### Surface structure and how to investigate it

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Low energy electron diffraction

Ab initio calculations of equilibrium geometry

Summary



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# Why are surface structures important?

Similar to the volume:

#### Structure very influences physical properties!

(e.g.  $\beta$ -Sn (tetragonal, metallic)  $\leftrightarrow \alpha$ -Sn (cubic, semiconducting) Fe (bcc, ferromagn.)  $\leftrightarrow$  Fe (fcc, paramagnet-ferromagn.) C (hexagonal, graphite)  $\leftrightarrow$  C (cubic, diamond)

#### Surface = Interface to the environment

important for (e.g.) contacts

- corrosion properties
- catalysis
- crystal growth
- epitaxy (new materials!)

Semiconductor miniaturisation: Surface area / volume gets ever larger



 $\implies$  Nanophysics

# Real surface - surface with defects



a terrace, 2. an emerging screw dislocation, 3. the intersection of an edge dislocation with the terrace, 4. an impurity adatom, 5. a monoatomic step in the surface, 6. a vacancy in the ledge, 7. a kink, 8. an adatom upon the ledge, 9. a vacancy in the terrace, 10. an adatom on the terrace.



# Bulk terminated fcc crystal surfaces





# Surface Crystallography

	2D	3D
number of space groups	17	230
number of point groups	10	32
number of Bravais lattices	5	17

2D- crystal system	symbol	lattice parameters	2D Bravais lattice	space group	point groups
oblique	m (mono- clin)	a, b, γ	$\frac{mp}{\gamma}$ b	2	1
rectangular	o (ortho- rhom- bic)	a, b $\gamma = 90^{\circ}$	op $b_a$ oc $b \bullet_a$	7	m (2mm)
square	t (tetra- gonal)	$\begin{array}{l}a=b\\\gamma=90^{\ 0}\end{array}$	tp a a	3	4 (4mm)
hexagonal	h (hexa- gonal)	a = b $\gamma = 120^{\circ}$	hp a a	5	3 6 3m 6mm

$a_1$
а <sub>1</sub>
$\mathbf{a}_1$

square	$a_1 = a_2$	$\gamma = 90^{\circ}$
hexagonal	$a_1 = a_2$	γ = 120°
rectangular	$a_1 \neq a_2$	γ = 90°
centered rectangular	a <sub>1</sub> ≠ a <sub>2</sub>	γ = 90°
oblique	<sup>a</sup> 1 ≓ <sup>a</sup> 2	γ ≠ 90°, 120°



# Adlayer, reconstruction - notation





# Surface relaxation and reconstruction



- a) Relaxation of the topmost atomic layer
- b) Reconstruction of the topmost atomic layer
- c) Missing row reconstruction (e.g.  $(2 \times 1)$ Pt(001)).



- GaAs(110) surface: a) Top view
- b) Side view
- c) Sphere model.



# Methods for structure determination - microscopies

#### **Electron Microscopy (imaging)**

for atomic resolution: lens aberrations must be reduced

- high electron energies (>50 keV)
- high sample penetration
- only projection visible
- Iow surface sensitivity
- Radiation damage!



Bright field imaging" of (220) net planes of Au

#### Special: Low Energy Electron Microscope (LEEM)

Electrons are retarded just before reaching the surface, so that there is only the surface penetration wanted. Resolution reached:  $\approx 5$  nm.

#### Scanning tunneling microscopy

Atomic resolution well achievable

- only top layer imaged
- electronic surface corrugation is imaged (rather than atoms).





# Methods for structure determination - microscopies



atomic resolution well achievable.

**Yet:** only atoms positions of high electric field or low work function are imaged. Also: application limited by the high fields applied; no subsurface atomic layers imaged.



# Methods for structure determination - diffraction methods

only intensities can be measured ("phase problem")

 $\implies$  "trial-and-error" methods to find the structure

#### Atom diffraction (thermal He, Ne, Ar)

Sensitive to surface corrugation of electron density. When correlated to atomic positions, accuracy < 0.1 Å achievable. **Yet:** *only top-layer diffraction (no sample penetration).* 

#### X-Ray Diffraction (XRD)

Atomic positions with accuracy < 0.1 Å well achievable.</li>
 Yet: Very oblique incidence of the primary beam necessary for surface sensitivity. Very accurate sample alignment necessary.



