Structure analysis: Electron diffraction

LEED: Low Energy Electron Diffraction
SPA-LEED: Spot Profile Analysis Low Energy Electron diffraction
RHEED: Reflection High Energy Electron Diffraction
TEM: Transmission Electron Microscopy

LEED

\[ k_i \rightarrow k_f \]

E = 10 – 500 eV

RHEED

\[ k_i \rightarrow k_f \]

E = 10 – 200 keV

TEM

\[ k_i \rightarrow k_f \]

E = 10 – 200 keV

Electron mean free path

\[ \lambda \text{ monolayers} \]
Basic theory of diffraction

By the principles of wave-particle duality, the beam of electrons may be equally regarded as a succession of electron waves incident normally on the sample. These waves will be scattered by regions of high localized electron density, i.e. the surface atoms, which can therefore be considered to act as point scatterers.

The wavelength of the electrons is given by the de Broglie relation:

\[ \lambda = \frac{h}{p} \]

( where \( p \) - electron momentum )

Now,

\[ p = m v = (2 m E)^{1/2} = (2 m e V)^{1/2} \]

\[ \lambda = \frac{h}{(2 m e V)^{1/2}} \]

- \( h \) Planck constant = 6.6 \( \times \) 10\(^{-34} \) J s
- \( m \) electron mass = 9.1 \( \times \) 10\(^{-31} \) Kg
- \( v \) electron velocity
- \( E \) electron kinetic energy
- \( e \) electron charge = 1.6 \( \times \) 10\(^{-19} \) C

Example:
1) Electron energy = 20 eV -> Wavelength = 2.7 Å
2) Electron energy = 200 eV -> Wavelength = 0.87 Å

\( \lambda \) comparable to the atomic spacing

N.B.: Electron energy = 2 eV -> Wavelength = 8.5 Å i.e. the hypothetical ‘RLEED’ would have low resolution
In the case of many scatter points the scattered wave is given by:
\[ \sum_j f_j(\theta, r_j) \ e^{ir_jk_f} \]

\( f_j(\theta, r_j) \) is the atomic structure factor
Elastic scattering: $|k_i| = |k_f|$ or the incident and reflected rays have the same wavelength $\lambda$

Constructive interference: $d \cos \theta_i + d \cos \theta_f = d (n_i - n_f) = m \lambda$

or

$d (k_i - k_f) = 2\pi m$  m integral

This is also equivalent to: $e^{-id(k_i - k_f)} = 1$

Bravais lattice

The condition of constructive interference has to be verified by all the lattice points, i.e.

$\mathbf{R} (k_i - k_f) = 2\pi m$  with $\mathbf{R}$ Bravais lattice vector,

or

$(k_i - k_f) = \mathbf{G}$  with $\mathbf{G}$ is a vector of the reciprocal lattice
Laue’s diffraction condition: $k_f = k_i \pm G$

Given an incident wave $k_i$, the diffraction spots are located by the $k_f$ vectors verifying:

1) $|k_i| = |k_f|
2) k_f = k_i \pm G$

2D case or the case of a surface

2D lattice described by $R_s$ implying $R_s (k_i - k_f) = 2\pi m$
or $(k_f - k_i)// = \Delta k// = \pm G_s$ with $G_s$ vector of the 2D reciprocal lattice

The diffraction spots is a map of the 2D reciprocal lattice

Example

\[ a_1^* = \frac{2\pi}{a_1} a_1 / a_1 \]
\[ a_2^* = \frac{2\pi}{a_2} a_2 / a_2 \]

$k_i = (0,0,1)$

$R_s = 1 a_1 + 1 a_2 = (a_1, a_2, 0)$

$G_s = s (1 a_1^* + 1 a_2^*) = s (2\pi/a_1, 2\pi/a_2, 0)$

$k_f = (2\pi s/a_1, 2\pi s/a_2, c)$

with $c^2 = 1 - (2\pi s/a_1)^2 - (2\pi s/a_2)^2$
Bravais lattice with basis

Consider the elementary cell located at $\mathbf{R}$ and assume the cell containing a basis of $N$ atoms. The coordinates of the $j$-atom in the cell are:

$$\mathbf{r}_j = \mathbf{R} + \mathbf{d}_j$$

with $\mathbf{d}_j$ the position vector inside the cell.

The amplitude of the diffracted wave is given by:

$$\Psi = \sum_{\text{all atoms}} f(\mathbf{r}_h) e^{i \mathbf{r}_h \cdot \mathbf{G}} = f \sum_{\text{Bravais}} \sum_{j=1}^{N} e^{i \mathbf{r}_j \cdot \mathbf{G}}$$

(f identical for all atoms)

In general $f$ is atom dependent -> spot intensity reflects the atomic structure factor.

Diffraction from $N = N_1 \times N_2$ lattice points

$$1 + e^{-i \alpha} + \ldots e^{-i (N_1-1) \alpha} + \ldots e^{-i (N_2-1) \alpha}$$

$$I(G_s) \propto |T(G_s)|^2 = \prod_{i=1}^{2} \sin^2(N_i R_i G_s /2)/ \sin^2(R_i G_s /2)$$

Peak width inversely proportional to $N$. 

![Graph of diffraction peaks](image)
LEED may be used in one of two ways

**Qualitatively**: the diffraction pattern is recorded; analysis of the **spot positions** yields information on the size, symmetry and rotational alignment of the surface unit cell with respect to the substrate unit cell.

**Quantitatively**: the intensities of the various diffracted beams are recorded as a function of the incident electron beam energy; comparison with theoretical curves, may provide accurate information on atomic positions.

### Experimental set-up

The LEED experiment uses a beam of electrons of a well-defined low energy incident normally on the sample.

