4. Techniques for Surface Structure Determination

Long-range order - size and symmetry of surface unit cell

Short-range order - atomic positions within unit cell

4.1 Low Energy Electron Diffraction (LEED)

Most suitable for long-range order determination (does not work on disordered or amorphous materials)

Can provide short range information using detailed theoretical analysis

4.1.1 General Diffraction Ideas

5000 eV photon (x-ray):

$$E = \frac{h\ c}{\lambda}$$

$$\lambda = \frac{6.63\text{x}10^{-34}\ \text{Js} \times 3.00\text{x}10^{8}\ \text{ms}^{-1}}{5\text{x}10^{3}\ \text{V}\ (= \text{JC}^{-1}) \times 1.60\text{x}10^{-19}\ \text{C}}$$

$$= 2.479\text{x}10^{-10}\ \text{m}$$

$$= 2.5\ \text{Å}$$

20 eV electron:

$$\lambda = \frac{h}{p} \qquad \text{de Broglie wavelength}$$

$$p = m\ v = \sqrt{2m(\text{KE})} = 2.42\text{x}10^{-24}\ \text{kg m s}^{-1}$$

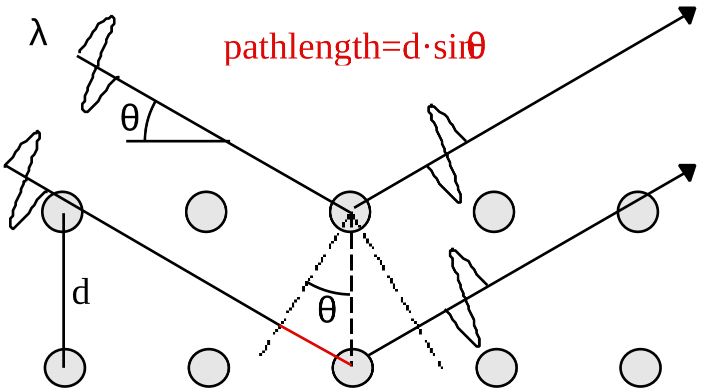
$$\lambda = \frac{6.63\text{x}10^{-34}\ \text{J s}}{2.42\text{x}10^{-24}\ \text{kg m s}^{-1}} \qquad (\text{J} = \text{kg s}^{-2}\ \text{m}^{2})$$

$$= 2.74\text{x}10^{-10}\ \text{m} = 2.7\ \text{Å}$$

Electrons of KE 20-200 eV can be diffracted by lattice of atomic dimensions

Low energy electrons are *strongly* back-scattered by the electrons of the surface atoms (unlike x-ray diffraction)

- electrons of 20-200 eV penetrate only ~10-50 Å into surface



$$n\lambda = 2d\sin\theta$$ Bragg Equation

$$n\left(\frac{h}{\sqrt{2meV}}\right) = 2d\sin\theta$$

Features to note:

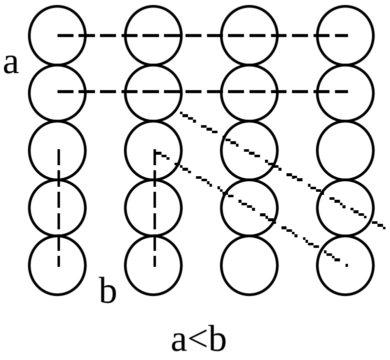
(1) Sinθ is proportional to $\frac{1}{d}$ - diffraction angle gets bigger as d becomes smaller

(2) Sinθ is proportional to $\frac{1}{\sqrt{eV}}$ - diffraction angle becomes bigger as electron KE becomes smaller

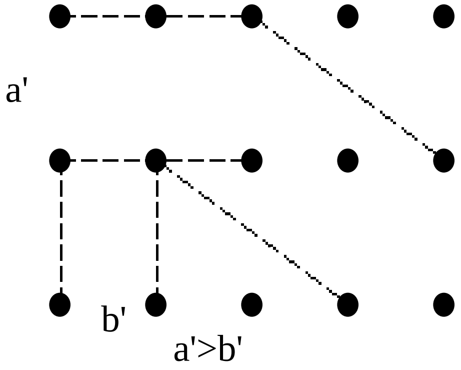
(3) Diffraction has same probability with n=1 and n=-1 - diffraction pattern is symmetric

- Possible to explain surface diffraction in terms of scattering from rows of atoms but quickly becomes cumbersome

Surface
FCC(110)



Diffraction Pattern



Can build a general theory based on reciprocal relationship of diffraction angle and electron wavelength

4.1.2 Ewald Sphere Construction in 3-D

Define wavenumber as reciprocal of wavelength

$$\vec{k} = \frac{2\pi}{\lambda}$$

It can be shown that $\vec{k}$ is really a measure of momentum

$$\lambda = \frac{h}{p} \qquad \vec{k} = \frac{2\pi}{\lambda} = \frac{p\ 2\pi}{h} = \frac{p}{\hbar}$$

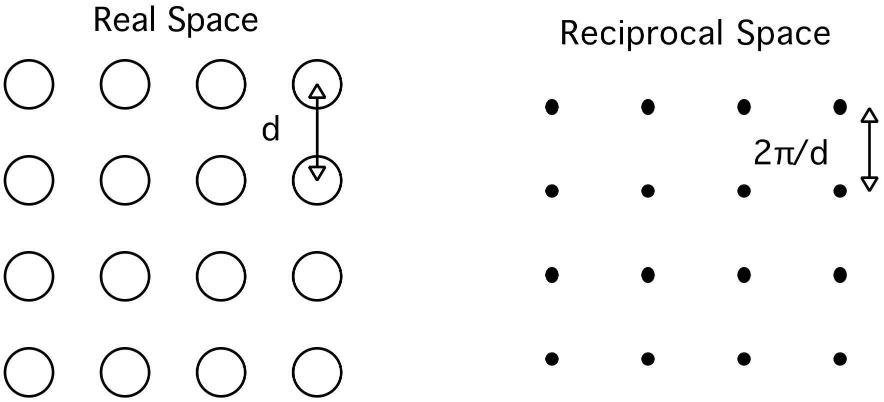
During scattering (diffraction):

- both energy and the magnitude of the electron momentum are conserved

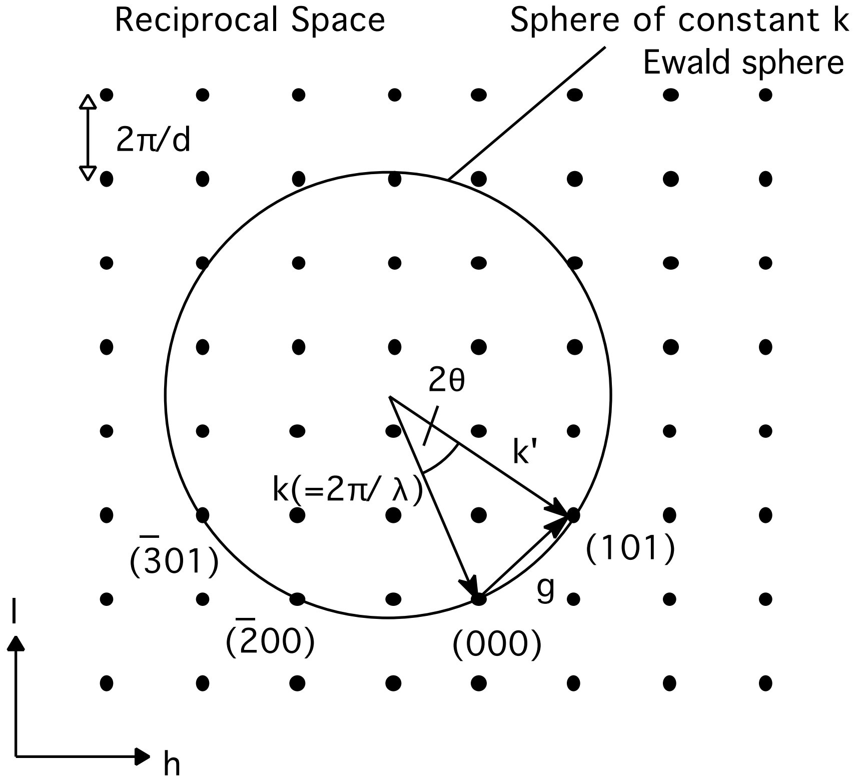
- direction of momentum is changed

So how do we determine scattering angle knowing $|\vec{k}|$ is conserved?

Draw *reciprocal lattice* (k-space lattice):



Reciprocal lattice is a scaled version of real lattice but lattice points are spaced proportional to k not d.



(1) Draw a scaled version of incident beam. The point of the beam should touch one lattice point. The direction of the arrow corresponds to the real-space angle with respect to the bulk lattice vectors

(2) This point is labeled as the origin hkl = (000).