# Methods for structure determination - diffraction methods

Low Energy Electron Diffraction (LEED = E ≤ 600 eV) ideal surface penetration (5-10 Å), experimentally "easy". Yet: Determination of atomic positions complicated by multiple electron scattering. Accuracy < 0.1 Å.



**Reflection High-Energy Electron Diffraction** (RHEED) (E ≤10 keV).

Multiple scattering less pronounced => simpler data evaluation compared to LEED (many beams!). Yet: to get surface sensitivity, (very) oblique incidence necessary; many beams; intensity measurement difficult.

Photo-Electron Diffraction (PED ) Angular Resolved Photo-Electron Spectroscopy (ARPES) Similar to LEED, except that a surface atom acts as electron source. Accuracy similar to LEED.

Surface Extended X-ray Absorption Fine Structure (SEXAFS) Only sensitive to bond lengths





# **Diffraction methods**

# - tools for surface topography





Low energy electron diffraction

Ab initio calculations of equilibrium geometry

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# Low Energy Electron Diffraction (LEED)

**LEED** is the principal technique for the determination of surface structures. It may be used in one of two ways:

Qualitatively : The analysis of the spot positions yields information on the size, symmetry and rotational alignment of the adsorbate unit cell with respect to the substrate unit cell.





**LEED** Si(111)7×7



RHEED Si(111)7×7

In the LEED image we can distinguish six additional spots between strong (0,-1), (0,0) and (0,1) patern.

In the RHEED-image we see six Laue-circles representing distorted order situated between the zero order Laue-circle and the first order Laue-circle.

Quantitatively : The intensities of the various diffracted beams are recorded as a function of the incident electron beam energy (I-V curves).

The comparison with theoretical curves may provide accurate information on atomic positions.

# LEED is surface sensitive



Low energy electrons interact strongly with matter: electron mean free path  $\lambda$  is small. Only electrons scattered from near surface can leave the surface.

The observation of a LEED pattern does not a guarantee that the surface is ordered: The coherence length of a standard LEED optics is only 10-20 nm!



# Electron scattering on 2D lattice

• Electron wave length: 
$$\lambda = \frac{h}{p} = \sqrt{\frac{h^2}{2mE}} \Longrightarrow \lambda[nm] \approx 0.1 \sqrt{\frac{150}{V[eV]}}$$

- Elastic scattering:  $E_f = E_i$
- Interference:

Intensity = Structure factor (unit cell geometry)

Interference function (scattering characteristics)

Maximum of interference function for k

$$ec{k_{||}^f} = ec{k_{||}^i} + ec{g}$$

$$ec{a_1}, ec{a_2}$$
 :  $ec{r}$ -space,  $ec{a_i} * ec{b_j} = 2\pi \delta_{ij}$   
 $ec{b_1}, ec{b_2}$  :  $ec{k}$ -space,  $ec{g} = hec{b_1} + kec{b_2}$ 

Laue conditions:

$$\vec{a_1} \cdot (\vec{k^f} - \vec{k^i}) = 2\pi h$$
$$\vec{a_2} \cdot (\vec{k^f} - \vec{k^i}) = 2\pi k$$

#### Bragg relation:

$$d_{hk} = (sin\Theta_f - sin\Theta_i) = n\lambda$$

 $\Theta_f, \Theta_i$  - angle between the incidence/reflected beam and the surface normal  $d_{hk}$  - interlayer distance,  $\Theta_f = \Theta_i$  - mirror reflection

# **Ewald construction**

**Ewald sphere construction** 

- plot reciprocal lattice (rods)
- plot direction of incident beam (s<sub>0</sub>) towards (00) spot
- go 1/λ along this direction
- make circle (sphere) with radius 1/λ
- direction from circle (sphere) center towards cut with reciprocal lattice rods gives direction of all possible diffraction spots (hk)

Usual arrangement: Normal incidence, symmetrical diffraction pattern





# Interpretation of LEED experiment

Simple: Kinematic theory (single scattering) Size, shape and symmetry of surface unit cell, Superstructures, domains only if long-range ordered No information about atomic arrangement within the unit cell

#### Less simple: Kinematic theory

Deviations from long-range order: Spot width  $\longrightarrow$  domain size Background intensity  $\longrightarrow$  point defect concentration Spot splitting  $\longrightarrow$  atomic steps

#### Difficult: Dynamical theory (multiple scattering)

Spot intensities  $I(E_0)$  or I-V curves  $\longrightarrow$  structure within unit cell



Increasing the incident beam energy means increasing 1/ $\lambda$ , i.e. more diffraction beams.



