Diffraction methods for crystallographic studies in the volume and at the surface

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.

Formation of diffraction pattern

Ertl/Küppers fig. 9.12, p. 217
Crystallographic information can be retrieved in scattering experiments performed by probe particles (electrons, He atoms, X rays) with appropriate wavelength. The scattered wave is described by:

\[
\Psi_j = \Psi_0 \frac{e^{i k \cdot R}}{R} f_j (k_0, k) e^{i(k-k_0) \cdot R_j}
\]

where \( f_j (k_0, k) \) is the atomic scattering factor and \( e^{i(k-k_0) \cdot R_j} \) is the dephasing between scattering centers.

Given \( R_j = (n_1 a_1, n_2 a_2) + r_j \) with a lattice spacing and \( r_j \) position within the unit cell, the scattered wavefunction can be divided into:

\[
\Psi = \sum_j \Psi_j \propto \sum_j f_j (k_0, k) e^{i(k-k_0) \cdot R_j} = F \cdot G
\]

- **Structure factor**: Depending only on the relative position of the unit cells.
- **Form factor**: Depending on the scattering within the unit cell.

\[
F_{\Delta k} = \sum_j f_j \exp \left( i \Delta \vec{k} \cdot \vec{r}_j \right)
\]

is the atomic factor factor depending on the electron–atom interaction.
Structure Factor $G$ (in 2D)

2 Dim. Case: \( R_j = (n_1 a_1, n_2 a_2) \) position of the unit cell we have \( M_1 \times M_2 \) unit cells:

\[
G = \sum_{n_1=0}^{M_1} e^{in_1a_1(k-k_0)} \sum_{n_2=0}^{M_2} e^{in_2a_2(k-k_0)}
\]

The intensity in each diffraction channel reads:

\[
G^2 = \frac{[\sin(\frac{1}{2} M_1 a_1 (k-k_0))]^2 \ [\sin(\frac{1}{2} M_2 a_2 (k-k_0))]^2}{[\sin(\frac{1}{2} a_1 (k-k_0))]^2 \ [\sin(\frac{1}{2} a_2 (k-k_0))]^2} \implies M_1^2 M_2^2
\]

Which has maxima for \( a \cdot (k-k_0) = 2n\pi \), i.e. in correspondence with the reciprocal lattice vectors:

\[
G = (2\pi n/a_1, 2\pi m/a_2).
\]

In the direction normal to the surface there is no periodicity: the peaks extend indefinitely and become rods.

The angular shape has the form of a Lorenzian curve.

The diffraction spots are narrow if \( M_1 e M_2 >> 1 \).

\( M_1 \) and \( M_2 \) are limited by:

**Coherence length** \( L \), depending on the order at the surface. It may exceed 1000 Å per monocrystals or be limited by dislocations.

**Transfer width** \( W \), depending on the experimental set up.
Definition of reciprocal Lattice and Brillouin Zone

3D case: given the unit cell vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ of the direct lattice, the reciprocal vector $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ is defined by:

$$
\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}
$$

$$
\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}
$$

$$
\mathbf{G} = \nu_1 \mathbf{b}_1 + \nu_2 \mathbf{b}_2 + \nu_3 \mathbf{b}_3 \quad \text{with } \nu_1, \nu_2, \nu_3 \text{ integer numbers}
$$

Dimensions of $\mathbf{R}$ [L]
Dimensions of $\mathbf{G}$ [1/L]

The **Brillouin Zone** is the unit cell in reciprocal space, defined in analogy to the **Wigner-Seitz cell** in real space.
Zone di Brillouin in 3D

