energy for one spot in the lab book. (Hand sketch, no computer evaluation required.)

3.3.10 Background

- Now look at the intensities in the LEED image between the spots. Change the electron energy to high values and note down your observations.

4 Evaluation

4.1 Orientation of the surface

For the tasks given in this section, you can neglect the complicated reconstruction of the Au(111) surface.

- Draw a hard-sphere model of the (111) surface and the photographed LEED image in a side-by-side manner with correct orientations.
- Mark the unit cell and the unit cell vectors of the (111) surface and denote their lengths.
- Determine the relative orientation of the vectors of the unit cell in real space to those of the diffraction image (reciprocal space).

4.2 Determination of the spot distances

- From the photos (see task 3.3.7), measure the distances x (in number of pixels) by which the (0,0)-spot was offset from the center of the LEED screen when rotating the sample by an angle Θ.
- From the x and values, determine the sample distance with respect to the LEED screen or, equivalently, the screen radius r in pixels. For this purpose, work out the relation that holds between Θ, x, and r

  Note: For the following, it is sufficient to obtain the screen radius r in number of pixels, i.e. in a relative unit.

- What could be the reason, if you find that the value determined for r changes continuously for increasing angles of rotation and is, thus, not constant? Consider the geometry of the sample with respect to the hemispherical LEED screen.

4.3 Determination of the lattice constant of the Au(111) surface

- Measure the spot distances (in pixels) with respect to the central, invisible (0,0)-spot from three diffraction patterns obtained in task 3.3.8.
- From these values (using the above value for r), determine the lattice constant of the Au(111) surface. Perform an error estimation. How well can you reproduce the literature value?

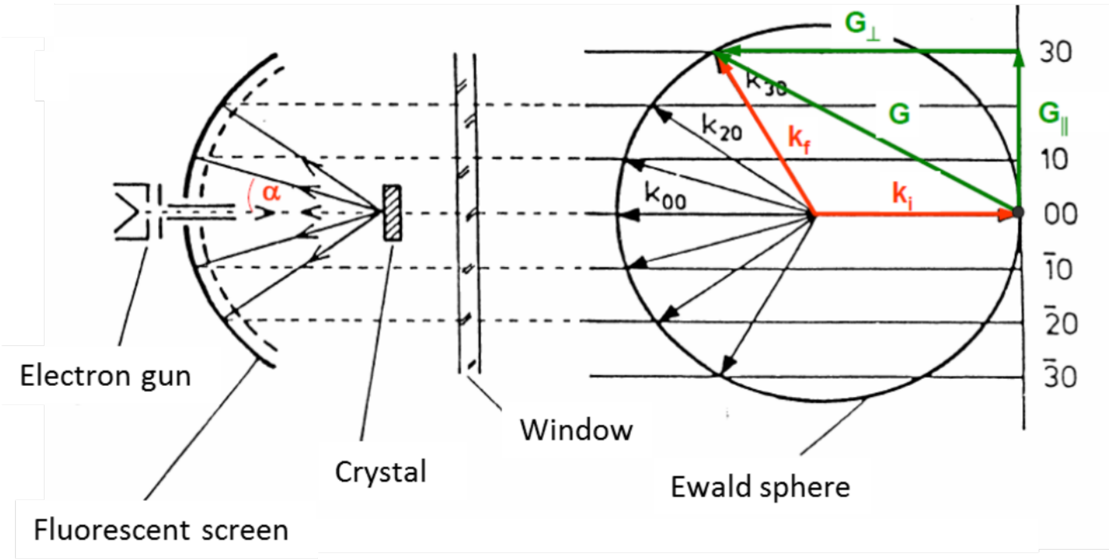

Figure 6: Schematic sketch of a LEED optics and the corresponding Ewald construction.

5 Advanced tasks

5.1 The reconstruction of the Au(111) surface

Observe the satellites around the (0,0)-spot and the spots of first order. Take pictures and draw the spots. Figure 7 shows a hard-sphere model of the reconstructed Au(111) surface. The unit cell is rectangular and exhibits a size of $\sqrt{3} \times 22$ in units of the lattice constant of the unreconstructed (111) surface. Explain the satellites around the (0,0)-spot in the LEED image on the basis of the *unit cell of the reconstruction* in reciprocal space. Figure 8 shows an appropriate LEED image for comparison and orientation that was recorded with a high-resolution LEED instrument.

