Low Energy Electron Diffraction (LEED) (CHM 409, MSc 4th Sem, Course Teacher BKK)

The LEED experiment uses a beam of electrons with well-defined low energy (typically in the range 20 - 200 eV) incident normally on the sample. The sample itself must be a single crystal with a well-ordered surface structure in order to generate a back-scattered electron diffraction pattern. LEED is a very useful technique for surface characterization, particularly for the determination of surface structure. It may be used in one of two ways (i) Qualitatively : where the diffraction pattern is recorded and analysis of the spot positions yields information on the size, symmetry and rotational alignment of the adsorbate unit cell with respect to the substrate unit cell, (ii) Quantitatively : where the intensities of the various diffracted beams are recorded as a function of the incident electron beam energy to generate so-called I-V curves which, by comparison with theoretical curves, may provide accurate information on atomic positions.

Experimental Details:

A typical experimental arrangement used in a LEED experiment is shown in Figure 1. An electron beam of variable energy is produced by an electron gun, and is incident on the sample. The electrons are then backscattered from the sample surface onto a system of grids surrounding the electron gun. The backscattered electrons are of two types; elastically scattered electrons forming a set of diffracted beams which create the LEED pattern, and inelastically scattered (low energy secondary) electrons, which may make up 99% of the total flux, but which are not required. After reaching the first grid, G1 (which is earthed) the elastically scattered electrons are accelerated towards the fluorescent screen, S, which carries a high positive potential (of the order of 5 kV). This provides the electrons in the diffracted beams with enough energy to excite fluorescence in the screen, so that a pattern of bright LEED spots is seen. The grids G2 and G3 are held at an adjustable negative potential, and are used to reject the majority of the electron flux, which is made up of inelastically scattered electrons and which otherwise contribute to a bright, diffuse background across the whole of the LEED screen. The potential on these grids is adjusted to minimize the diffuse background to the LEED pattern. The LEED pattern which is observed may be recorded using a still or video camera mounted onto a chamber window placed directly opposite the LEED screen. **The LEED pattern what we observe is a representation in reciprocal space not in real space. So, simple understanding on lattice representation in reciprocal space is necessary to analyze the LEED patterns.**

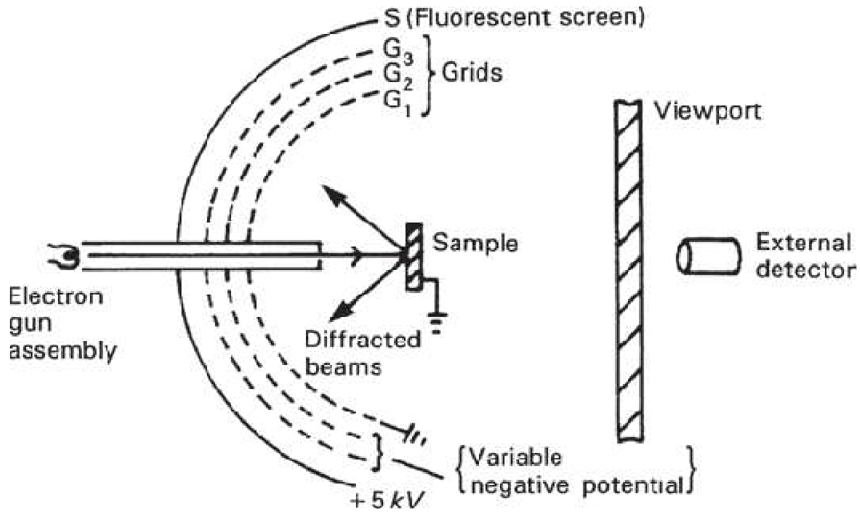


Fig.1 Schematic diagram of conventional LEED optics

Basic principle: From the consideration of wave-particle duality, the beam of electrons may be regarded as a succession of electron wave's incident normally on the sample. These waves will be scattered by regions of highly localized electron density, i.e. the surface atoms, which can therefore be considered to act as point scatterers.