(3) A sphere of constant $|\vec{k}|$ is drawn with center at the start of the incident beam.

(4) Diffraction will occur for any reciprocal space point that crosses this circle such that

$$\vec{k}' = \vec{k} + \vec{g}$$

where $\vec{g}$ is the scattering vector.

(5) Draw a scattered reciprocal k-space vector, $\vec{k}'$, for the outgoing wavevector from the center of the Ewald sphere (circle) to any point where the sphere and reciprocal lattice points intersect

Pythagoras' theorem (in 3-D) gives

$$|\vec{g}|^2 = \left(h^2 + k^2 + l^2\right) \frac{2\pi}{d}$$

$$|\vec{g}| = \sqrt{\left(h^2 + k^2 + l^2\right)} \frac{2\pi}{d}$$

and since

$$|\vec{k}| = \frac{2\pi}{\lambda} \text{ and } \sin\theta = \frac{|\vec{k}|}{|\vec{g}|/2}$$

$$\sin\theta = \frac{\frac{2\pi}{\lambda}}{\sqrt{\left(h^2 + k^2 + l^2\right)} \frac{2\pi}{2d}}$$

$$= \sqrt{\left(h^2 + k^2 + l^2\right)} \frac{2d}{\lambda}$$

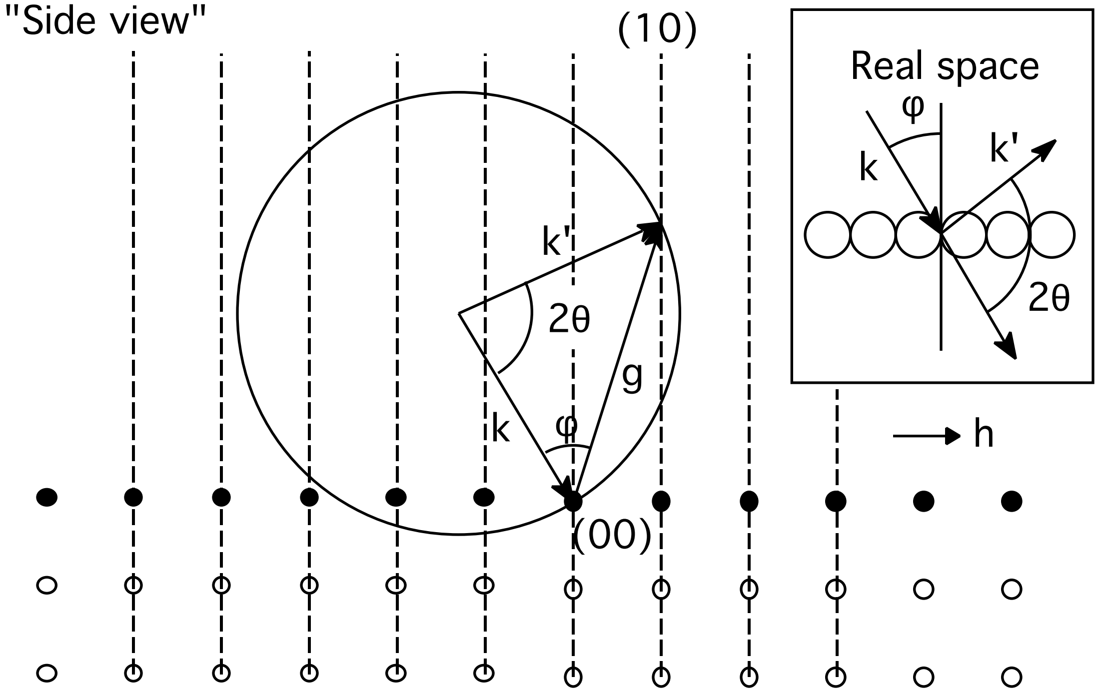
This is essentially the Bragg equation ($n\lambda = 2d \sin\theta$) where $(h^2+k^2+l^2)^{1/2}$ is the diffraction order

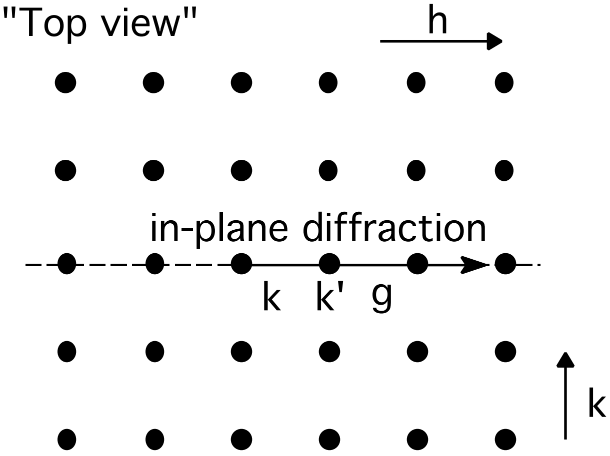
Remember that the above drawing is a 2-D "slice" through true 3-D reciprocal lattice

4.1.3 Ewald Sphere Construction in 2-D

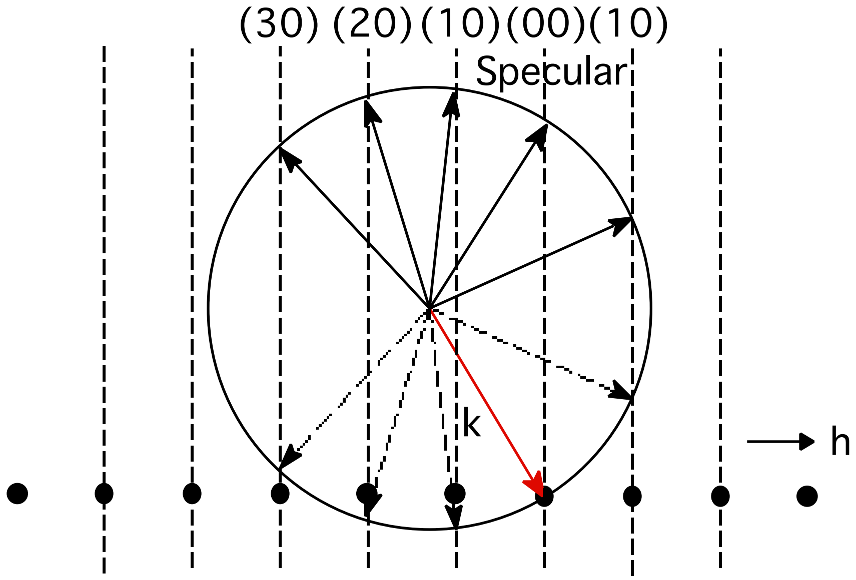
For surface scattering, we are only concerned with periodicity in 2-D of surface, not into bulk.

Can remove one dimension from reciprocal lattice - points become "rods"





In fact, will get diffraction for many beams including forward and back-scattered and a specular beam (00) "reflected" at the incidence angle.



Note:

Only a few beams diffracted

Some beams scattered into surface (invisible)

Some beams back-scattered towards source

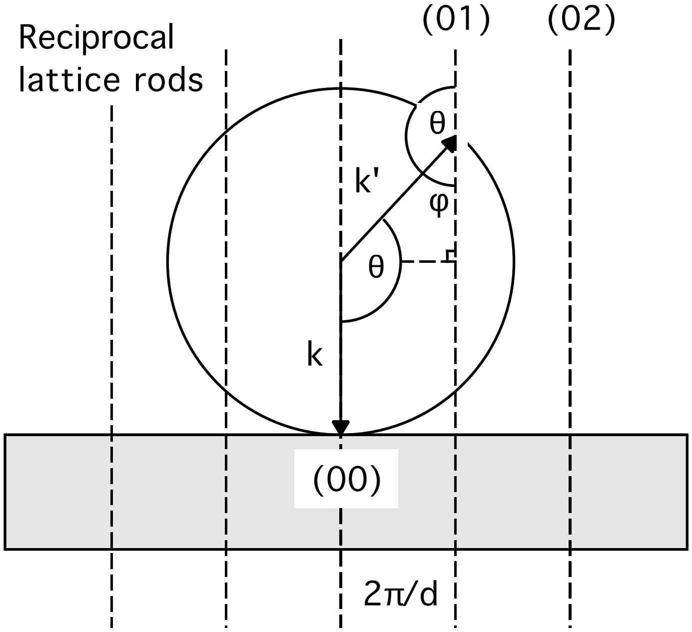
More beams visible as $|\vec{k}|$ increases (smaller λ, larger KE)

4.1.4 Ewald Sphere Construction for LEED

- In LEED, electron beam incident along surface normal

- 2d becomes d in Bragg equation $2d\ \sin\theta = \sqrt{\left(h^2 + k^2\right)}$

