Surface crystallography

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Part of the lecture is taken from Wolfgang Rankes LEED-Script

Literature:
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1. Bravais lattices
2. Structure examples: Overlayers
3. Method: LEED, low energy electron diffraction
4. LEED principle in one and two dimensions
5. Reciprocal lattice
6. Ewald sphere construction
7. LEED and symmetry: glide lines
8. Astonishing example
9. LEED and defects
10. Comparison with other methods
11. LEED I-V measurement
12. Reality – an example from heterogeneous catalysis
Bravais lattices

INTERNATIONAL TABLES
FOR
CRYSTALLOGRAPHY

or

### Bravais lattices

Table 9.1.7.1. Two-dimensional Bravais lattices

<table>
<thead>
<tr>
<th>Bravais lattice*</th>
<th>Lattice parameters</th>
<th>Metric tensor</th>
<th>Relations of the components</th>
<th>Projections</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional</td>
<td>Primitive</td>
<td>Conventional</td>
<td>Primitive/transf.†</td>
</tr>
<tr>
<td><strong>mp</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a, b$</td>
<td>$a, b$</td>
<td>$g_{11}$</td>
<td>$g_{11}$</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>$\gamma$</td>
<td>$g_{12}$</td>
<td>$g_{12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$g_{22}$</td>
<td>$g_{22}$</td>
</tr>
<tr>
<td><strong>op</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a, b$</td>
<td>$a, b$</td>
<td>$g_{11}$</td>
<td>$g_{11}$</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 90^\circ$</td>
<td>$\gamma = 90^\circ$</td>
<td>$g_{12}$</td>
<td>$g_{12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$g_{22}$</td>
<td>$g_{22}$</td>
</tr>
<tr>
<td><strong>oc</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_1 = a_2$</td>
<td>$a_1 = a_2$</td>
<td>$g_{11}$</td>
<td>$g_{11}$</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>$\gamma$</td>
<td>$g_{12}$</td>
<td>$g_{12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$g_{22}$</td>
<td>$g_{22}$</td>
</tr>
<tr>
<td><strong>tp</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_1 = a_2$</td>
<td>$a_1 = a_2$</td>
<td>$g_{11}$</td>
<td>$g_{11}$</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 90^\circ$</td>
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<td>$g_{12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$g_{22}$</td>
<td>$g_{22}$</td>
</tr>
<tr>
<td><strong>hp</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_1 = a_2$</td>
<td>$a_1 = a_2$</td>
<td>$g_{11}$</td>
<td>$g_{11}$</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 120^\circ$</td>
<td>$\gamma = 120^\circ$</td>
<td>$g_{12}$</td>
<td>$g_{12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$g_{22}$</td>
<td>$g_{22}$</td>
</tr>
</tbody>
</table>

* The symbols for Bravais lattices were adopted by the International Union of Crystallography in 1985; cf. de Wolff et al. (1985).
† $T(C) = \frac{1}{2}(11/11)$. 
Structure examples: Overlayers

Overlayer structures

Ertl/Küppers fig. 9.2, p.204

p(2x2) c(2x2) (√3x√3)R30°
on square lattice on hex. lattice

Three possible arrangements yielding c(2x2) structures.
Note: different symmetry but the same LEED pattern!

Superstructure nomenclature

<table>
<thead>
<tr>
<th>Wood: Simplest in most cases</th>
<th>Matrix notation (Park and Madden)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p or c(n×m)R9°</td>
<td>more general</td>
</tr>
<tr>
<td>unit cell vector lengths</td>
<td></td>
</tr>
<tr>
<td>b₁ = n a₁</td>
<td>m₁₁  m₁₂  b₁ = m₁₁ a₁ + m₁₂ a₂</td>
</tr>
<tr>
<td>b₂ = m a₂</td>
<td>m₂₁  m₂₂  b₂ = m₂₁ a₁ + m₂₂ a₂</td>
</tr>
<tr>
<td>rotation 9</td>
<td></td>
</tr>
<tr>
<td>p=primitive, c=centered</td>
<td></td>
</tr>
</tbody>
</table>

Wood

<table>
<thead>
<tr>
<th>2 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 2</td>
</tr>
</tbody>
</table>

(2×2) [9=0 is omitted]  (√3×√3)R30°

<table>
<thead>
<tr>
<th>1 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 -1</td>
</tr>
</tbody>
</table>

Overlayer structures

Ertl/Küppers fig. 9.6, p.208

on top  bridge  4-fold hollow

Wood

(2×2)
Method: LEED, low energy electron diffraction

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

De Broglie wavelength: \( \lambda = \frac{h}{mv} \)

For electrons: \( \lambda = \sqrt{\frac{150}{E_0}} \) \( E_0 \) in eV, \( \lambda \) in Å.

For 100 eV-electrons: \( \lambda(100) = 1.22 \) Å (low energy)

corresponds to atomic dimensions, similar to XRD
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 LEED requires crystalline surfaces.