Fig. 3.8. The Brillouin zones of the face-centered cubic, body-centered cubic and hexagonal lattices. Points of high symmetry are denoted by $\Gamma, L, X$ etc. The surfaces enclosing the Brillouin zones are parts of the planes that perpendicularly bisect the smallest reciprocal lattice vectors. The polyhedra that are produced by these rules of construction can be drawn about every point of the reciprocal lattice. They then fill the entire reciprocal space. The cell produced by the equivalent construction in real space is known as the Wigner-Seitz cell. It can be used to describe the volume "belonging" to each point of the real crystal lattice.
The probe particles may bounce elastically conserving energy \( (\hbar^2 k^2 / 2m) \) and quantity of motion \( \hbar k \)

\[
k^2 = (k')^2 \quad \text{Conservation of energy}
\]

\[
\vec{k}' = \vec{k} + \vec{g}_{hkl} \quad \text{Conservation of the quantity of motion}
\]

where \( \vec{g}_{hkl} \) is a reciprocal lattice vector, (2 indexes in 2D, 3 in 3D). To have diffraction the modulus of \( \vec{k}' - \vec{k} \) must be comparable or larger than \( \vec{g} \).
Ewald Sphere Construction in 3D Reciprocal Space

\[ k = \frac{2\pi}{\lambda} = \left(\frac{2mE}{\hbar^2}\right)^{1/2} \]

1) A vector \( k \) is drawn terminating at the origin of the reciprocal space.
2) A sphere of radius \( k \) is constructed about the beginning of \( k \).
3) For any point at which the sphere passes through a reciprocal lattice point, a line to this point from the center of the sphere represents a diffracted beam \( k' \).
4) Notice the reciprocal lattice vector \( g_{hkl} \).
Diffraction Techniques in 3D Space

There is a variety of techniques based on the diffraction process suitable for volume structural determination:

Electrons IN/Electrons OUT
TED (Transmission High Energy Electron Diffraction)

Photons IN/Photons OUT
XRD (X-Ray Diffraction)

Neutrons IN/Neutrons OUT
.... (Elastic Neutron Scattering)

....Photon IN/Electron OUT : EXAFS (see later ...)

The best probe particles to study 3D crystallography by diffraction are neutrons and X-rays, for which the single scattering approximation holds. Inverting the scattered intensities allows to reconstruct the position of the scatterers in direct space.

Electrons are suited for microscopes since they can be easily focused.
Diffraction in 2D

$k^2 = (k')^2$

$\vec{k}^2 + \vec{k}_\perp^2 = \vec{k}'^2 + \vec{k}'_\perp^2$

$k'_\parallel = k_\parallel + \hat{g}_{hk}$

Conservation of Energy

Conservation of Momentum

$\vec{k}_\perp$ is not conserved since the translational symmetry normal to the surface is now broken

The indexing of the diffracted beams is, by convention, referenced to the substrate real and reciprocal net.

If the selvedge or adsorbate structures have larger periodicities, the surface reciprocal net is smaller than that of the substrate alone. The extra reciprocal net points and associated diffracted beams are denoted by fractional rather than integral indices.
Ewald Sphere Construction in 2D Reciprocal Space

Notice that the reciprocal lattice is now replaced by infinite reciprocal lattice rods perpendicular to the surface and passing through the reciprocal net points.

1) At surfaces 2D translational symmetry holds thereby only the wave vector parallel to the surface is conserved with the addition of a reciprocal net vector.
2) The dashed scattered wave vectors propagate into the solid and are not observable.
2D Crystallography: Surface Reciprocal Lattice

The reciprocal net vectors $c_1^*$ and $c_2^*$ of the surface mesh are defined as

\[ c_1 \cdot c_2^* = c_2 \cdot c_1^* = 0 \]
\[ c_1 \cdot c_1^* = c_2 \cdot c_2^* = 2\pi \text{ (or 1)} \]

The reciprocal net points of a diperiodic net may be thought of (in 3D space) as rods.

Fig. 3.9. Construction of the surface first Brillouin zone of the (110) surface of a BCC crystal, $d$ is the bulk lattice parameter

The rods are infinite in extent and normal to the surface plane where they pass through the 3D reciprocal net points.