For this purpose use the program ”Spot-Plotter” provided on ecampus. On the basis of your LEED image, quantify (including an error estimation) the size of the unit cell of the reconstruction and check the agreement with the unit cell shown in Figure 7. Comment on your result.

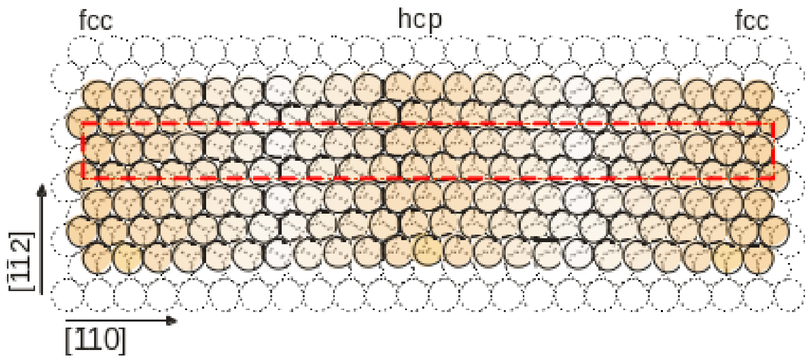

Figure 7: Hard-sphere model of the reconstructed Au(111) surface. (Source: Bachelor thesis, E. Rojo-Wiechel, Bonn 2010 with data taken from refs. [4,5].)

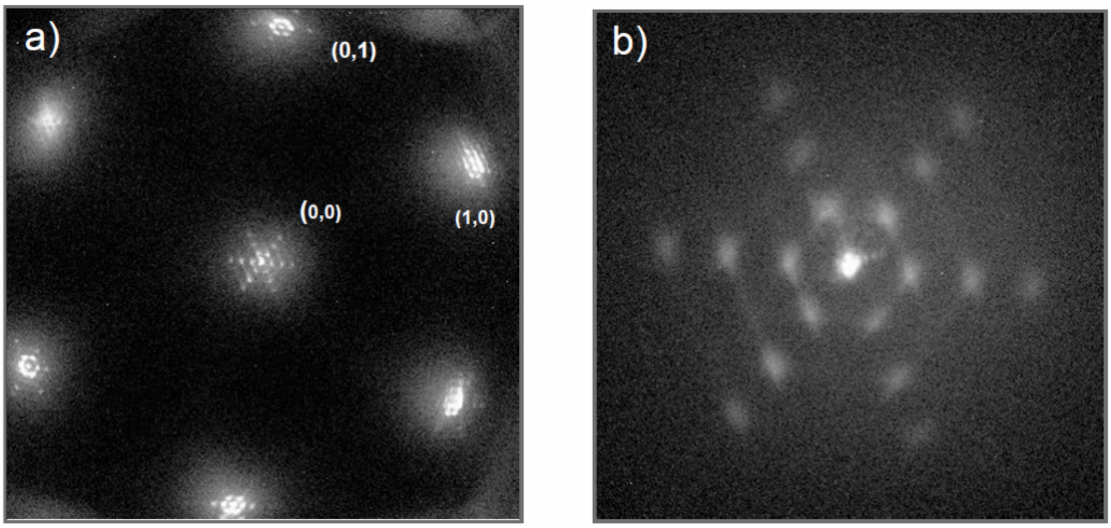

Figure 8: LEED images of the reconstructed Au(111) surface obtained with a high-resolution LEED device. Electron energy: 68.5 eV. a) Overview. b) Details around the (0,0)-spot. (Source: Master thesis, Saskia Spitzer, Bonn 2013.)

5.2 Preparation of an organic adlayer on the Au(111) surface by epitaxial growth

PTCDA is known as the "poster-child" of surface science as it forms ordered monolayers on most metal substrates. Investigate the structure of PTCDA on Au(111) by preparing an ordered monolayer on the Au(111) substrate. Take photos of the observed LEED images, preferrably at low electron energies (≈20-30 eV).

