Low Energy Electron Diffraction - LEED

Wolfgang Ranke
Dep. Inorganic Chemistry
Group Model Surface Analysis
Fritz-Haber-Institut der MPG

For script:
see homepage

or

mail to: ranke@fhi-berlin.mpg.de

Literature:
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 6,
1. Introduction, General

Surface science, UHV, p~10^{-10} mbar

De Broglie wavelength: \[ \lambda = \frac{h}{mv} \]

For electrons: \[ \lambda = \sqrt{\frac{150}{E_0}} \quad E_0 \text{ in eV, } \lambda \text{ in Å.} \]

For 100 eV-electrons: \[ \lambda(100) = 1.22 \text{ Å} \] (low energy)

corresponds to atomic dimensions, similar to XRD

Si(111)-(7x7)

LEED display system

Ertl/Küppers fig. 9.7, p. 210
Low energy electrons interact strongly with matter: 

- electron mean free path \( \lambda_e \) is small.
- Only e\(^-\) scattered from near surface can leave the surface, surface sensitive.

The observation of a LEED pattern does not guarantee that the whole surface is ordered!

Coherence of e\(^-\) -beam limited by \( \Delta E \) and beam divergence. 
Coherence length = diameter of coherently scattering area.

The coherence length of a standard LEED optics is only 10 – 20 nm!
1st approximation:  
Scattering from 2-D lattice.

Analogy to optical grating.

Constructive interference:  
Enhancement of intensity only in certain directions:

\[ n \lambda = d \sin \varphi \]

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.
Useful: Introduction of reciprocal lattice

Real lattice vectors \( \mathbf{a}_1, \mathbf{a}_2 \)
Reciprocal lattice vectors \( \mathbf{a}_1^*, \mathbf{a}_2^* \)

Definitions: \( \mathbf{a}_1^* \) perpendicular to \( \mathbf{a}_2 \)
\( \mathbf{a}_2^* \) perpendicular to \( \mathbf{a}_1 \)

\[ \mathbf{a}_1^* = 1/(a_1 \sin \gamma) \]
\[ \mathbf{a}_2^* = 1/(a_2 \sin \gamma) \]
\( \gamma \) angle between \( \mathbf{a}_1 \) and \( \mathbf{a}_1 \)

Constructive interference for:
\[ \mathbf{a}_1 (\mathbf{s} - \mathbf{s}_0) = h \lambda \]
\[ \mathbf{a}_2 (\mathbf{s} - \mathbf{s}_0) = k \lambda \]
(Laue conditions for 2 dimensions)
Real 2D system: 3rd Laue condition always fulfilled.

It follows for the direction of beams:
\[ 1/\lambda (\mathbf{s} - \mathbf{s}_0) = 1/\lambda \Delta \mathbf{s} = h \mathbf{a}_1^* + k \mathbf{a}_2^* = \mathbf{g} \]
\( \mathbf{g} = \) reciprocal lattice vector

Example

Ertl/Küppers fig. 9.11, p 216
Ewald sphere construction

- plot reciprocal lattice (rods)
- plot direction of incident beam ($s_0$) towards (00) spot
- go $1/\lambda$ along this direction
- make circle (sphere) with radius $1/\lambda$
- 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
Expected diffraction pattern for (001) surface, e.g. Pt(001) (unreconstructed), $E_0 = 313$ eV
Surface diffraction with X-rays, He-atoms and electrons.
Example: diamond-type (111) surface like C, Si, Ge.
The darkness of rec. latt. spots and rods symbolizes diffraction intensity

Horn-von Hoegen, fig. 2.1
LEED:

2. 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

3. Less simple
   Kinematic theory
   Deviations from long-range order:
   Spot width $\rightarrow$ domain size
   Background intensity $\rightarrow$ point defect concentration
   Spot splitting $\rightarrow$ atomic steps

4. Difficult
   Dynamic theory (multiple scattering)
   Spot intensities $I(E_0)$ or I-V curves $\rightarrow$ structure within unit cell
2. LEED – simple

Superstructures result from:

- Reconstruction = rearrangement of surface atoms on clean surfaces
- Ordered adsorption
Structure examples

Overlayer structures

Ertl/Küppers fig. 9.2, p.204

p(2x2) on square lattice

\[ \sqrt{3} \times \sqrt{3} \] R30° on hex. lattice

Superstructure nomenclature

Wood: Simplest in most cases
p or c(n×m)R\(\vartheta\)°
unit cell vector lengths
\(b_1 = n a_1\quad b_2 = m a_2\)
orientation \(\vartheta\) p=primitive, c=centered

Matrix notation (Park and Madden)
more general
\[ \begin{array}{ccc}
m_{11} & m_{12} & b_1 = m_{11} a_1 + m_{12} a_2 \\
m_{12} & m_{22} & b_2 = m_{12} a_1 + m_{22} a_2
\end{array} \]

Wood

(2×2) \[ \vartheta=0 \text{ is omitted} \] (\(\sqrt{3} \times \sqrt{3}\)) R30°

Matrix

2  0  1  1
0  2  2  -1

Three possible arrangements yielding c(2x2) structures.
Note: different symmetry!