Solving for θ by geometry using Ewald sphere construction:



We have enough information to solve for θ:

For the (01) beam -

$$\sin\varphi = \frac{2\pi/d}{|\vec{k}'|}$$

$$\text{since}\ |\vec{k}'| = |\vec{k}| \quad \text{and} \quad \sin\varphi \equiv \sin\theta$$

$$\theta = \sin^{-1}\left(\frac{2\pi/d}{|\vec{k}|}\right)$$

$$= \sin^{-1}\left(\frac{\lambda}{d}\right)$$

In fact, for any beam along this azimuth - (01), (02), (03)… - 2π/d can be replaced by k(2π/d) where k is Miller index of the beam. In general

$$\theta = \sin^{-1}\left(\frac{k(2\pi/d)}{|\vec{k}|}\right)$$

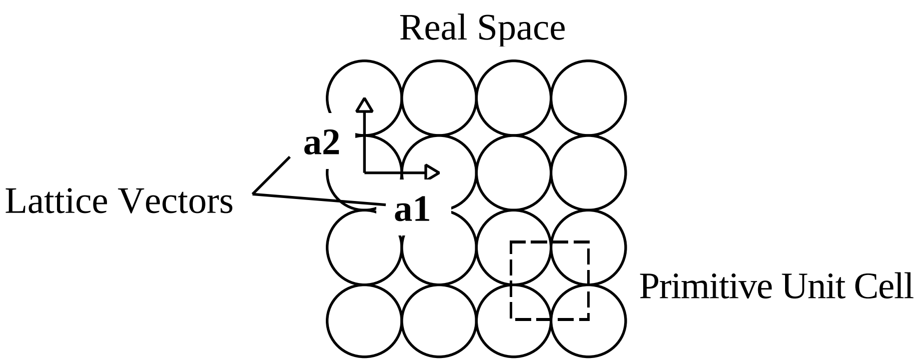
$$= \sin^{-1}\left(\frac{k\lambda}{d}\right)$$

Remember: k is just $\sqrt{\left(h^2 + k^2\right)}$ for constant h in along this azimuth!

4.2 Surface Reciprocal Lattices

4.2.1 Bulk Termination

Let's define a real space plane lattice (surface net) by lattice vectors $\mathbf{a_1}$ and $\mathbf{a_2}$:



Reciprocal lattice (net) defined by reciprocal lattice vectors $\mathbf{a'_1}$ and $\mathbf{a'_2}$ (surface) or $\mathbf{b'_1}$ and $\mathbf{b'_2}$ (adsorbate) defined by:

$$\left.\begin{array}{l}\mathbf{a}_1\;\;\mathbf{a}'_2 = 0\\ \mathbf{a}_2\;\;\mathbf{a}'_1 = 0\end{array}\right\}\text{implies } \mathbf{a}_1 \text{ and } \mathbf{a}'_2 \text{ perpendicular}$$

$$\left.\begin{array}{l}\mathbf{a}_1\;\;\mathbf{a}'_1 = 1\\ \mathbf{a}_2\;\;\mathbf{a}'_2 = 1\end{array}\right\}\text{implies inverse relation } \mathbf{a}_1 \text{ and } \mathbf{a}'_1$$

(Remember dot product $\mathbf{a_1}\cdot\mathbf{a'_1}$ means $|a_1 \text{ x } a'_1|\text{Cos}\alpha$)

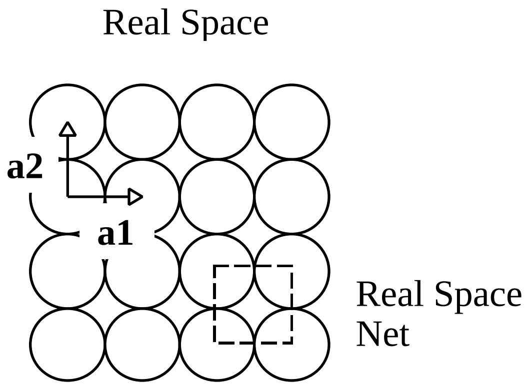
When α=0° (ie $\mathbf{a_1}$ and $\mathbf{a'_1}$ parallel)

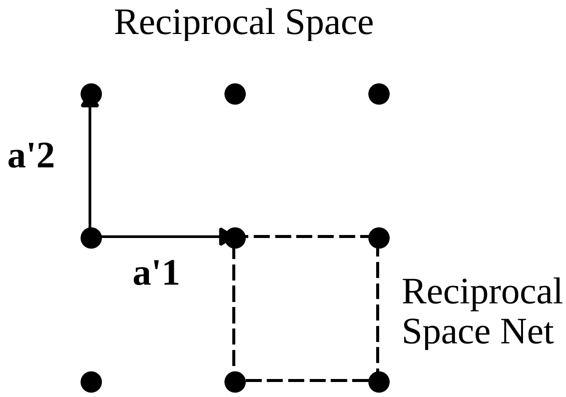
$$\mathbf{a_1} \quad \mathbf{a'_1} = 1$$

$$\left|\mathbf{a_1} \times \mathbf{a'_1}\right| \mathrm{Cos}\alpha = 1 \qquad \text{Reciprocal relationship}$$

$$\left|\mathbf{a_1}\right| = \frac{1}{\left|\mathbf{a'_1}\right|}$$

(1) FCC(100):





$\mathbf{a'_1} \quad \mathbf{a_2}$ and $\mathbf{a'_2} \quad \mathbf{a_1}$

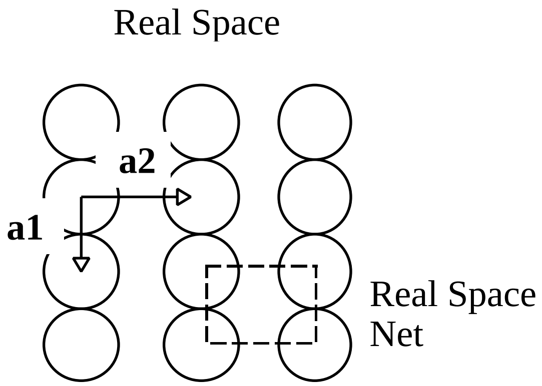
α (angle between $\mathbf{a_1}$ and $\mathbf{a'_1}$ is 0°), Cosα=1

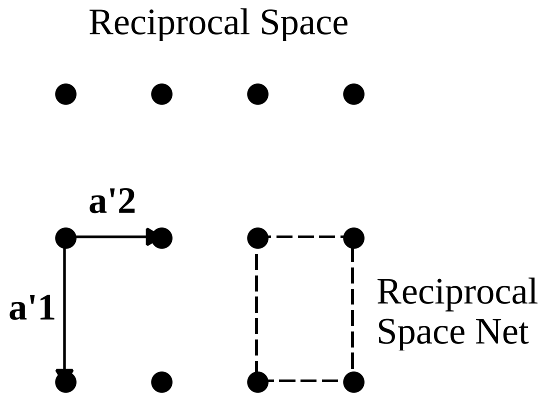
$$\mathbf{a_1} \quad \mathbf{a'_1} = 1$$

$$\left|\mathbf{a_1} \times \mathbf{a'_1}\right| \mathrm{Cos}\alpha = 1$$

$$\left|\mathbf{a_1}\right| = \frac{1}{\left|\mathbf{a'_1}\right|}$$

(2) FCC(110):





$\mathbf{a'}_1$ $\mathbf{a}_2$ and $\mathbf{a'}_2$ $\mathbf{a}_1$

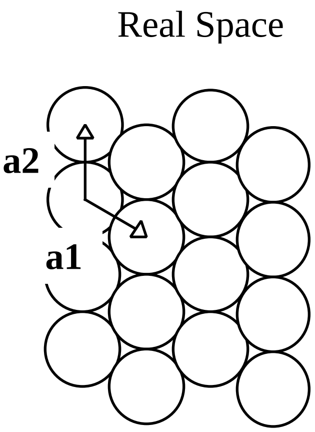
α (angle between $\mathbf{a}_1$ and $\mathbf{a'}_1$ is 0°), Cosα=1

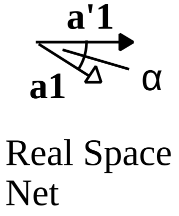
$$\mathbf{a}_1 \;\; \mathbf{a'}_1 = 1$$

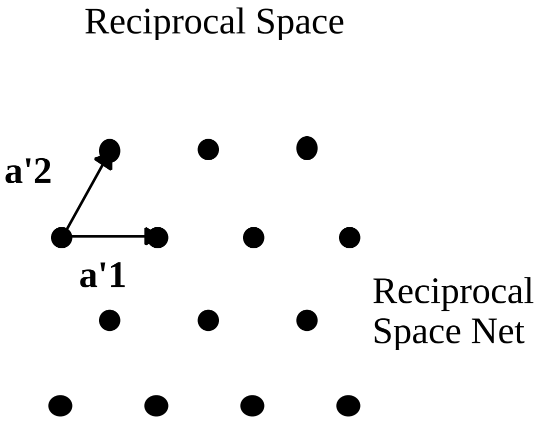
$$\left|\mathbf{a}_1 \times \mathbf{a'}_1\right| \mathrm{Cos}\alpha = 1$$

$$\left|\mathbf{a}_1\right| = \frac{1}{\left|\mathbf{a'}_1\right|}$$

(3) FCC(111):