Experimental spectrum is total different from kinematic approximation. This is not an "approximation"for LEED intensity! We need to consider multiple scattering / diffraction.

# LEED - interference

1st approximation: Scattering from 2-D lattice.

Analogy to optical grating.

Constructive interference: Enhancement of intensity only in certain directions:

 $n\lambda = d\sin \phi$ 

For 2D arrangement (plane lattice): scattering conditions have to be fulfilled in both directions

#### Note:

If the lattice constant(s)  $a_1 (a_2)$  increase, the scattering angle for the beam h (k) decreases.

This is the reason for the reciprocity of the real and the s.c. reciprocal lattice.





# LEED - spot intensities

Spot intensities contain information on structure within the unit cell

 $\mathbf{I} \sim |\mathbf{F}|^2 \cdot |\mathbf{G}|^2$ 

G <sup>2</sup> = structure factor or lattice factor contains shape and arrangement of repeat units (unit cells) yields reciprocal lattice determines location and shape of spots, kinematic theory

|F|<sup>2</sup> = structure factor or form factor

contains contribution from all atoms within the repeat unit, includes multiple scattering, in-depth attenuation, dynamic theory





# Scattering of low energy electrons

- elementary introduction into the theory
   Translation symmetry: V(*i*) = V(*i* + mai + nai),

$$\psi_{cr}(ec{r})=e^{iec{k_{||}}ec{r}}U_{ec{k_{||}}}(ec{r})$$

- *muffin-tin* potential from the selfconsistent surface el. struct. calculation
- optical potential fenomenological description of nonelastic processes



- scattering on an atom described in spherical wave basis  $\delta_l$
- scattering on an atomic layer reflection and transmission matrices  $R^{\pm\pm}$



# Atomic scattering

Polar angle representation more intuitive:





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# Surface diffraction





# LEED - multiple scattering process



Dynamic LEED analysis: No direct deduction of structure from I-V-curves:

Guess structure model calculate I-V-curves compare with measured curves modify model check if improval if yes: proceed modifying in this direction if no: modify in another direction or guess new model

Disadvantage: Only for ordered structures Much computer time

#### But:

One of very few methods for structure analysis of first few atomic layers (~1 nm)



# Comparison of calculated and measured data

To find the correct structure, the exp. spectra must be reproduced by model calculations

- one needs a quantitative measure to compare spectra
- R-factors
   ("reliability factors", as widely used in XRD)



At the time being, mainly two different R-factors are used:

a) mean square deviation



Similar mean square deviation, though spectral features are better reproduced on the left.

#### b) Pendry R-factor

Conceptional idea:

The location of both maxima and minima reflect the structure because they mirror de- and constructive interference. The height of maxima is less important, all maxima (small or high) are equally important!!



# Pendry R-factor

=> use transformed spectra

$$I(E) = \frac{1}{I} \frac{dI}{dE} = L(E)$$

or better, to avoid singularities  $Y(E) = \frac{L(E)}{1 + (V_{0i}L)^2}$ 





# Experiment versus theory - an example

trial and error method

$${\it R}_{ZJ} = rac{{\it A}_{ZJ}}{\delta E} \int \omega(E) |c{\it I}_{\it th}' - {\it I}_{\it exp}'| dE$$

where 
$$c = \frac{\int I_{exp}}{\int I_{th}}$$
,  $\omega = \frac{|cl'_{th} - l''_{exp}|}{|l'_{exp}| + \epsilon}$ ,  $\epsilon = |I'_{exp}|_{max}$ 

empirically: R = 0.2 - good, R = 0.35 - mediocre, R = 0.5 - bad agreement

$$R_{tot} = \frac{\sum_{\vec{g}} R_{\vec{g}} \Delta E(\vec{g})}{\sum_{\vec{g}} \Delta E(\vec{g})}$$

Example:  $(\sqrt{3} \times \sqrt{3})30^{\circ}$  S on Pd(111)



Simplest model:

- three adsorption sites respect observed symmetry of diffraction patterns (top, fcc, hcp)
- only top surface layer distance  $d_{\perp}$  varied
- surface barrier hight  $V_{0r}$  is an other parameter
- $\implies$  searching the minimum of  $R_{tot}(d_{\pm}, V_{0r})$

# $(\sqrt{3} \times \sqrt{3})30^{o}$ S on Pd(111)







Contour plot from the LEED R-factor analysis for the hollow 1 site.