$\lambda = h/p, \quad \lambda = h/\sqrt{2mE}$

Where λ is wavelength, m mass, E energy and h Plank constant. For electron, λ in Angstrom can be written as

$\lambda = \sqrt{150/E_0}$ where E_0 is the energy in eV.

For example, the wave length of electron with energy 150 eV, can be calculated from the above equation and will be around 1Å which is comparable or slightly smaller than a typical inter-atomic spacing and hence suitable for electron diffraction. In LEED, electrons with low energy in the range 20-200 eV is used for diffraction experiment. As these low energy electrons (20-200 eV) interact strongly with matter, they can only penetrate ~10-15Å into the surface. Only electron scattered from near surface can leave the surface and give pattern in the fluorescent screen. So LEED is a surface characterization technique and give only information regarding the structure of the surface.

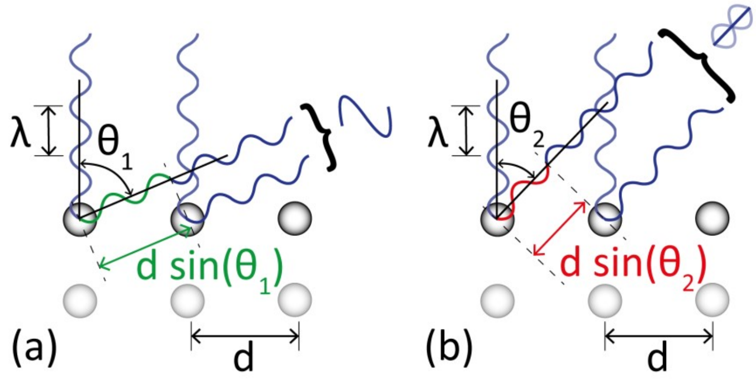


Figure 2. *Diagram of Bragg diffraction. The incident beams are shown normal to the lattice planes of the sample, as in LEED. Different angles of the diffracted waves exhibit **(a)** constructive and **(b)** destructive interference, depending on whether the path difference (shown in green for constructive and red for destructive interference. λ is the wavelength of the incident beam, d is the in-plane atomic spacing and θ is the angle between the incident beam and the atomic layers.*

In case of LEED, the incident beam direction is along the normal to the surface. The relation derived by Bragg for constructive interference between two waves at normal incidence (From Fig. 2) is

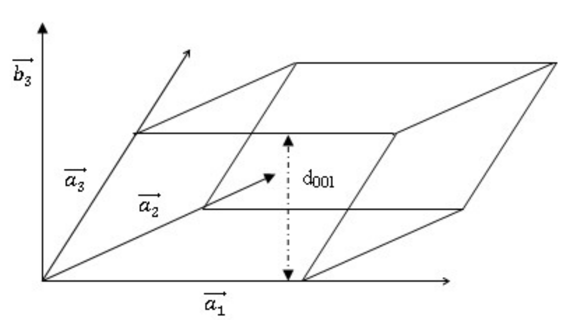
$n\lambda = d \sin\theta$ -----------------------------------(1)

where n is the order of the diffraction

It is clear from equation 1 that some angles will lead to maxima in the diffracted beam intensity. But it should be noted that in the case of the diagram (Fig. 2), if only two atoms are involved, there will be a smooth transition between maxima and minima. In practice, the size of the electron beam in LEED means that many atoms diffract the beam, mainly sharp peaks are observed, surrounded by areas of destructive interference. For this reason LEED is an averaging technique.

Bragg diffraction (and hence LEED) does not directly measure real-space atomic distances. Instead, the distance between diffraction spots is inversely proportional to the inter-atomic spacing, d, and the nλ term is related to the number of wavelengths that fit between atoms. **Therefore, a LEED pattern describes reciprocal space.**

The reciprocal lattice:



For an infinite 3-dimensional lattice, defined by its primitive vectors ($\vec{a_1}$, $\vec{a_2}$, $\vec{a_3}$), the reciprocal lattice ($\vec{b_1}$, $\vec{b_2}$, $\vec{b_3}$) is defined as:

$$\vec{b_1} = 2\pi \frac{\vec{a_2} \text{ X } \vec{a_3}}{\vec{a_1}\,(\vec{a_2}\,.\vec{a_3})} \quad , \quad \vec{b_2} = 2\pi \frac{\vec{a_3} \text{ X } \vec{a_1}}{\vec{a_2}(\vec{a_3}\,.\vec{a_1})} \quad , \quad \vec{b_3} = 2\pi \frac{\vec{a_1} \text{ X } \vec{a_2}}{\vec{a_3}(\vec{a_1}\,.\vec{a_2})}$$

(where X *and . denotes sign and cross product respectively.*

Surface diffraction

Consider a beam of electrons impinging on a 3-dimensional crystal as shown in fig. 3

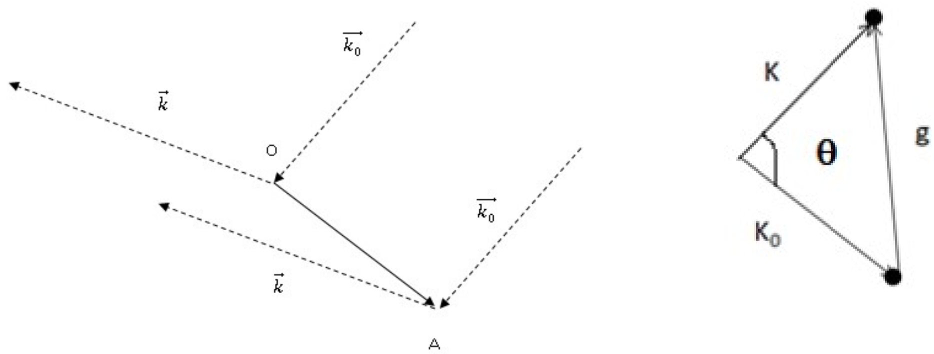


Fig. 3 Diffraction of wave from two lattice point with direction of incident and diffracted beams, where k_0 and k are the wave vector of incident and diffracted beam.

For an incident electron with wave vector $\vec{k_0} = 2\pi/h\lambda_0$, and a scattered wave vector $\vec{k} = 2\pi/h\lambda$, the von Laue condition for constructive interference states that:

$\vec{k} - \vec{k_0} = g = h\,\vec{b_1} + k\,\vec{b_2} + l\,\vec{b_3}$……………………………(2)

where g is a reciprocal lattice vector, where h, k, l must be integer.

Only elastic scattering is considered, and so energy is conserved, i.e. $\vec{k} = \vec{k_0}$. As mentioned, the mean free path of electrons within a crystal is small and so only the first few atomic layers play a role in the diffraction. Therefore, there is no diffraction elements perpendicular to the surface, and the lattice can be considered as a 2-dimensional series of rods extending from the surface lattice points.

Following from this, the 2-dimensional simplification of Equation (2) and the reciprocal lattice vectors become

$\overrightarrow{k^{2D}}$-$\overrightarrow{k_0^{2D}}$ = g = h $\overrightarrow{b_1}$ + k $\overrightarrow{b_2}$ ……………………………….(3)

Where

$\overrightarrow{b_1} = 2\pi \frac{\overrightarrow{a_2} \times \vec{n}}{\overrightarrow{a_1} \times \overrightarrow{a_2}}$, $\overrightarrow{b_2} = 2\pi \frac{\vec{n} \times \overrightarrow{a_1}}{\overrightarrow{a_1} \times \overrightarrow{a_2}}$

where $\hat{n}$ is the surface normal unit vector.

$\overrightarrow{b_1}$ perpendicular to $\overrightarrow{a_2}$, $\overrightarrow{b_2}$ perpendicular to $\overrightarrow{a_1}$

$\overrightarrow{b_1} \cdot \overrightarrow{a_2} = 0$, $\overrightarrow{b_2} \cdot \overrightarrow{a_1} = 0$,

$\overrightarrow{b_1} \cdot \overrightarrow{a_1} = \overrightarrow{b_2} \cdot \overrightarrow{a_2} = 1$

Real Space (i.e. spacing of surface atoms in nm), Reciprocal space (i.e. spacing of diffraction spots in nm^{-1}*)*

A useful visualisation of the effect of Equation 3 is the Ewald sphere, shown in Figure 4.
The Ewald sphere illustrates the points of constructive interference formed by the incident and diffracted electron waves. The upper half of the sphere can be considered as the hemispherical fluorescent screen of the LEED apparatus, and from Figure 4b it is clear how a higher kinetic energy leads to more LEED spots visible on the screen.