$\mathbf{a'}_1$ not $\mathbf{a}_2$ and $\mathbf{a'}_2$ not $\mathbf{a}_1$

α (angle between $\mathbf{a}_1$ and $\mathbf{a'}_1$ is 30°), Cosα=√3/2

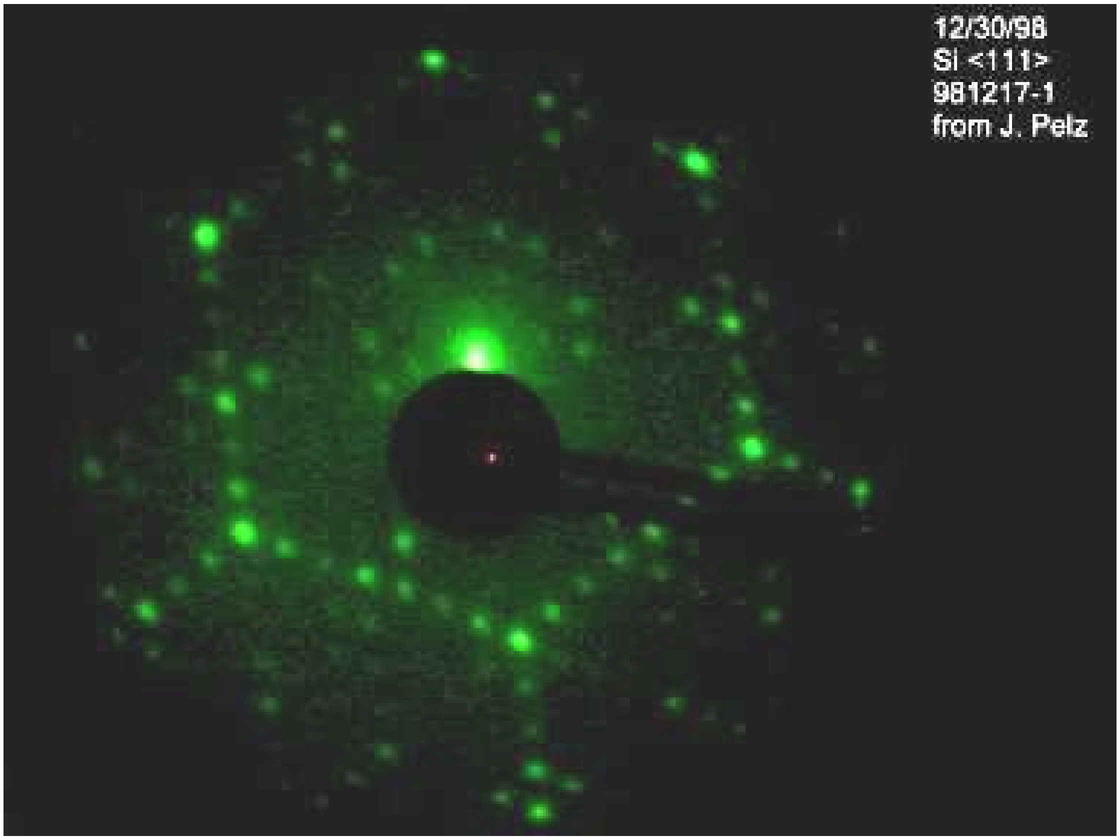
$$\mathbf{a_1} \quad \mathbf{a'_1} = 1$$

$$|\mathbf{a_1} \times \mathbf{a'_1}| \mathrm{Cos}\alpha = 1$$

$$|\mathbf{a_1} \times \mathbf{a'_1}| \frac{\sqrt{3}}{2} = 1$$

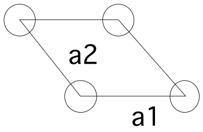
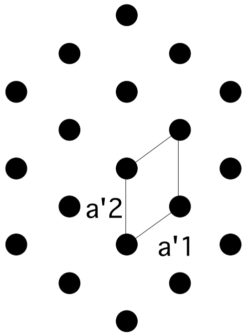
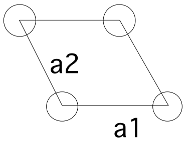
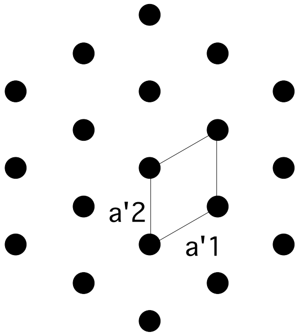
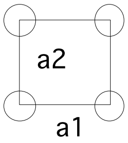
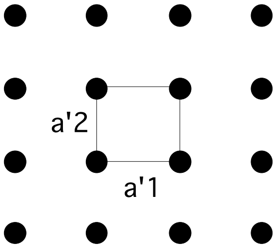
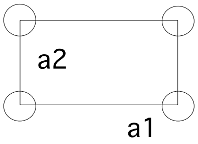
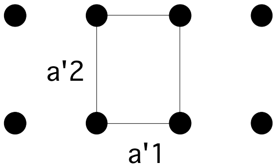
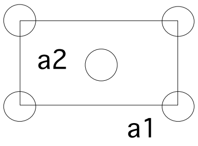
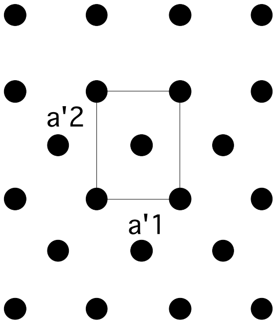
$$|\mathbf{a_1}| = \frac{2}{\sqrt{3}} \frac{1}{|\mathbf{a'_1}|}$$

In fact, for qualitative picture, no need to worry about Ewald sphere - *diffraction pattern is just a scaled version of reciprocal lattice!*



LEED pattern obtained from Si(111)7x7 reconstructed surface

Diffraction Patterns of 5 Plane Lattices:

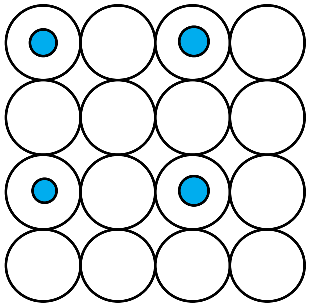
Lattice	Plane Lattice	Diffraction Pattern
Oblique (general)		
Hexagonal		
Square		
Rectangular		
Centered Rectangular		

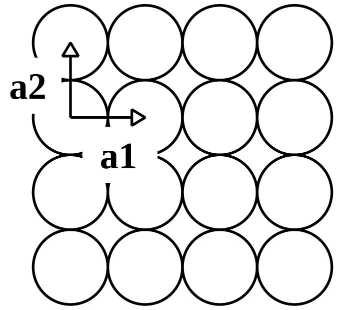
4.2.2 Adsorbate-Covered Surfaces

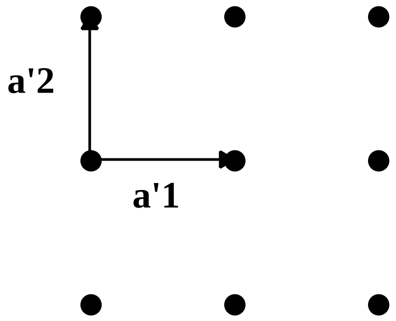
How does the presence of adsorbates influence the electron diffraction pattern?