# Tensor LEED

Experience: if structural parameters are changed gradually, the spectra change gradually, too



Can we get the changing spectra by the perturbation of a reference spectrum?

#### Scattering of a displaced atom



Scattering factor of the undisplaced atom:  $t_i$ 

Scattering factor of the displaced atom:  $t_j = t_j + \delta t_j (\delta_j^2)$ 

#### How to calculate



$$\delta t_j (\delta \vec{r}_j) = P(\delta \vec{r}_j) t_j P(\mathbf{r}_j)$$
propagate to the scatter!
new position!

propagate back to the old position!

(All this is done in angular momentum space, so the quantities P and t are matrices)



Ni(100) (1 1)  $d_{12}(\hat{A})$   $d_{12}(\hat{A})$   $d_{12}(\hat{A})$   $d_{12}(\hat{A})$  1.86  $d_{1.76}$  1.66  $d_{1.76}$  1.66  $d_{1.76}$ 1.56

full dynamical calculation

# Tensor LEED

The atomic displacement cause a change in the scattering amplitude of the total surface. In 1. order perturbation this can be written as  $\delta A_j$ 

$$\delta A_{j} = \langle \psi_{f} | \delta t_{j} | \psi_{i} \rangle$$

In angular momentum representation this writes as  $\delta A_j = \sum T_{jLL'} \delta_{jLL'}$ 

with the tensor T depending only on the unperturbed structure (=reference structure)

For many displaced atoms:  $\delta A = \sum_{j;LL'} T_{jLL'} \delta_{jLL'}$ 

The intensity of the new structure is simply:

$$I = \left| A_0 + \delta A \right|^2$$

Once the Tensor has been computed, the new intensity results just by matrix multiplications

> In many cases atoms can be displaced by as much as 0.5 Å off the position in the reference structure

(This is 1. Born (i.e. kinematic) approximation with respect to the scattering at  $\delta_{t}$ 





# Structure of the Fe<sub>3</sub>O<sub>4</sub>(111) surface





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# Atomic force minimization

#### Hellmann-Feynman teorem

$$\begin{array}{rcl} \mathcal{H}\Psi &=& \mathcal{E}\Psi & \\ \\ \frac{\partial \mathcal{E}}{\partial \lambda} &=& \frac{\partial}{\partial \lambda} < \Psi |\mathcal{H}|\Psi > &=& < \Psi |\frac{\partial \mathcal{H}}{\partial \lambda} |\Psi > + \mathcal{E} \frac{\partial}{\partial \lambda} < \Psi |\Psi > \\ \\ \frac{\partial \mathcal{E}}{\partial \lambda} &=& < \frac{\partial \mathcal{H}}{\partial \lambda} > \end{array}$$

In adiabatic approximation (Born-Oppenheimer):

$$\mathcal{H} = \mathcal{H}(\{\vec{R_I}\}) = \mathcal{T} + \mathcal{U}_{ee} + \mathcal{U}_{el}(\{\vec{R_I}\}) + \mathcal{U}_{ll}(\{\vec{R_I}\})$$

 $\implies$  total energy  $\mathcal{E}(\{R_l\})$  and the force on the J-th atom

$$-\frac{\partial}{\partial X_{\alpha J}}\mathcal{E}(\{R_l\}) \equiv \mathcal{F}_{\alpha J} = \int d^3r \frac{e^2(\vec{r}-\vec{R_J})_{\alpha}}{|\vec{r}-\vec{R_J}|^3} (n_+(\vec{r})-n(\vec{r}))$$



# Surface relaxation



- Surface atoms push for increasing the number of bonds
   surface layer relaxed usually inwards.
- Interlayer distances are usually oscillating from the top surface to bulk.