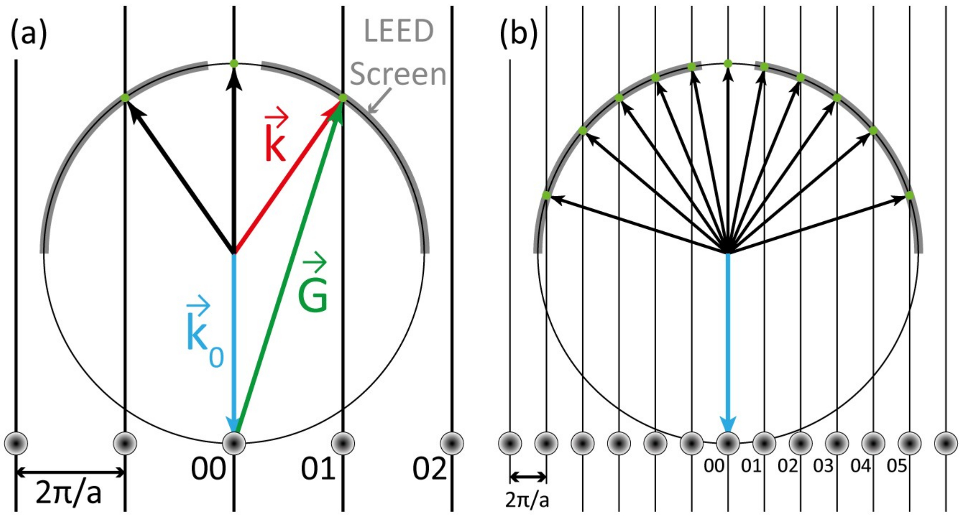


Figure 4: *The Ewald sphere construction. The sphere has a radius $|\overrightarrow{k_0}|$, and because LEED is performed using a beam of electrons impinging normal to the surface, by default the incident wave vector lies parallel to the vertical 00 rod. The spots (rods) are numbered by their hk value. Points where the rods cross the sphere coincide with the Laue condition (Equation 3).* ***(a)*** *Spots are then formed on the fluorescent LEED screen at these points of constructive interference.* ***(b)*** *at higher kinetic energies, the Ewald sphere radius increases and more rods cross the sphere, thus more LEED spots (circles) are visible.*

A LEED pattern obtained from the clean Mo(110) surface is shown in Figure 5, showing the hexagonal reciprocal lattice representative of the close-packed (110) surface of a body-centred cubic crystal.

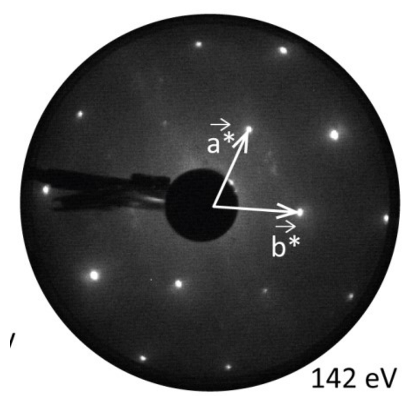


Fig. 5 LEED pattern recorded from the clean Mo(110) surface at an energy of 142 eV. The primitive reciprocal lattice vectors $\overrightarrow{a^*}$ and $\overrightarrow{b^*}$ are shown in white.

Figure 6.a shows a model of an unreconstructed (100) face of a simple cubic crystal and the expected LEED pattern. The spots are indexed according to the values of *h* and *k*.