Only the elastically-scattered electrons contribute to the diffraction pattern; the lower energy (secondary) electrons are removed by energy-filtering grids placed in front of the fluorescent screen that is employed to display the pattern.
fcc(110)

$\mathbf{a}_1^\ast = \frac{2\pi}{\mathbf{a}_1}$

$\mathbf{a}_2^\ast = \frac{2\pi}{\mathbf{a}_2}$

(0,0) represents the reflected beam along the surface normal
fcc(100) (2x2)

fcc(100) (√2x√2) R45  [c(2x2)]
Ideal surface

Real surface

Three possible domains rotated by 60° depending on the terrace
Spot diffraction due to surface defects

Arrangement

regular step array
monotonous

up and down

random steps
two layers

many layers

adsorbate islands

Intensity

$I_0$ $I_{\text{steps}}$ $I_{\text{atoms}}$

$k_{ij}$

$I_{\text{down}}$ $I_{\text{up}}$
LEED is sensible to surface defects

Steps behave like 1D adsorbate nets

Figure 4. (a) STM topography of the clean Cu(223) surface, (500 Å)², from [17]. (b) LEED image (inverted grey scale) at 115 eV. The (0, 1) spot is split into two single spots, separated by the reciprocal superlattice periodicity.
Spot Profile Analysis

**Ideal case**: the diffraction spots are described by $\delta$ functions

**Real case**: the diffraction spots are described by Gauss’s functions

Reasons of the intrinsic width of the diffraction spot:
1) Electron energy non perfectly monochromatic
2) Electron beam non perfectly normal to the sample surface
3) Incident wave non perfectly plane
4) Aberrations of the optics

but also

The sample surface is not a ideal flat surface steps, islands, adsorbates, etc.

The observed spot $O(G)$ is the convolution of the ideal diffraction spot $I(G)$ with the instrumental transfer function $T(G)$ and the surface defect diffraction $S(G)$:

$$O(G) = I(G) * T(G) * S(G)$$

The Fourier transform of $T(G)$ is a gaussian function
The HWHM is defined as the **transfer width** and define the maximum surface distance on which the diffraction is coherent (about 30-50 nm)
SPA-LEED

Large transfer width 100 – 200 nm

STM images of Cu(100) ion sputtered at room temperature. Ion sputtering at normal incidence produces square pits

http://ssp.tnw.utwente.nl/english/onderzoek/stripes/ibmm.html
Surface morphology for different ion sputtering direction

STM

350 x 350 nm²

SPA-LEED

Electron penetration depth $\lambda = 10$-30 nm at 40 keV for normal incidence

Surface sensibility if $\cos \varphi = d/\lambda$ with $d = 1$-2 atomic layers or $\varphi$ about $89^\circ$

Vertical bars in place of spots because due to the geometry the technique is strongly sensible to surface defects (in the impinging direction)

Due to the grazing incidence the surface is seen as a continuous along the incidence direction (no diffraction) and consequently only the periodicity perpendicularly to the incidence direction is detected
The spectrum is visible only if the incident beam is aligned with a symmetry direction of the substrate.
RHEED sensibility to surface defects

Growth of GaAs(100) by Molecular Beam Epitaxy (MBE)


The intensity oscillations are a measure of the surface disorder

Oscillation period: 1 atomic layer
Intensity: decreasing with the number of deposited layers

Imperfect layer by layer growth

Maximum disorder at 0.5 ML during layer by layer growth
What advantages does RHEED offer over LEED?

**Pro:** 1) The geometry of the experiment allows much better access to the sample during observation of the diffraction pattern. This is particularly important if it is desired to make observations of the surface structure during growth of a surface film by evaporation from sources located normal to the sample surface or simultaneous with other measurements (e.g. AES, XPS).

2) Experiments have shown that it is possible to monitor the atomic layer-by-atomic layer growth of epitaxial films by monitoring oscillations in the intensity of the diffracted beams in the RHEED pattern.

**Con:** 1) Quality of the diffraction pattern frequently lower

2) Diffraction patterns have to be observed for at least two sample alignments with respect to the incident beam in order to determine the surface unit cell.
Transmission Electron Microscope (TEM)

Conceptually is identical to an optical microscope where electrons are used in place of photons.

\[ E = 75 \text{ keV} \rightarrow \lambda = 0.05 \text{ Å} \]

Theoretical resolution about hundred thousands times better than that of light.
Unfortunately, this theoretical resolution has never come even close to being attained. The basic draw back is that magnetic fields can not be manipulated, shaped and grouped the way an optical engineer does with glass lenses.

There are several disadvantages of electron optics.
1) Electrons are easily effected by any mater they encounter. When they do encounter mater the interaction results in the emission of all the lower forms of energy. Such as x-rays, secondary electrons, ultraviolet, heat etc.
2) Complicate to describe the scattering process inside the object
3) The wave function resulting from the scattering process is falsified by the optical system
4) The electrons can not pass through air. As a result the microscope has to be kept in a high vacuum.
5) Our eyes are not sensitive to electrons so the operator must learn to focus the instrument using different focal cues than he is used to.

Advantages of TEM over light microscopes:
1) about a thousand fold increase in resolution
2) a hundred fold increase in depth of field.

TEM image of DNA
TEM images of a single-crystal MTJ with the Fe(001)/MgO(001)(1.8 nm)/Fe(001) structure. b is a magnification of a. The vertical and horizontal directions respectively correspond to the MgO(001) (Fe(001)) axis and MgO(100) (Fe(110)) axis. Lattice dislocations are circled. The lattice spacing of MgO is 0.221 nm along the [001] axis and 0.208 nm along the [100] axis. The lattice of the top Fe electrode is slightly expanded along the [110] axis.