Ertl/Küppers fig. 9.6, p.208

on top  bridge  4-fold hollow
coincidence latt.  
commensurate  
incommensurate 

coincidence latt.  
simple overlayer struct. 

not distinguishable
Real and reciprocal space lattices

Van Hove et al. fig. 3.5, p.55
Superstructures,
example 1

GaAs(001)
clean,
different preparations

As(31)/Ga(55)
Auger peak height ratios:
c(8x2) 1.74
(4x6) 1.77
c(6x4) 1.92
(1x6) 2.12
c(2x8) 2.25
c(4x4) 2.7

Information from patterns:
- symmetry of unit cell
- size and shape of surface unit cell
- sharpness of spots → domain size
- background intensity → concentration of point defects

Drathen, Ranke, Jacobi, 1978
Superstructures, example 2
Si(001) clean

no 2x2 structure!
central spots missing
→ two-domain 2x1

C, Si, Ge (001)

(1x1)

no 4-fold rotation symmetry!

(2x1) and (1x2)

Wasserfall, Ranke, 1994
Figure 3. Buckled dimer reconstructions on the (001) surface of germanium: (a) b(2 × 1); (b) c(4 × 2); (c) p(4 × 1); (d) p(2 × 2).
### 3. LEED – less simple

Information from spot shape (profile), background, $E_0$-dependence ($k_\perp$-dependence)

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Beispiele An</th>
<th>Einfluß auf Reflexprofil</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Punktfehler thermische Bewegung statische Unordnung</td>
<td>Anordnung: statistisch korreliert</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_\perp$ Abhängigkeit keine</td>
</tr>
<tr>
<td>1</td>
<td>Stufenkanten Domänen (Größe, Grenzen)</td>
<td>statistisch regelmäßig oder periodisch (Stufen) keine (Domänen)</td>
</tr>
<tr>
<td>2</td>
<td>Überstruktur Facetten</td>
<td>keine periodisch</td>
</tr>
<tr>
<td>3</td>
<td>Volumendefekte (Mosaik, Verspannung)</td>
<td>monoton</td>
</tr>
<tr>
<td></td>
<td>ideale Oberflächen</td>
<td>keine</td>
</tr>
</tbody>
</table>

Henzler, Göpel Abb. 3.8.10, p.176
Facets and mosaic

Henzler, Göpel
Abb. 3.8.4, p.167

Oberfläche mit Facetten

Facette 1

Facette 2

Mosaik Struktur
Regular atomic steps

Van Hove et al., fig. 3.6, p.58

Henzler, Göpel, fig. 3.8.3, p.165
Pt(9,11,11)

T = 1000K

0.2 ML

1 ML

7 MLE*
Example: Si(001)vic

Si(001) vic, 5° → [110]

Wasserfall, Ranke, 1994
4. LEED – difficult

Spot intensities contain information on structure within the unit cell

\[ I \sim |F|^2 \cdot |G|^2 \]

\[ |G|^2 = \text{structure factor or lattice factor} \]
- contains shape and arrangement of repeat units (unit cells)
- yields reciprocal lattice
- determines location and shape of spots,
  kinematic theory

\[ |F|^2 = \text{structure factor or form factor} \]
- contains contribution from all atoms within the repeat unit,
- includes multiple scattering, in-depth attenuation,
  dynamic theory

Multiple scattering

Henzler/Göpel fig. 3.7.3, p.151
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 improvement
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)
Fe₃O₄(111),
(inverse spinel)
10 nm thick
on Pt(111)

LEED-I-V analysis is one of very few reliable surface structure analysis methods!

Michael Ritter, Werner Weiss Guido Ketteler
FeO/Pt(111), satellite pattern: multiple scattering, kinematic

0.9 ML FeO(111) on Pt(111), „structure 1“

M. Ritter, W. Ranke, W. Weiss
5. LEED in model catalysis - example

UHV
LEED, AES, TDS
p = 10^{-6} to 10^{-10} mbar

Preparation reactor
p = 1000 to 10^{-6} mbar

Ethylbenzene $\xrightarrow{+ \text{Fe}_x\text{O}_y, \text{K, H}_2\text{O}}$ Styrene

$T = 870 \text{ K}$
$\Delta H = 125 \text{ kJ/mol}$

Manfred Swoboda
Christian Kuhrs
Werner Weiss
Distinguish different Fe-O-phases

FeO(111)/Pt(111), 1 ML

Starting surface: 
\( \alpha-\text{Fe}_2\text{O}_3(0001) \) (hematite), defective

After reaction
- no long-range order
- strong C peak in AES

After mild TPO (thermal programmed oxidation)
- reordered
- no longer hematite but \( \text{Fe}_3\text{O}_4(111) \) (magnetite)
6. Conclusions

For qualitative information on surface structure very simple (display LEED)
• Order
• Periodicity
• Symmetry

For quantitative information on deviations from ideal order (SPA-LEED)
• Domain size
• Antiphase domains
• Atomic steps

For quantitative analysis of surface structure (dynamic I-V-curve analysis)
• Precise atomic arrangements
• Relaxations
• Reconstructions