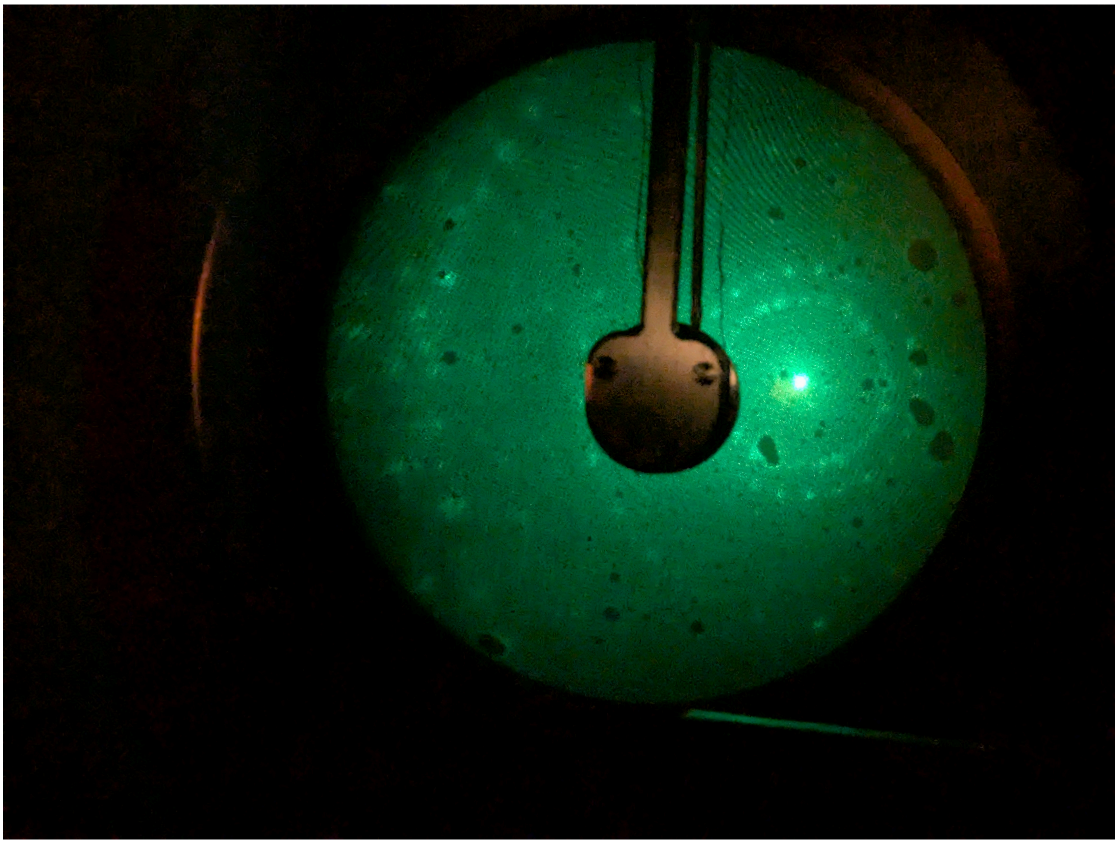

Figure 9: LEED image of PTCDA on Au(111) at room temperature, $E_{\mathrm{kin}} = 25$ eV

Procedure for the preparation of the organic layer:

- Position (together with the supervisor) the sample in front of the evaporator. Settings: x = 22.5; y = 12.5; z = 47; Θ = 40°.
- Connect the power supply from the shelf to the black P evaporation source on the UHV chamber.
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- Connect a digital thermometer to the evaporation source switch it on.

