### 3.3 Determination of Surface Structure - Reciprocal-Space Techniques

Far-field microscopy cannot image surface details finer than the wavelength of radiation used. This fact forces us to image the surface in reciprocal space (Frauenhofer diffraction) instead of in real space. Subsequent to the recording process the information is transferred into real space. In order to visualize the processes, we now transport the Bravais lattice into reciprocal space, as we did for 3DIM (cf. Eq. 2.4).

If \( \mathbf{a}^* \) and \( \mathbf{b}^* \) are the basis vectors in reciprocal space, we write

\[
\mathbf{a}^* \cdot \mathbf{a} = 2\pi \quad \mathbf{b}^* \cdot \mathbf{b} = 2\pi \quad \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \end{pmatrix} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix} = 4\pi
\]

\[
\mathbf{a}^* \cdot \mathbf{b} = 0 \quad \mathbf{b}^* \cdot \mathbf{a} = 0 \quad \text{d.h.} \quad \mathbf{a} \perp \mathbf{b}^* \quad \text{and} \quad \mathbf{b} \perp \mathbf{a}^*.
\]

We present an example for the relationship of basis vectors in real and reciprocal lattice in Fig. 3.37. Translational invariance means that each point of the lattice can be reached from the origin:

Real lattice \( \mathbf{T} = p \mathbf{a} + q \mathbf{b} \)

Reciprocal lattice \( \mathbf{G} = h \mathbf{a}^* + k \mathbf{b}^* \)

For superstructures we express the reconstructed surface as a linear combination of the vectors of the unreconstructed lattice:

\[
\begin{pmatrix} \mathbf{a}_s \\ \mathbf{b}_s \end{pmatrix} = \mathbf{M} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix}
\]

where \( \mathbf{M} \) is the definition matrix for the superstructure.

In reciprocal space

\[
\begin{pmatrix} \mathbf{a}_s^* \\ \mathbf{b}_s^* \end{pmatrix} = \mathbf{M}^* \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \end{pmatrix}
\]

Note that \( \mathbf{M}^* = \mathbf{M}^{-1} \) or \( \mathbf{M} = (\mathbf{M}^*)^{-1} \), where “\(^*\)” stands for the transposed matrix.

In nature, \(|\mathbf{a}_s| \geq |\mathbf{a}|\), i.e., the increased periodicity of the reconstructed surface is manifested by the presence of additional diffraction spots.

Recall that

\[
\begin{pmatrix} \mathbf{a}_s \\ \mathbf{b}_s \end{pmatrix} = \mathbf{M} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix} \quad \begin{pmatrix} \mathbf{a}_s^* \\ \mathbf{b}_s^* \end{pmatrix} = \mathbf{M}^* \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \end{pmatrix}
\]

\[
\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix} = \mathbf{M}^{-1} \begin{pmatrix} \mathbf{a}_s \\ \mathbf{b}_s \end{pmatrix} \quad \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \end{pmatrix} = (\mathbf{M}^*)^{-1} \begin{pmatrix} \mathbf{a}_s^* \\ \mathbf{b}_s^* \end{pmatrix}
\]

\[
\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix} \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \end{pmatrix} = 4\pi \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = 4\pi
\]

\[
\mathbf{M}^{-1} \begin{pmatrix} \mathbf{a}_s \\ \mathbf{b}_s \end{pmatrix} \begin{pmatrix} \mathbf{a}_s^* \\ \mathbf{b}_s^* \end{pmatrix} = (\mathbf{M}^*)^{-1} \begin{pmatrix} \mathbf{a}_s \\ \mathbf{b}_s \end{pmatrix} = 4\pi
\]

\[
(\mathbf{M}^*)^{-1} \begin{pmatrix} \mathbf{a}_s \\ \mathbf{b}_s \end{pmatrix} = \mathbf{M} \quad \text{or} \quad \mathbf{M}^* = (\mathbf{M}^T)^{-1}
\]
3.3.1 Low-Energy Electron Diffraction

De Broglie has postulated the wave nature of particles in his historical work.\textsuperscript{21} According to him, the nonrelativistic electrons have a wave length $\lambda = h/p$. Only one year later Davisson and Germer\textsuperscript{22} proved this postulate for electrons in scattering experiments with Ni(110).