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

Advantage:
• can look into the unit cell

Disadvantage:
• only local (statistics)
LEED principle in one dimension

\[ g = n\lambda = d - d_0 = a\left(\sin\alpha - \sin\alpha_0\right) \]

\[ \frac{x}{R} = \sin\alpha = \frac{n\lambda}{a} \]

\[ \frac{x}{R} = \sin\alpha = \frac{1}{a} = \frac{n}{\lambda} \]
Useful: Introduction of reciprocal lattice

Real lattice vectors \( a_1, a_2 \)

Reciprocal lattice vectors \( a_1^*, a_2^* \)

Definitions:
- \( a_1^* \) perpendicular to \( a_2 \)
- \( a_2^* \) perpendicular to \( a_1 \)

\[
\begin{align*}
    a_1^* &= 1/(a_1 \sin \gamma) \\
    a_2^* &= 1/(a_2 \sin \gamma) \\
    \gamma &= \text{angle between } a_1 \text{ and } a_1
\end{align*}
\]

Example

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

- plot reciprocal lattice (rods)
- plot direction of incident beam ($s_0$) towards origin of the reciprocal space (0,0)
- go from (0,0) $1/\lambda$ 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) (here k=0)

Usual arrangement:

Normal incidence, yields a symmetrical diffraction pattern
LEED principle in two dimensions

Formation of diffraction pattern

h, k
(order)

Ertl/Küppers fig. 9.12, p. 217

LEED pattern of HOPG?

circle
LEED and symmetry

Table 2.2.13.3. Reflection conditions for the plane groups

<table>
<thead>
<tr>
<th>Type of reflections</th>
<th>Reflection condition</th>
<th>Centring type of plane cell; or glide line with glide vector</th>
<th>Coordinate system to which condition applies</th>
</tr>
</thead>
<tbody>
<tr>
<td>$hk$</td>
<td>None</td>
<td>Primitive $p$</td>
<td>All systems</td>
</tr>
<tr>
<td></td>
<td>$h + k = 2n$</td>
<td>Centred $c$</td>
<td>Rectangular</td>
</tr>
<tr>
<td></td>
<td>$h - k = 3n$</td>
<td>Hexagonally centred $h^*$</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>$h0$</td>
<td>$h = 2n$</td>
<td>Glide line $g$ normal to $b$ axis; glide vector $\frac{1}{2}a$</td>
<td>Rectangular, Square</td>
</tr>
<tr>
<td>$0k$</td>
<td>$k = 2n$</td>
<td>Glide line $g$ normal to $a$ axis; glide vector $\frac{1}{2}b$</td>
<td></td>
</tr>
</tbody>
</table>

* For the use of the unconventional $h$ cell see Chapter 1.2.
Glide line symmetry and LEED

Real space  Reciprocal space  LEED pattern

(0,0)  (2,0)  (0,1)
Ewald sphere construction and beam energy

Increasing the beam energy means increasing $1/\lambda$, i.e. a larger Ewald sphere.
Experiment

• 10 nm TiO$_2$ deposited on Re(10-10) (known from XPS)

• Surface crystallography? LEED!
Ewald sphere construction with facets
Result of the experiment

Rutile (011)-(2x1) crystallites with facets according to the Wulff-construktion

Glide line symmetry
LEED and defects

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

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Beispiele An</th>
<th>Nachweis von Oberflächendefekten mit Beugung</th>
<th>Einfluß auf Reflexprofil</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Punktefehler thermische Bewegung statische Unordnung</td>
<td>Anordnung: statistisch</td>
<td>$k_{\perp}$ Abhängigkeit keine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>korreliert</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Stufenkanten Domänen [Größe, Grenzen]</td>
<td>statistisch regelmäßig</td>
<td>oder periodisch (Stufen)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>oder keine (Domänen)</td>
</tr>
<tr>
<td>2</td>
<td>Überstruktur Facetten</td>
<td>keine</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Volumendefekte (Mosaik, Verspannung)</td>
<td>periodisch</td>
<td>monoton</td>
</tr>
<tr>
<td></td>
<td>ideale Oberflächen</td>
<td>keine</td>
<td></td>
</tr>
</tbody>
</table>

Henzler, Göpel Abb. 3.8.10, p.176

Special method: SPA-LEED (spot profile analysis), complementary to STM
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 – intensities

Spot intensities contain information on structure within the unit cell

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

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

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

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)
Fe$_3$O$_4$(111),
(inverse spinel)
10 nm thick 
on Pt(111)

Michael Ritter,
Werner Weiss
Guido Ketteler

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

\[
\begin{array}{|c|c|}
\hline
\text{Fe} & \text{O} \\
\hline
\text{Fe}_1 & \text{O}_1 \\
\text{Fe}_2 & \text{O}_2 \\
\hline
\end{array}
\]
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{T = 870 \text{ K}} \Delta H = 125 \text{ kJ/mol} \rightarrow \text{Styrene} + \text{H}_2

ISS, PEEM
(Samer Aburous)

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

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)

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

\( \text{Fe}_3\text{O}_4(111) \)

\( \alpha-\text{Fe}_2\text{O}_3(0001) \)