Fig. 3.8. Real (basis vectors: $a, b$) and reciprocal (basis vectors: $A, B$) lattices of the (110) surface of a BCC crystal, $d$ is the bulk lattice parameter
Brillouin Zones 2D

Fig. 3.10a, b. Surface first Brillouin zones of low index faces of cubic crystals: a BCC, b FCC, d is the bulk lattice parameter
Diffraction Techniques in 2D Space

Techniques based on the diffraction process suitable for surface structural determination:

Electrons IN/Electrons OUT
- **LEED** (Low Energy Electron Diffraction)
- **RHEED** (Reflected High Energy Electron Diffraction)

Photons IN/Photons OUT
- **GIXD** (Grazing Incidence X-Ray Diffraction)

Atoms IN/Atoms OUT
- **ABS** (Atom Beam Scattering)

Electrons are the least expensive tool for diffraction experiments, but multiple scattering is important which makes the inversion of the diffraction intensities complicated.
The atomic scattering factor depends on the electron energy. At high energy (1100 eV) the cross section is peaked in the forward direction (0°). At smaller energies (300-500 eV) the backscattering peak (180°) becomes important, while at low energies (<100 eV) interference effects lead to intensity also at large angles from the incident trajectory (peaks at 60° and 120° in the figure).
Examples of LEED Patterns

(a) Si(111)  (b) GaAs(110)  (c) Sr$_2$CuO$_2$Cl$_2$

Notice that the LEED spots span a variety of relative intensities (see below)

$20 \text{ eV} < E_i < 500 \text{ eV}$
2D-Superstructures and nomenclature

Superstructures correspond to the formation of larger lattices due to surface reconstruction or to the presence of an adsorbate layer at the surface.

Fig. 2.5 Examples of overlayer structures in which the open circles represent the periodicity of the substrate while the crosses show adsorbate or selvedge mesh periodicity. In each case the substrate Bravais net is shown dashed while the full surface Bravais net is shown with full lines. (a) shows a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure on an hexagonal substrate, the matrix notation being \(
\begin{pmatrix}
2 & 1 \\
-1 & 1 \\
\end{pmatrix}
\). (b), (c) and (d) show $(2 \times 2)$ or \(
\begin{pmatrix}
2 & 0 \\
0 & 2 \\
\end{pmatrix}
\), $(\sqrt{2} \times \sqrt{2})R45^\circ$ or \(
\begin{pmatrix}
1 & 1 \\
-1 & 1 \\
\end{pmatrix}
\) and $(2 \times 1)$ or \(
\begin{pmatrix}
2 & 0 \\
0 & 1 \\
\end{pmatrix}
\), structures. Note in case (c) that the dash–dot net is centred but not rotated relative to the substrate unit mesh so that this structure is often referred to as c$(2 \times 2)$, necessitating the notation p$(2 \times 2)$ for structure (b).
**LEED Process**

1) The incident wave is exponentially attenuated while the electron propagates in the solid. Inelastic mean free path depends on electron energy and is smallest around 100 eV.

2) Since atom-electron scattering cross sections can be very large ($\approx 1 \text{ Å}^2$, i.e. $10^{10}$ times larger than in X-ray diffraction), multiple scattering must be included. This means that each incident electron is treated as a superposition of the primary wave and the scattered waves.

3) The atomic scattering cross section ($f_j$) involves a phase shift (also dependent on $k$) and is thus complex.

4) The diffraction intensity is modulated by the Bragg conditions in vertically to the surface.
LEED
Since the penetration depth of the primary electrons is finite, one has thickness-modulated vertical reciprocal rods instead of infinite uniform-thickness reciprocal rods within the Ewald sphere construction.
Dynamical LEED: the intensity depends on interference conditions. Inverting the intensities one can determine the position of the scattering centers.

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 (\sim 1 \text{ nm})
The position of the maxima is given by positive interference conditions for scattering off the atomic planes. The peak position is shifted because of the internal potential in the solid which affects the kinetic energy of the electrons. Extra peaks are caused by multiple scattering.
LEED
Examples of spot profiles as a function of the primary beam energy

Spot profile analysis reveals the inadequacy of the simple scattering approach. Multiple scattering plays a major role and it must be included in the theory.
Example: thin Fe$_3$O$_4$ film epitaxially grown on Pt(111)

Fe$_3$O$_4$(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 Kettleier
Basic Instrumental Components of a LEED Experiment

• UHV Apparatus

• Sample

• Sample Preparation Facilities

• LEED Optics
  • Electron Gun
  • Grids & Fluorescent Screen

• CCD Camera/Computer
Usually the electron beam at a selected kinetic energy hits the surface along the normal direction.