Consider a transmission experiment through a thin specimen thickness $d$ as shown in Fig. 3.38. We write $I_T = I_o e^{-n\sigma d}$, with $\sigma$ the scattering cross section, $n$ density of particles, and $n\sigma = \mu$, the absorption coefficient. $1/\mu = \Lambda(E)$ is called the penetration depth or the mean free path. X-rays are used to determine the 3DIM structure of the bulk, because $1/\mu \approx 1000 - 10000 \text{ Å}$ (at approximately 1.5 keV). Electrons scatter at valence and core electrons of the target material, and excite bulk and surface plasmons. These are inelastic interactions with large energy transfer with almost no momentum transfer, i.e., they are strong in the forward-scattering direction. Electrons that lose energy do not take part in interference. For

\textsuperscript{21}L. de Broglie, J. Physique 7, 1 and 321 (1926).
\textsuperscript{22}C.J. Davisson and L.H. Germer, Phys. Rev. 30, 705 (1927).
elastically scattered electrons, on the other hand, the mean free path is very short, and the information is limited to a surface region. For electron energies $30 - 300$ eV the mean free path $\Lambda(E)$ is limited to atomic distances as seen in Fig. 1.14.

Elastic scattering is strong at such energies and occurs at the Coulomb potential of the target atoms. There is no energy transfer, but considerable momentum transfer (This was briefly mentioned in the classical limit and given in Eq. 1.3). Since Coulomb potentials are located where the atoms are, the resulting interference pattern carries information on the location of target atoms at the surface. This is the working principle of LEED.\(^{23}\)

\[ I_R = I_o e^{-2d/\Lambda} \]

Figure 3.39: The surface sensitivity is enhanced by a factor of 2 in the exponent in case of elastic reflection of electrons.

How surface sensitive is a LEED experiment? The intensity of electrons prior to an elastic scattering at a depth $z$ can be written as $I(z) = I_o e^{-z/\Lambda}$ with $I_o$ the intensity of the primary electrons. The intensity of electrons that can leave the surface after an elastic scattering is $I_R = I_o e^{-2d/\Lambda}$. The doubling of the exponent renders additional surface sensitivity to LEED. For several other surface-sensitive techniques the sampling depth is given by $e^{-d/\Lambda}$.

Another description divides the intensity of electrons $I_R$ reflected from the surface in two component, if $I_o$ is the intensity of the impinging electrons. $I_d$ originates from a depth between 0 and $d$. $I_V$ originates from $\infty$ to $d$ (Fig. 3.39).

\[ dI_R = I_o e^{-z/\Lambda} \cdot (SN\,dz) \cdot e^{-z/\Lambda} = A e^{-2z/\Lambda} \, dz, \]

where $S$ is the elastic scattering factor, $N$ the number of scattering centers pro unit area parallel to the surface and $Nd\,dz$ number of atoms per volume. $A = I_oSN$ is a constant.

\[ I_d = A \int_0^d e^{-2z/\Lambda} \, dz = A\Lambda/2 \left(1 - e^{-2d/\Lambda}\right) \quad \text{(3.7)} \]

\[ I_V = A \int_d^\infty e^{-2z/\Lambda} \, dz = A\Lambda/2 \; e^{-2d/\Lambda} \quad \text{(3.8)} \]

Important are relative values: The ratio of surface-to-volume contribution is

\[ \frac{1 - e^{-2d/\Lambda}}{e^{-2d/\Lambda}} = e^{2d/\Lambda} - 1. \]  \hspace{1cm} (3.9)

When normalized, the surface contribution reads \( e^{-2d/\Lambda} \) with the corresponding bulk value of \( (1 - e^{-2d/\Lambda}) \).

This consideration holds true for most of the metals and for normal incidence at \( E = 30 - 300 \) eV. Varying the angle of incidence facilitates better surface sensitivity.

If we are interested for a slab of \( d = 3 \) Å at the surface, we obtain with \( \Lambda \approx 5 \) Å \( I_a/I_V = 2.3 \), which means that 70\% of the signal originates from the near-surface region (approximately one single atomic layer) and 30\% from the bulk. Variation of the angle of incidence enhances the surface sensitivity.

If we chose to work between \( E = 30 - 300 \) eV to exploit the extreme surface sensitivity as seen in Fig. 1.14, we obtain \( \lambda \approx 2.2 - 0.7 \) eV for the wavelength of electrons, using Eq. 2.9. The wavelength is comparable with the interatomic distance in most of the elemental solids, which leads to interference effects.

Now we focus on the diffraction of plane waves at 2DIM lattices. First, we make three assumptions:

a - only surface scattering (not realistic, because we have seen that about 30\% intensity originates from the bulk)

b - no multiple scattering (Born approximation)

c - elastic scattering, i.e., \( |\mathbf{k}_i| = |\mathbf{k}_r| \)

First we draw a geometric 1DIM picture (cf. Fig. 3.40). In order to have constructive interference in the direction \( \alpha \), the path difference must be \( a - b = d(\sin \alpha - \sin \beta) \). It follows

\[ d(\sin \alpha - \sin \beta) = n\lambda. \]  \hspace{1cm} (3.10)

The difference between Eq. 2.10 and Eq. 3.10 exhibits the crucial difference between the 3DIM bulk and 2DIM surface diffraction.