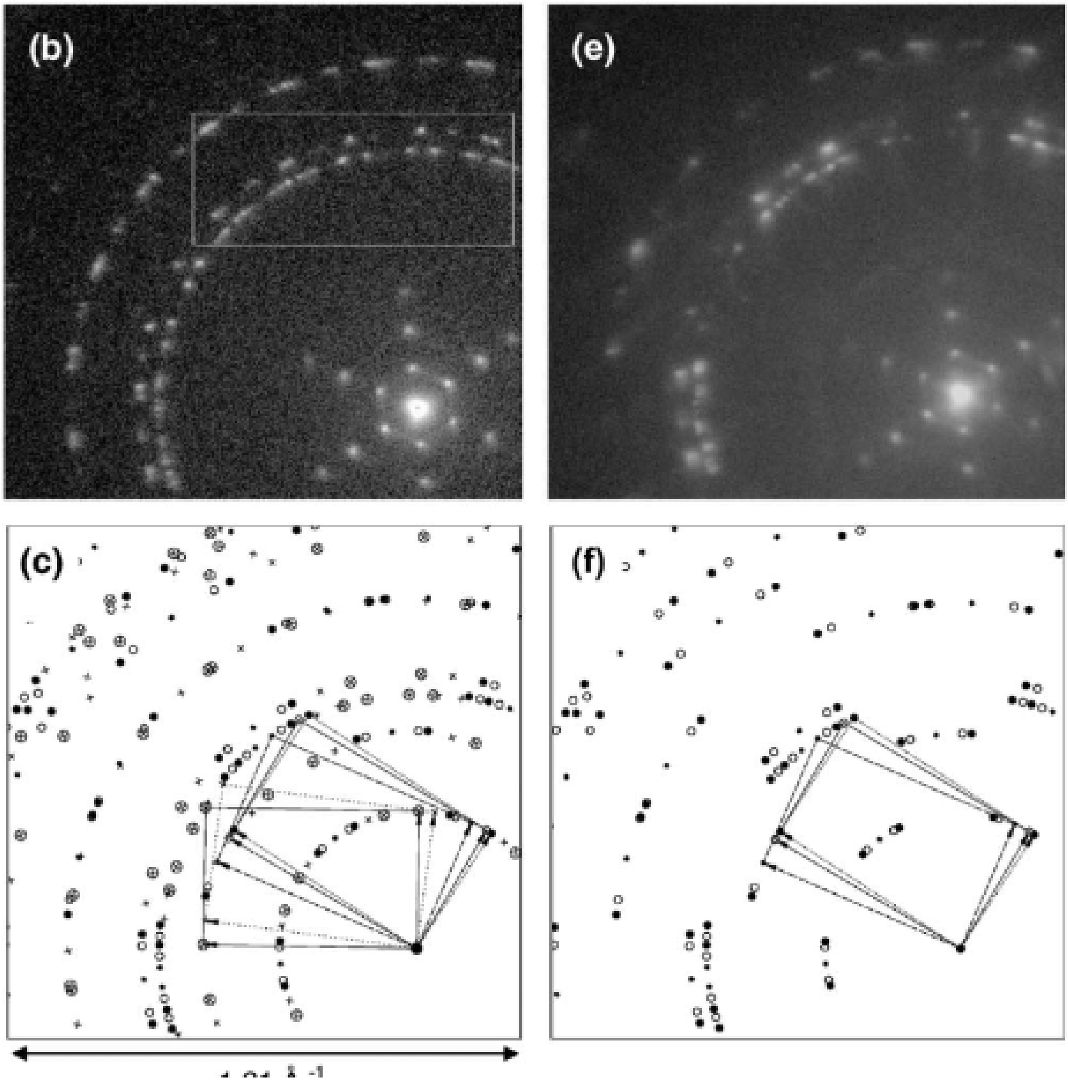

Figure 10: SPA-LEED images and geometric simulations of LEED patterns from Kilian et al.

- Make sure that the potentiometers (rotary knobs) on both power supplies (for voltage and current) are set to 0. Turn on the power supplies. Turn up the potentiometers for the current until they stop. (No current is flowing yet.)
- **Evaporator:** Slowly turn up the voltage potentiometer a few tens of scale divisions. Heat the evaporation source to 450°C and hold it at this temperature for 10 min before increasing it slowly to 500°C. The pressure in the vacuum chamber should rise to about 1×10^{-8} mbar
- Open the shutter of the evaporation source for 1 min.
- Close the shutter.
- Turn off the voltage and the current on the power supplies and turn it off.
- Carefully (!) move the crystal away from the evaporation source and place it in front of the electron gun.
- Inspect the sample via LEED and enjoy!

Optimize the lens voltages and take photos of the diffraction images of the resulting superstructure. The voltages found for a good diffraction image are given in Table 2 below.

Table 2: Overview of the lens voltages at 82 eV.

Energy	$\mathbf{Y_1}$	$\mathbf{Y_2}$**/Anode/Focus**	$\mathbf{X_2}$	$\mathbf{X_3}$	**Wehnelt**	**Supressor**
23 eV	76.1 V	90.9 V	88.4 V	76.7 V	86.5 V	74.8 V

5.2.1 Evaluation

The structure of PTCDA on Au(111) is complicated and requires a superposition of multiple structures to understand. Try to simulate the LEED pattern using Spot-Plotter (or any other suitable program of your choosing) given any of the superstructure matrices given in literature. Try to find an agreement with at least some of the spots and provide a corresponding length of the real-space vectors.

Discuss the structures of PTCDA on Au(111) considering the following aspects:

- Is the structure commensurate given the unreconstructed Au(111) surface? What do you conclude regarding the adsorbate/substrate-interactions?
- Is the reconstruction of the Au(111) surface preserved, or lifted for PTCDA/Au(111), again, think about the conclusions you can draw regarding adsorbate/substrate-interactions

6 Literature

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