Surface sensitivity in LEED is achieved by combining the low IMFP ($\approx 5 \text{ Å}$) with the high backscattering probability (ion core cross section as high as $1 \text{ Å}^2$).
LEED Optics

In this case one UHV flange is just needed
Recording LEED with a CCD Camera
Effect of incident energy

Real Space – fcc(110) surface

Diffraction Pattern

Cu(110)

90 eV

140 eV

90 eV
Effect of incident energy

Real Space – fcc(110) surface

Diffraction Pattern

140 eV

Cu(110)

90 eV

140 eV
Effect of Superstructures
Effect of Superstructures p(2x2)
Effect of Superstructures $c(2\times2)$
RHEED: Reflection high energy electron diffraction

The primary beam hits the surface and the diffracted beam emerges at very grazing incidence (<5°). This, combined with the high forward scattering probability and notwithstanding the high primary energy (30÷100 keV), ensures a high surface sensitivity. This primary-beam/sample/screen geometry is typically preferred during MBE growth, i.e. when the sample must face the Knudsen cells. The Ewald sphere is now very large relative to the spacing of the reciprocal net rods (see LEED) and cuts these rods at grazing angles. The combination of the very grazing angle of intersection of the Ewald sphere with the broadened reciprocal net rods (due to the real quality of surface order and the instrumental transfer width) leads to streaking of the diffraction spots.
Reciprocal Lattice Rods

Ewald sphere

Allowed Reciprocal Lattice Vectors

Reciprocal Lattice Vectors

Ewald sphere

Reciprocal lattice points

Perfectly flat surface Reciprocal rods have no width

Surface with monolayer roughness. Broadened rods.

Surface with large roughness. Transmission features.
RHEED: Ideal Pattern

The spacing gives the surface lattice constant.

Fractional-order spots in some azimuths indicate surface reconstruction.

Splitting of the beams indicates a faceted surface. The separation gives the surface tilt.

This distance gives the angle of incidence.

Image of the incident electron beam
RHEED Apparatus    RHEED and Ewald Sphere

Fig. VIII.4. (a) Schematic of the experimental set-up for RHEED. The inset shows two different scattering situations on a highly enlarged surface area: surface scattering on a flat surface (below) and bulk scattering by a three-dimensional crystalline island on top of the surface (above). (b) The Ewald sphere construction for RHEED. $k$ and $k'$ are primary and scattered wavevectors, respectively. The sphere radius $k = k'$ is much larger than the distance between the reciprocal lattice rods (hk). For more details, see Sect. 4.2 and Figs. 4.2, 3.
RHEED
Scattering and Diffraction Geometry
Figure 3.5. RHEED patterns (20 kV) of Si(111) with the 7 × 7 reconstruction along: (a) [121] and (b) [011] incidence. Note the reciprocal lattice unit cell O'ACB, and the six superlattice spots in each direction between these fundamental spots (from Ino 1977, reproduced with permission).

Figure 3.6. RHEED patterns (20 kV) of Si(111) in the ‘\(\sqrt{3}\)’ structure associated with the ML phase of Ag deposited at 500°C: (a) in the normal view, (b) in the perpendicular view, showing reciprocal lattice unit cell O'ACB, and the two spots between these spots (from Gotoh & Ino 1978, reproduced with permission).
RHEED oscillations

How RHEED oscillations are applied to monitor MBE growth processes.

The (0,0) beam is recorded for destructive interference conditions for scattering from the first layer and from the added layer. The scattered intensity is lowest when the added layer has half a monolayer coverage. Monitoring the beam intensity vs layer growth time allows therefore to determine when the layer is complete.
The intensity of the spots oscillates as layers are deposited if the surface becomes alternately rough and smooth.

The period of the oscillation gives the growth rate and can be used to determine composition in some cases.

Envelope shows the surface roughness evolution.

Surface smoothness recovers if growth is stopped.
High Resolution in k space

High k-resolution is needed to observe large objects since scattering must be coherent over them. Large objects give rise to small momentum transfers \(\rightarrow\) small angle scattering.