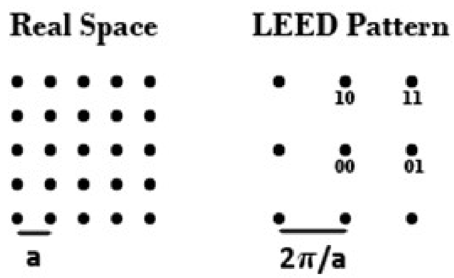
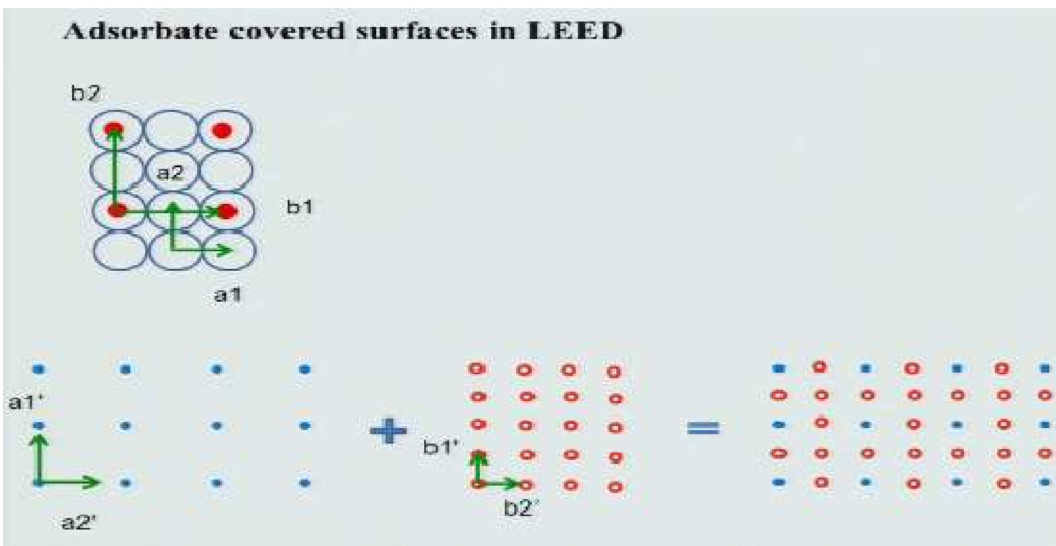


Fig. 6 Real space and reciprocal lattices for the case of a (100) face of a simple cubic lattice.

Low energy electron diffraction can be used not only to study the structure of the surface, but also to study the structure of the absorbent as well as the substrate.



Lets a_1 and a_2 are the basis vector for the pure substrate two dimensional lattice in real space. Now the absorbent are sitting at a particular location and you will get some absorbent lattice which is characterized by b_1 and b_2 in real space. Now if we construct the reciprocal net for the pure substrate and for the absorbent and superimpose these two reciprocal net we will get the reciprocal net of the composite substrate in LEED.

Application: Using simple (display) LEED one can get useful qualitative information on surface structure like order, periodicity and symmetry.

A real surface is not perfectly periodic but has many imperfections in the form of dislocations, atomic steps, terraces and the presence of unwanted adsorbed atoms. This departure from a perfect surface leads to a broadening of the diffraction spots and adds to the background intensity in the LEED pattern. Spot Profile Analysis – low energy electron diffraction (SPA-LEED) is a technique where the profile and shape of the intensity of diffraction beam spots is measured. The spots are sensitive to the irregularities in the surface structure and their examination therefore permits more-detailed conclusions about some surface characteristics. Using SPA-LEED may for instance permit a quantitative determination of the surface roughness, terrace sizes, dislocation arrays, surface steps and adsorbates.

A more quantitative analysis of LEED experimental data can be achieved by analysis of so-called I-V curves, which are measurements of the intensity versus incident electron energy. The I-V curves can be recorded by using a camera connected to computer controlled data handling or by direct measurement with a movable Faraday cup. The experimental curves are then compared to computer calculations based on the assumption of a particular model system. The model is changed in an iterative process until a satisfactory agreement between experimental and theoretical curves is achieved. A quantitative measure for this agreement is the so-called reliability- or R-factor. This method gives many quantitative analysis of surface structure like precise atomic arrangements, relaxations and reconstructions.