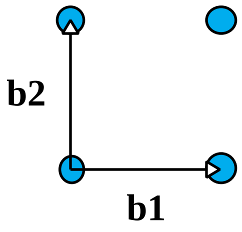
Real Space

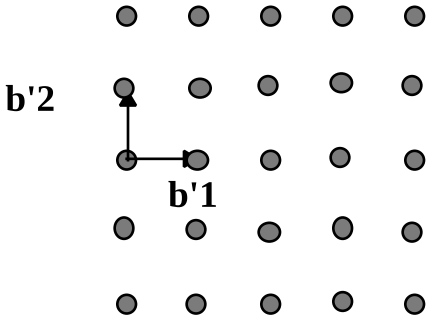
Reciprocal Space



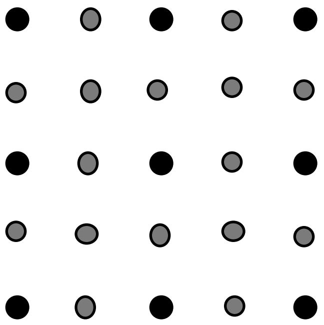




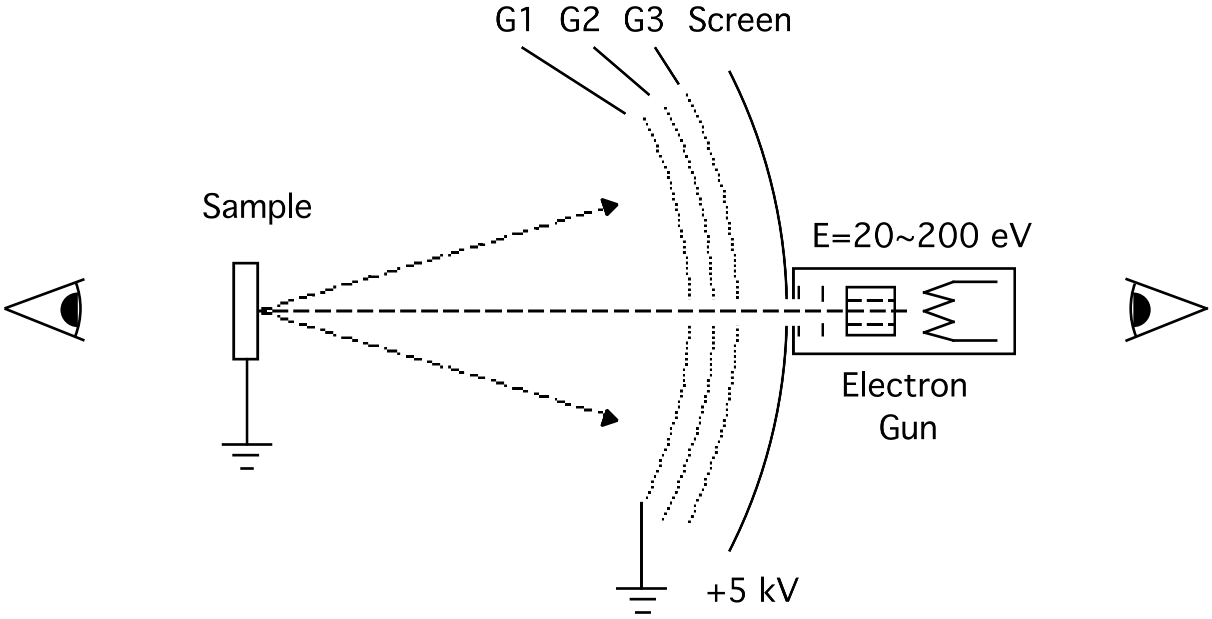




Diffraction Pattern ->



4.2.3 Instrumentation for LEED



Electron gun produces focussed e^- beam 10 nA-10 μA E 20-200 eV

Magnetic shield expels residual magnetic fields

Sample positioned at "focus" of hemispherical grids

Diffracted electrons (elastically scattered) and secondary electrons (inelastically scattered) back-scattered towards LEED optics in field free region

Diffracted electrons - spots

Secondary electrons - diffuse background

After passing through G1 (ground) accelerated towards phosphor screen

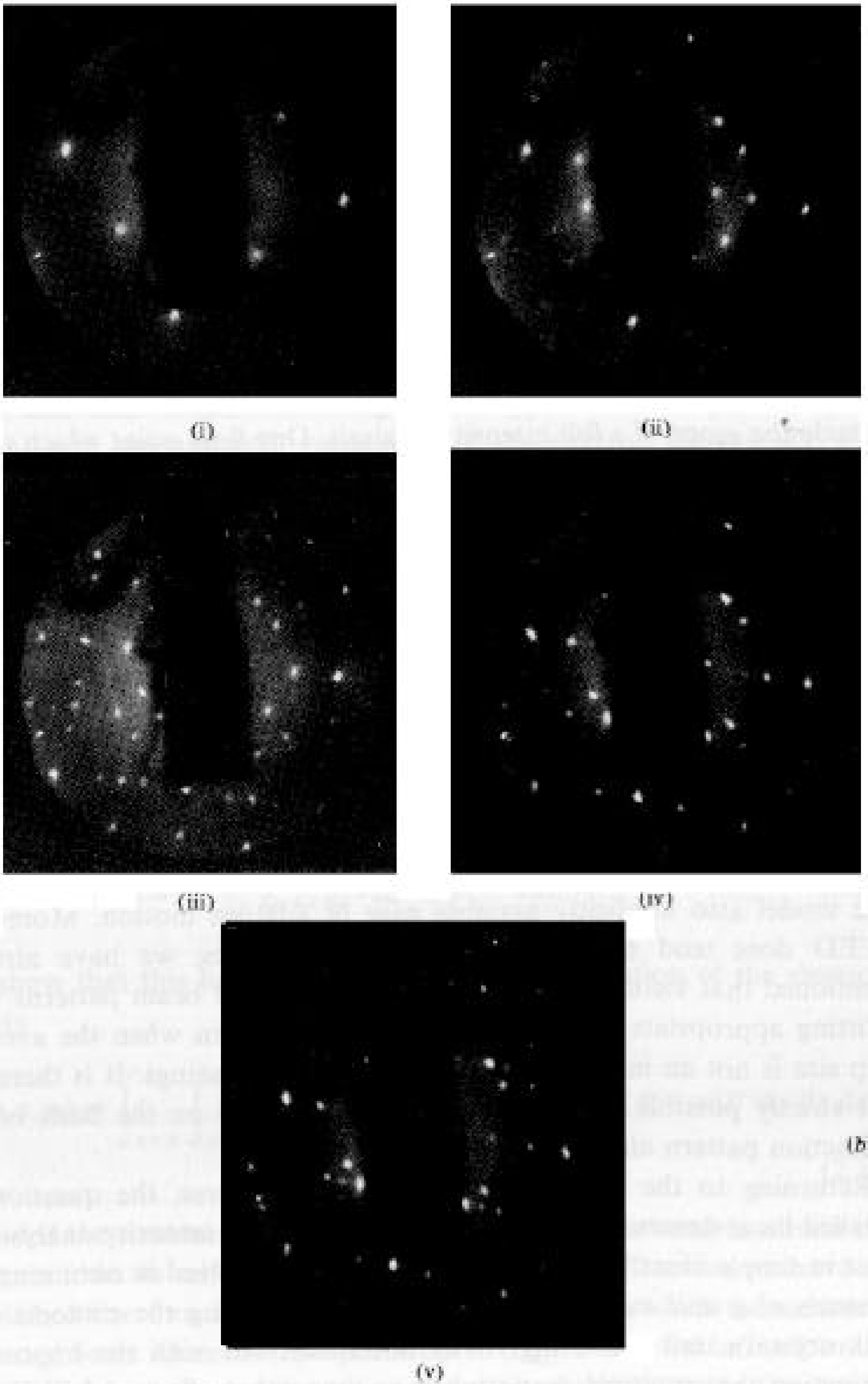
Negative potentials applied to G2 and G3 to repel secondary electrons

Electrons strike phosphor → photons

Front-view LEED versus rear-view LEED

Image captured on photographic film or video camera

Rear-view LEED system. Width about 10", height about 12 ". The grids, G1, G2 and G3, are visible at the top of the picture and the view-port is at the bottom. The magnetic shield has been removed.


(i) (ii) (iii) (iv) (v)

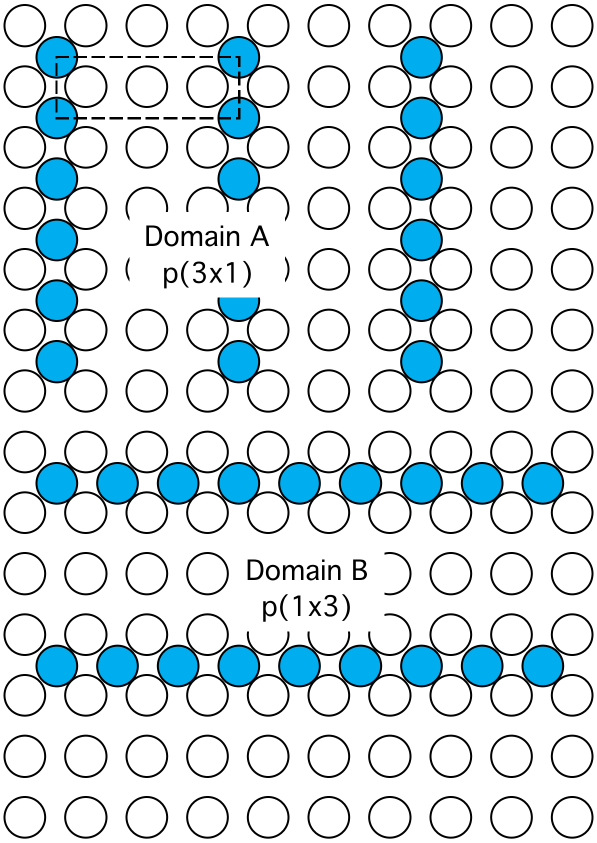
(*b*)