Easily achieved with neutrons and TEAS for which the sources are far away from the target, more difficult with electrons which may easily be deflected by stray fields.
Transfer width

The transfer width $w$ corresponds to the size of the area over which the wave associated with the incident particles is coherent (it has a well defined phase relationship)

\[ q_\parallel = k_\parallel - k_i \parallel \]

\[ q_\parallel = k |\sin \theta_f - \sin \theta_i| \]

\[ w = 2\pi/\Delta q_\parallel \]

with $\Delta q_\parallel$ uncertainty over $q_\parallel$ (width of diffraction spots)

\[ \Delta q_\parallel = (\partial q_\parallel / \partial E) \Delta E + (\partial q_\parallel / \partial \theta) \Delta \theta \]

one obtains two contributions:

\[ w_\theta = 2\pi/(k \cos \theta_i \Delta \theta_i) \]

\[ w_E = 2\pi 2 k/(\Delta E |\sin \theta_f - \sin \theta_i|) \]

For low energy electron diffraction (LEED)

$k \approx 0.51 \sqrt{E} \text{ (Å}^{-1})$ for $E$ given in eV

In LEED $E \approx 100 \text{ eV}$ and $\Delta \theta_f \approx 10^{-2} \text{ rad}$ \quad $w_\theta \approx 100 \text{ Å} \ll w_E$

The resolution is thus limited by the angular divergence of the electron beam.
At the atomic distances the incident wave is *spherical* rather than *plane* introducing additional phase shifts which destroy constructive interference.
### Diffraction Intensities for particular configurations

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Spot Separation ((\text{relative to } 2\pi/a))</th>
<th>Halfwidth</th>
</tr>
</thead>
<tbody>
<tr>
<td>One atom</td>
<td>(\infty)</td>
<td>(\infty)</td>
</tr>
<tr>
<td>Two atoms (distance (a))</td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>(N) atoms in a row (regular distance (a))</td>
<td>1</td>
<td>1/(N)</td>
</tr>
<tr>
<td>Several ((M)) groups of (N) atoms each (regularly spaced) [distance of group centers ((N+1/2)a)]</td>
<td>1/([N+(1/2)])</td>
<td>1/({M[N+(1/2)]})</td>
</tr>
<tr>
<td>Several groups of varying size (arranged as in (d))</td>
<td>1</td>
<td>depending on spot size and mixture</td>
</tr>
<tr>
<td>(N) atoms randomly distributed over 2N regular sites</td>
<td>1</td>
<td>1/(2(N))</td>
</tr>
</tbody>
</table>

**Fig. 2.11** Calculated diffraction intensities, \(I\), for one-dimensional scattering models. (a) A single atom; (b) two atoms with spacing of \(a\); (c) \(N\) atoms in a row, spacing \(a\); (d) several groups of \(N\) atoms, each with spacing \(a\) but with the distance between the groups being \((N + \frac{1}{2})a\); (e) several groups of atoms of varying size but otherwise as for (d); (f) \(N\) atoms randomly distributed over 2N sites with regular spacing of \(a\) (Henzler, 1977).
Fig. 4.9. Ewald construction for a surface with a regular step array. The steps with a height \( d \) and a terrace width \( \alpha N \) (\( \alpha \) is the lattice constant) cause an inclination angle \( \alpha \) between the macroscopic surface and the main lattice plane. Corresponding to the lattice distance \( \alpha \), the reciprocal lattice vector is \( G_{||} \). The step array is described by a superimposed inclined reciprocal lattice of periodicity \( Q = 2\pi/Na \). The primary electrons are described by the wavevector \( k \) (two different primary energies with two different lengths of \( k \) are considered) and two different scattered beams (\( k' \) and \( k'' \)) are plotted (\( k = k' \) and \( k = k'' \)).
LEED
How surface defects affect the reciprocal lattice rods and the resultant LEED spot profile

Fig. 3.8. Possible surface defect structures, the corresponding modification of the reciprocal lattice rods and the resultant LEED spot profile (Henzler, 1982).
Figure 3.3. LEED apparatus types, illustrating schematically the configurations of normal and reverse view LEED, and spot profile analysis. The +5 kV is applied to a fluorescent screen, which for reverse view must be transparent (after Bauer 1975, redrawn with permission).
The deflection is achieved via an octupole field. Since the reciprocal space is scanned changing also the angle of incidence the Ewald construction implies a twice as large “modified Ewald sphere.”
SPA-LEED