First-principle LDA calculations[Bohnen, Ho] - d in %

Al(110)	$\Delta d_{12}$	-6.8	Cu(110)	$\Delta d_{12}$	-9.3	Na(110)	$\Delta d_{12}$	-1.6
	$\Delta d_{23}$	0.0		$\Delta d_{23}$	2.8		$\Delta d_{23}$	0.0
	$\Delta d_{34}$	-2.0		$\Delta d_{34}$	-1.1		$\Delta d_{34}$	0.6
Al(100)	$\Delta d_{12}$	1.2	Cu(100)	$\Delta d_{12}$	-3.0	Au(110)	$\Delta d_{12}$	-9.2
	$\Delta d_{23}$	0.2		$\Delta d_{23}$	0.1	(1×1)	$\Delta d_{23}$	7.7
	$\Delta d_{34}$	-0.1		$\Delta d_{34}$	-0.2		$\Delta d_{34}$	0.7
AI(331)	$\Delta d_{12}$	-11.3	Cu(111)	$\Delta d_{12}$	-1.3	Au(110)	$\Delta d_{12}$	-16.0
	$\Delta d_{23}$	-6.3		$\Delta d_{23}$	0.6	(1×2)	$\Delta d_{23}$	2.0
	$\Delta d_{34}$	10.1		$\Delta d_{34}$	-0.3		$\Delta d_{34}$	3.0
	$\Delta d_{45}$	-4.4		-			$Z_3$	7.0
	$\Delta d_{56}$	-1.8		-			<b>y</b> 2	0.05 Å
	$\Delta d_{67}$	4.8		-			-	

# 0.5 ML Co on p(1×2)Pt(110)



Comparison: LEED and DFT	results
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Parameters	LEED	DFT
b <sub>1</sub>	-0.01±0.03	-0.11
$\Delta d_{12}$	-0.31±0.01	-0.40
$p_2$	$0.09{\pm}0.05$	0.08
$\Delta d_{23}$	+ $0.14 \pm 0.03$	+0.17
$b_3$	+0.07±0.04	+0.06
$\Delta d_{34}$	-0.04 $\pm$ 0.0025	-0.05
$p_4$	$0.04{\pm}0.04$	0.02
$\Delta d_{45}$	+0.00 $\pm$ 0.024	+0.00
$b_5$	+0.03±0.04	-
<b>d</b> <sub>bulk</sub>	1.386	1.385
R <sub>Pendry</sub>	0.24	-

Here,  $d_{ij}$  denote the averaged vertical distance between layer *i* and layer *j*,  $b_i$  and  $p_i$  represent the buckling and lateral displacements (pairing) of the atoms in the layer *i*, respectively. All values are given in Å.

# Total energy calculations





#### See the accuracy of calculations! (1 htr = 27.2 eV)

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# Summary

- Surface:
- ideal  $\iff$  real (relaxation, reconstruction, defects, ...)
- vacuum, T = 0  $\iff$  atmosphere, T > 0

- Tensor LEED combination of perturbation theory and full dynamical calculations (small/large elementary cell —> simple/complicated analysis)
- LEED simulations use results of charge distribution: potential
- Closed packed surfaces relaxed slightly (a few % of bulk interlayer distance), open surfaces relaxed strong (up to 20%).
- ► Equilibrium = minimization of free energy, i.e. for T = 0 minimization of system total energy. Forces acting on an atom → 0, can be evaluated.



To understand electronic charge redistribution in the surface region the electronic structure calculations are needed.
(next: electronic structure from bulk => surface)

# References

- J. B. Pendry: Low Energy Electron Diffraction, Academic Press, London, 1974.
- M. A. Van Hove, W. H. Weinberg, C.M. Chan: Low-Energy Electron Diffraction: Experiment, Theory and Surface Structure Determination, Springer Series in Surface Sciences, Vol 6, Springer, Berlin, 1986.
- G. Ertl, J. Küpers: Low energy electrons in surface chemistry, VCH, Weinheim, 1985.
- K. Heinz: LEED and DLEED as modern tools of quantitative surface structure determination, Prog. Surf. Sci. 58 (1995) 637-704.
- F. Máca in Metody analýzy povrchu: Elektronová mikroskopie a difrakce, ed. L. Eckertová, L. Frank, 281-308, Academia, 1996.