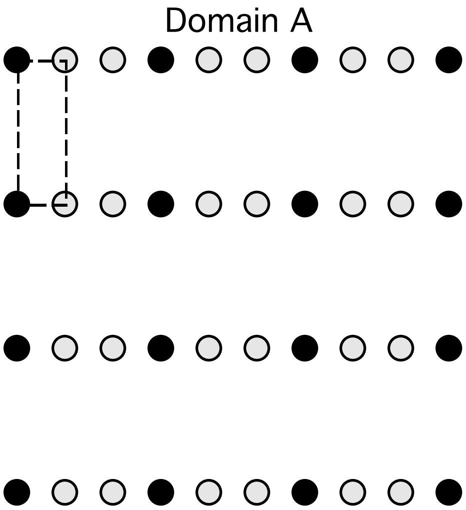
Fig. 2.17 (*continued*) (*b*) Actual LEED patterns at various coverages: (i) $c(2 \times 2)$, $\theta = \frac{1}{2}$; (ii) incommensurate, $\theta = 0.313$; (iii) $c(2 \times 3)$, $\theta = \frac{1}{3}$; (iv) incommensurate, $\theta = 0.359$; (v) $c(2 \times 8)$, $\theta = 0.375$. LEED beam energies are 70 eV except for (iii) which is at 89 eV (after Jones & Woodruff, 1981).

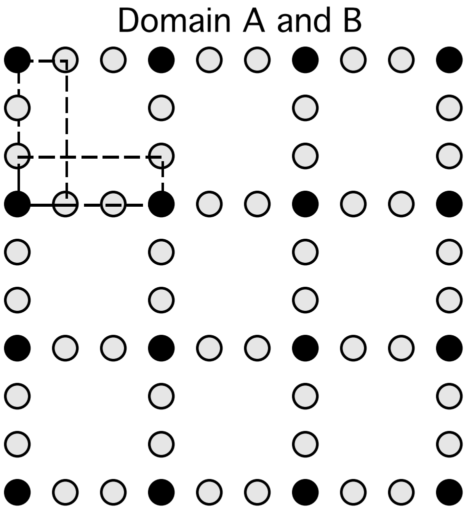
4.2.4 Real Surface Diffraction Patterns

If electron beam diameter is larger than *domain* size on surface - presence of multiple (rotational) domains increases complexity of diffraction pattern

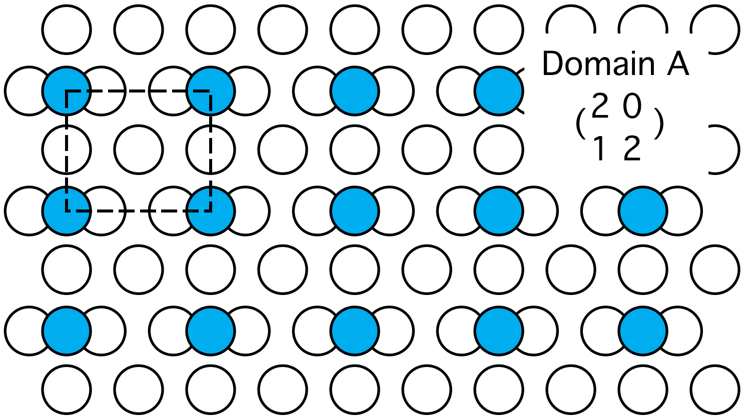
Example 1:

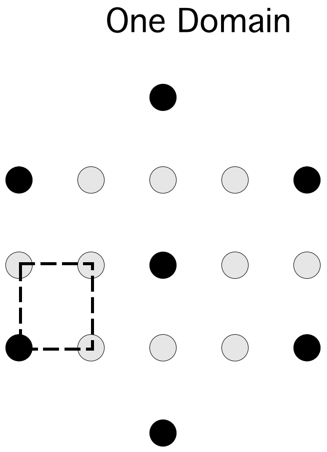


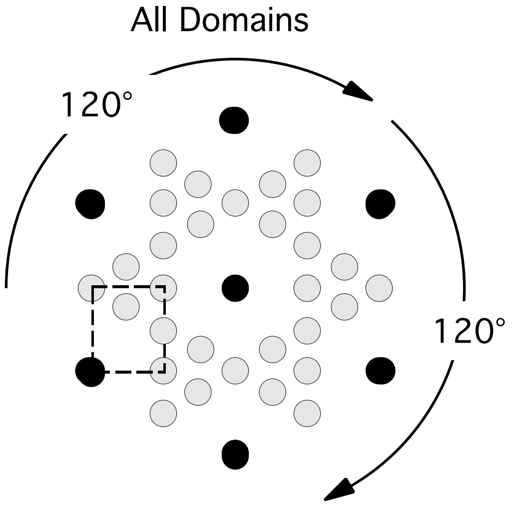




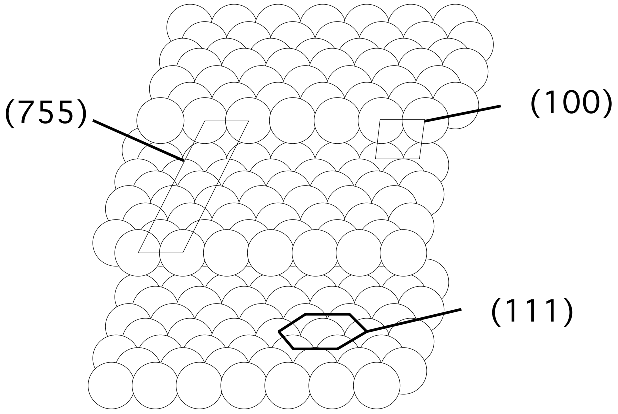
Example 2:



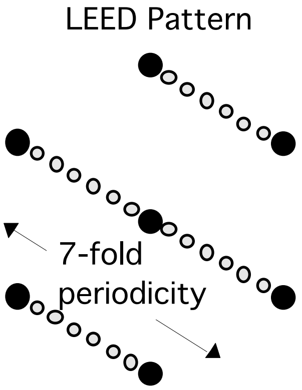




Vicinal surfaces with regularly spaced steps behave like large (1-D!) adsorbate nets



Pt(755)
Pt (S)-[7(111)x(110)]



Irregularly-spaced steps produce "streaky" or blurred LEED spots or rows of spots

Kinked surfaces produce additional spots or rows of spots in different direction to step spots

Amorphous, disordered or *glassy* surfaces produce no LEED pattern - only diffuse background

4.3 Dynamical LEED

So far, only considered position of spots

More information in intensity of spots?

> *Kinematic* LEED considers incident electron scattered once (top layer of atoms) - works fine for symmetry/size of adsorbate or unit cell
>
> *Dynamical* LEED considers incident electron scattered multiple times (1st, 2nd, 3rd… layers of atoms) - necessary to account for intensity of spots

Essential ingredients of dynamical LEED theory:

Calculation of amplitude (A) and phase (δ) due to -

(a) ion core scattering

(b) multiple scattering

(c) inelastic events

(d) surface vibration (effect of temperature)

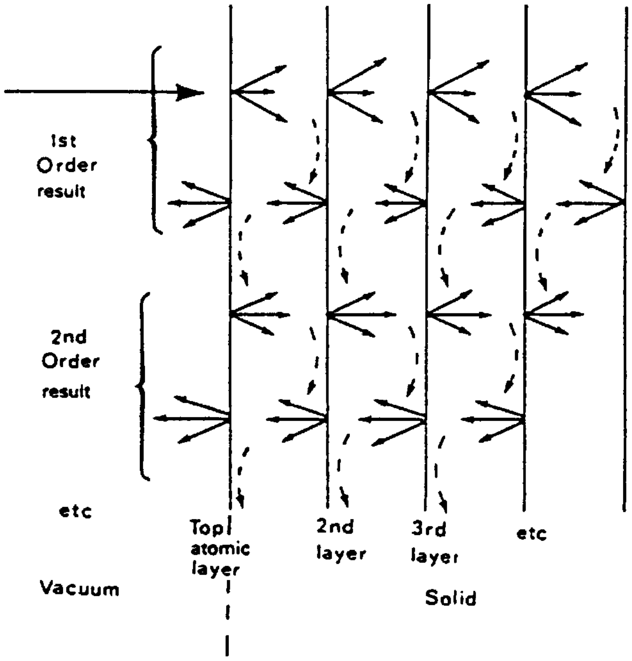


FIG. 3.17. Sequential 'passes' of the electron scattering processes involved as a renormalized forward-scattering scheme is used to compute the intensities of beams leaving a surface. Convergence is usually obtained after a few passes.