Figure 3.40: The path difference between the rays is given by \( a - b \).
Following a more physical consideration (Fig. 3.41) we realize that
a) $k^\parallel$ is conserved.
b) crystal momentum $G^\parallel$ can always be added parallel to the surface
\[ \Delta k^\parallel = k^\parallel_r - k^\parallel_i = nG^\parallel = n2\pi/d. \]
It follows $|k_r| \sin \alpha - |k_i| \sin \beta = n/d k_o \lambda$ or with $|k_r| = |k_i| = |k_o|
\[ d(\sin \alpha - \sin \beta) = n\lambda. \]

Figure 3.41: Electron momentum parallel to the surface is conserved.

Here is $2\pi/d = |G|$ the reciprocal lattice vector or the unit vector of the reciprocal space. We have constructive interference whenever $\Delta k^\parallel$ is a multiple of the reciprocal lattice vector $G^\parallel$. In 1DIM $\Delta k^\parallel = nG^\parallel$, where $|G^\parallel| = \frac{2\pi}{a}$ and in an additional dimension $\Delta k^\parallel = mG^\parallel$, where $|G^\parallel| = \frac{2\pi}{b}$. $n$ and $m$ represent the order of the interference. Zeroth order diffraction means, $\beta = \alpha$, $n = m = 0$, specular (= mirror) reflection, which is encountered for the 00 beam.

Figure 3.42: Rods in the reciprocal space of 2DIM diffraction.

The conditions for the constructive interference is best represented by the Ewald-construction in the reciprocal space. The 3DIM case relevant for x-ray diffraction
was shown in Fig. 2.10 where the Ewald sphere goes through a reciprocal point in order to fulfill the condition for constructive interference. In general (3DIM), $G = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*$, where $h, k,$ and $l$ are integers. In 2DIM, there is no condition obeyed in the third dimension, and, therefore, $l$ is arbitrary and $\mathbf{c}^*$ is any vector perpendicular to the surface. This results in rods in the reciprocal space instead of points as shown in Fig. 3.42.

Thus in 2DIM the Ewald sphere always intersects with the rods and the condition for constructive interference is always fulfilled for a set of $n$ and $m$ as seen in Fig. 3.43. In 3DIM the radius of the Ewald sphere, i.e., the electron energy, must exactly be tuned for the condition of constructive interference to be met.

![Diagram](image_url)

Figure 3.43: Ewald construction for diffraction in 2DIM.

In Fig. 3.43, $G = 2\pi/d$, (00) is the origin of the reciprocal space, $\mathbf{k}_i$ the incident and $\mathbf{k}_r$ the reflected beam, and the Ewald sphere has the radius $2\pi/\lambda$. Wherever the sphere cuts the rods, the diffraction condition is met. This results at all energies in bright spots on the fluorescent screen in the LEED experiment. Therefore, we realize that the LEED pattern represents a projection of the unit cell of the surface reciprocal lattice. From the pattern, we extract the size $G$ of the unit cell and its symmetry $(nm)$. Fig. 3.44 illustrates a typical pattern obtained from a reconstructed Mo(110) surface.\(^{24}\)

Figure 3.45 schematically shows the experimental details. The sample surface is placed at the center of the concentric and spherical multiple-grid system where primary electrons hit the surface. The first grid is on the same potential as the sample to maintain a field-free region and not to influence the path of the scattered

---

electrons. The second grid suppresses inelastically scattered electrons and transmits elastically scattered ones onto a spherical fluorescent collector screen. Thus electrons backscattered from the sample surface are visualized as diffraction spots which can be viewed without angular distortion.
We have to consider three issues:

1. The condition for constructive interference is \(2k_{\text{min}} \geq |\mathbf{G}| = 2\pi/d\) or \(\lambda \leq 2d\). Otherwise the Ewald sphere is too small to cut the rods. In that case we have **evanescent** waves propagating into the crystal with imaginary \(k\) and exponentially diminishing intensity, as it is known for surface states.

2. In LEED we have a case of surface diffraction where the 00 beam always exists because the Ewald sphere always cuts the reciprocal space rods.

3. In 3DIM we have bulk diffraction. In x-ray scattering, the energy must be varied considerably in order to fulfill the condition for constructive interference, i.e., for the Ewald sphere to go through a reciprocal-space spot [Fig. 3.46(right panel)].