If multiple scattering occurs then all the waves scattered into a particular direction in many different scattering sequences must be added up with due regard for their correct amplitudes and phases. Such a treatment is referred to as a *dynamical theory* and it is essential in the description of LEED.

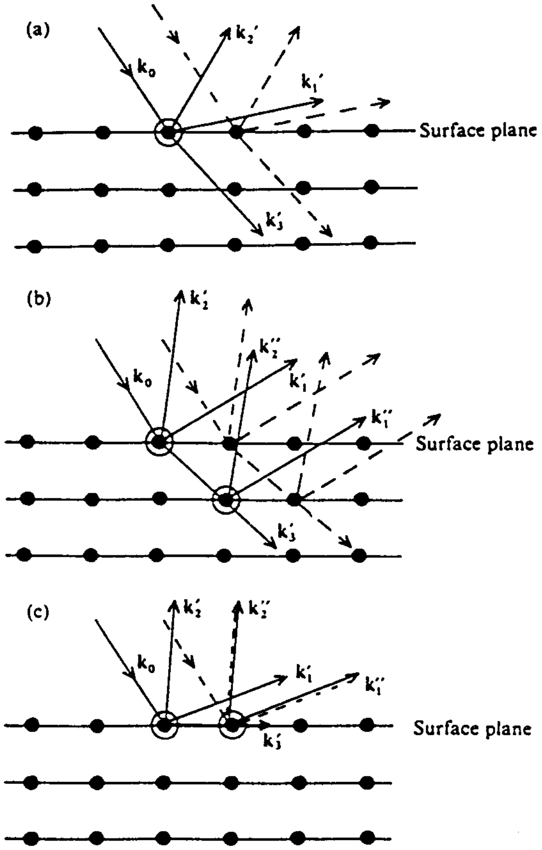


FIG. 3.15. The scattering of waves from a solid surface. The filled-in circles indicate the atomic positions and the open circles are added when a scattering event occurs. (a) Single scattering. Kinematical theory would describe such an event. Diffraction occurs when the 'dashed' wave adds up in phase with the 'solid' wave. (b) Double scattering. The forward-scattered beam k_3' is scattered into two beams k_1'' and k_2'' adding to beams k_1' and k_2' generated at the first scattering event. (c) A case of double scattering involving a surface wave k_3'.

4.3.1 Measurement of LEED Spot Intensities

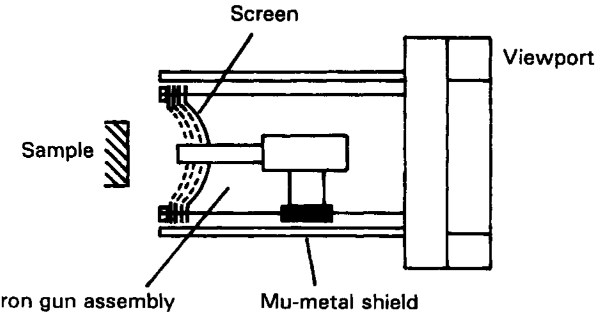


Figure 8.7. Schematic diagram of a reverse view LEED/Auger system (courtesy of Omicron)

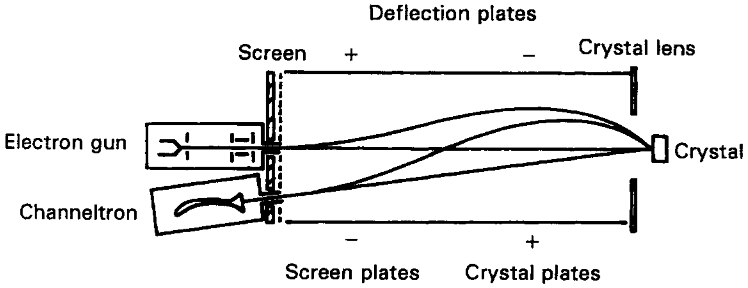


Figure 8.8. Schematic diagram of the SPA-LEED system, showing the beam paths with and without deflection voltages applied. Reproduced by kind permission of Elsevier Science – NL from ref. [4]

Digital video camera (CCD) used to measure intensity

Computer-controlled potentials "steer" one diffracted beam towards electron multiplier as primary beam energy is changed

4.3.2 Dynamical LEED Methodology

Intensity tells us about interlayer spacing

When combined with multiple scattering theory, gives information about "height" of adsorbate atoms and relaxation phenomena

Can measure intensity in two ways:

(1) vary incidence angle - I(θ) curves

(2) vary incidence energy - I(V) curves

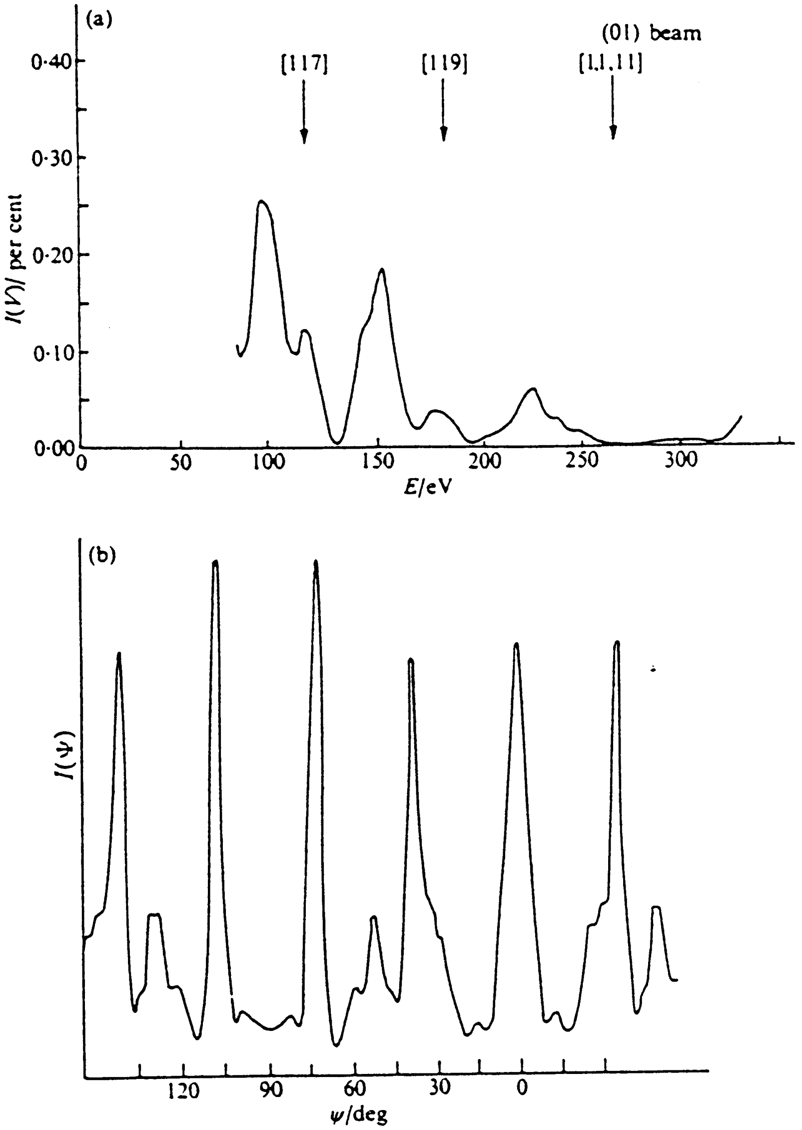


FIG. 3.16. (a) An $I(V)$ plot from Mg(100) in normal incidence. The energies of the Bragg peaks are marked and indexed. The shift between the large observed peaks and the calculated Bragg peak positions is due to the 'inner potential' in the crystal. (b) A rotation diagram I (ψ) from W(110). The primary energy is 595 eV and the diffraction geometry is set so that the (550) beam is being measured. (After Gervais, Stern, and Menes 1968.)