![Figure 3.46: The intensity \(I\) vs. energy of the diffracted beams in 2D and 3D.](image)

In 2DIM, however, we always have constructive interference. Figure 3.46 shows on the left-hand side that the cross section for elastic scattering decreases constantly with increasing energy and scattering angle. Its dependence on \(Z\) is not unique and an atomic identification of the target is not possible.

![Figure 3.47: Selected LEED patterns from Si(111) with different reconstructions, see text. Ref. [23].](image)
Figure 3.47 displays diffraction pattern obtained from the Si(111) surface with different surface phases: (a) impurity stabilized \((1 \times 1)\) pattern, (b) \((7 \times 7)\) pattern of the clean surface, (c) \((\sqrt{19} \times \sqrt{19}) - R(23.56^\circ)\) - Ni pattern, (d) \((5 \times 5)\) - Cu pattern, (e) \((6 \times 6)\) - Au pattern, (f) \((7 \times 7)\) pattern.\(^\text{25}\)

### 3.3.1.1 Intensity of Diffracted Beams

We have dealt with the geometry and the symmetry of the atomic distribution at the surface. Equally useful information can be extracted from the investigation of the intensity of diffracted beams.

![Figure 3.48: A plane wave is incident onto the surface with the unit cell that contains \(L\) atoms. We receive the scattered wave at \(X\) in a distance \(R\) from the surface.](image)

In general terms, we consider a plane wave \(\Psi_o = \Phi_o e^{i\mathbf{k}_o \cdot \mathbf{r}}\) incident onto the surface in the direction \(\mathbf{s}_o\) with the momentum \(\mathbf{k}_o = \frac{2\pi}{\lambda}\mathbf{s}_o\).

\(\mathbf{r}_j\) – position of the primitive cell \(j\) in the 2D lattice. In Fig. 3.48 we identify \(\mathbf{r}_j = p\mathbf{a} + q\mathbf{b}\)

\(\mathbf{r}_l\) – position of the scattering center \(l\) in the primitive cell with total \(L\) atoms.

There are \(M_1 \times M_2\) primitive cells aligned periodically, i.e., \(1 \leq p \leq M_1\) and \(1 \leq q \leq M_2\). \(M_1 \times M_2\) or \(aM_1 \times bM_2\) is called the region of coherence. We have to consider all atoms in the cell and all the cells.

The total scattered wave at \( X \)

\[
\Psi(k) \propto \sum_{l,j} f_l(|k_r - k_o|) e^{i(k_r - k_o) \cdot (r_j + r_l)}
\]

\( f_l \) is the scattering amplitude of the atom \( l \). More elegantly:

\[
\Psi(k) \propto \sum_{l} f_l(|k_r - k_o|) e^{i(k_r - k_o) \cdot r_l} \cdot \sum_{j} e^{i(k_r - k_o) \cdot r_j}
\]

The first factor is equal for each cell and depends only on the atomic species.

\[
\Psi(k) \propto \sum_{l=1}^{L} f_l(|k_r - k_o|) e^{i(k_r - k_o) \cdot r_l} \cdot \sum_{p=1}^{M_1} e^{i(k_r - k_o) \cdot a_p} \cdot \sum_{q=1}^{M_2} e^{i(k_r - k_o) \cdot b_q}
\] (3.11)

The first term is the scattering factor \( F \) for the primitive cell. It also depends on the phase factor: \(|k_r - k_o| = 2|k| \sin(\theta/2)|^2\).

The product of the other two terms is called the interference function or the lattice contribution \( G \). It depends on the 2DIM periodicity as well as on \((k_r - k_o)\). Hence

\[
\Psi \propto F \cdot G
\]

In the experiment, only the intensity is accessible but not the amplitude:

\[
I = |\Psi|^2 \propto |F|^2 \cdot |G|^2
\]

It is because of the lattice contribution that the intensity varies if we move on a circle of radius \( R \). So far, this description holds for the dynamic as well as the kinematic theory.

The difference between the two approaches lies in the treatment of the scattering factor \( F \). The dynamic approach considers all the scattering paths into the unit cell and among unit cells. It includes multiple-scattering effects. It correctly treats \( F \) as dependent on both \( k_o \) and \( k_r \). In the kinematic approach one only considers a weak interaction of the plane wave with matter. Only simple single-scattering events take place. This approximation works well for x-ray or high-energy electron scattering. Its validity is doubtful for slow electrons. Yet it is very popular, because
- the calculations are relatively simple,
- the spatial distribution of the spots are correct,
- relative magnitudes are often correct.