Set of I(V) curves with variable θ:

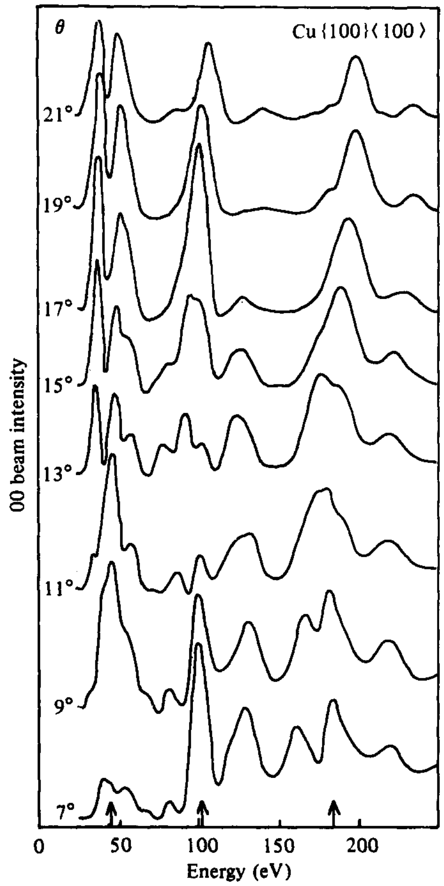


Fig. 2.19 LEED experimental intensity–energy spectra for the 00 beam from a Cu{100} surface in a ⟨100⟩ azimuth for different incidence angles. The arrows indicate the predicted positions of kinematical 'Bragg peaks' at normal incidence for energies in the crystal.

Methodology -

1. Initial guess for structure
2. Calculate I(V) or I(θ) curves using dynamical LEED theory
3. Compare theory and experimental data
4. Refine guessed structure until best agreement is obtained

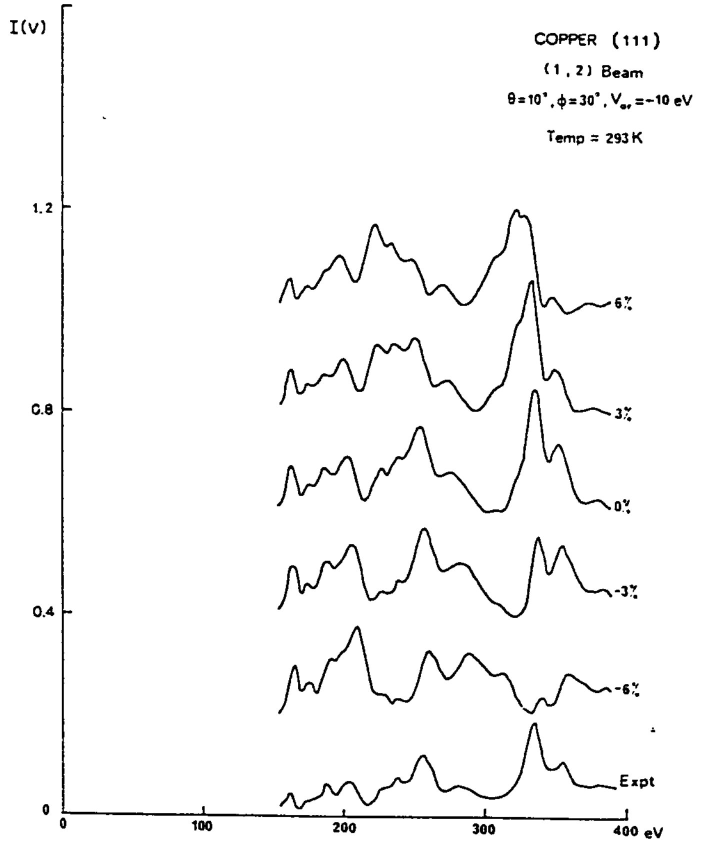


FIG. 3.18. LEED $I(V)$ curves for the (11) beam from a Cu(111) surface. The geometry is for angle of incidence of 10° and azimuth of 30°. The bottom curve is the experimental data. The five top curves are for top layer relaxations of ±6%, ±3%, and 0% of an interlayer spacing of bulk Cu.

Agreement between theory and experimental data given by "goodness of fit" Pendry R-factor

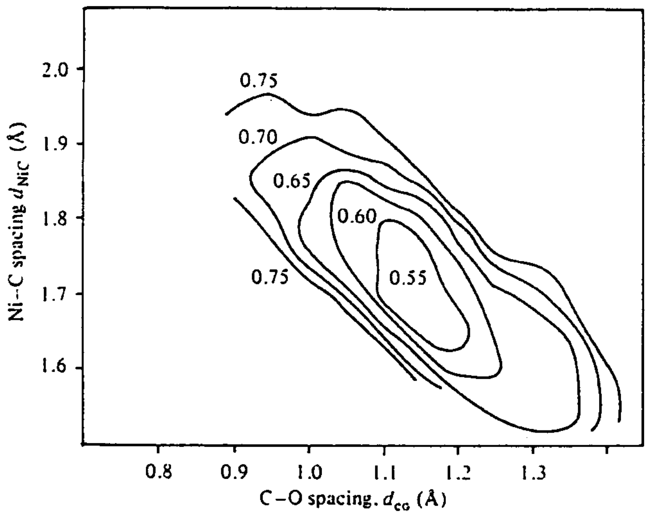
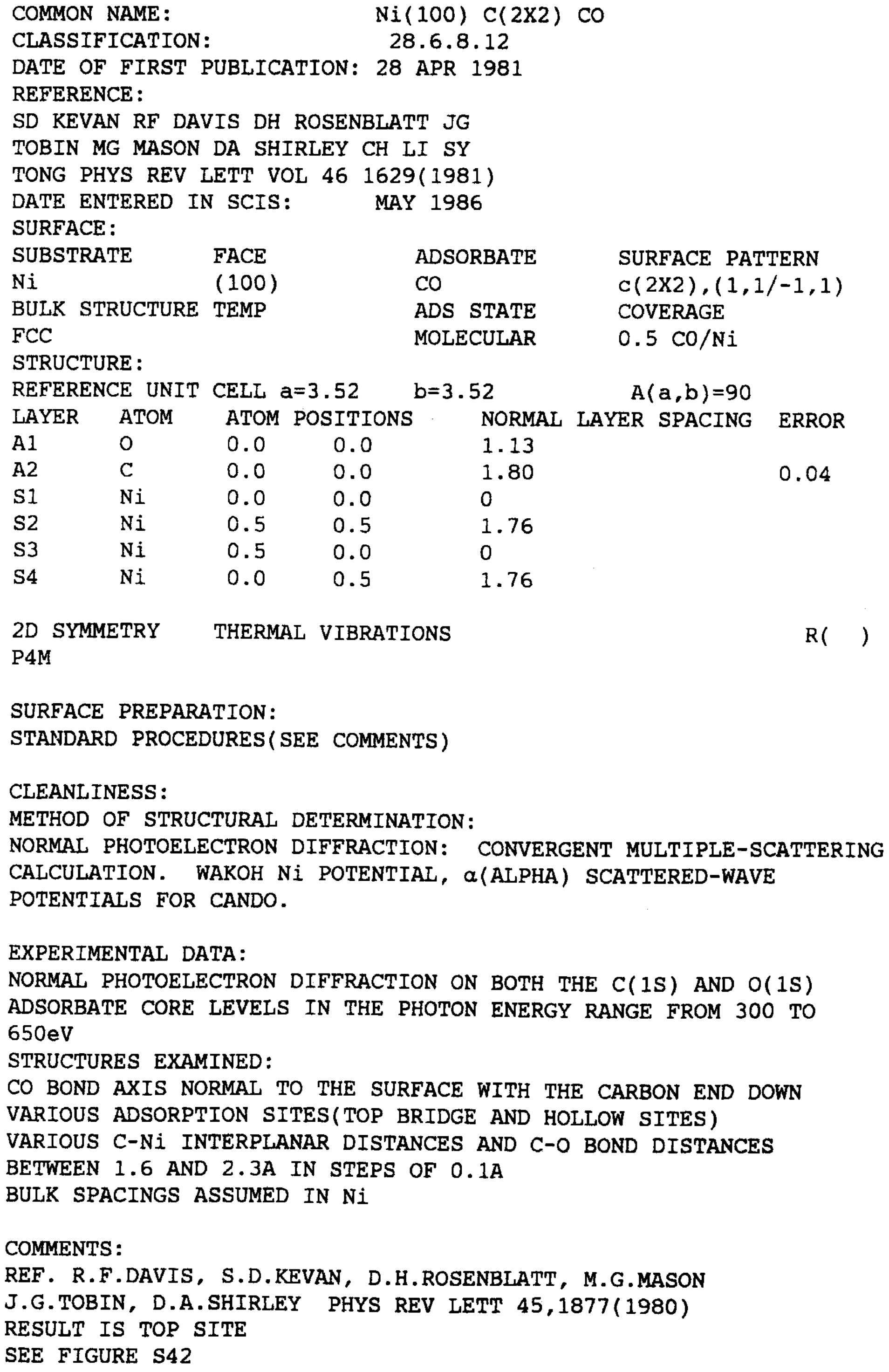


Fig. 2.24 Pendry R-factor contour map for a study of the Ni{100}($\sqrt{2} \times \sqrt{2}$)$R45°$–CO structure using the Ni–C and C–O spacings as parameters but assuming a CO molecule perpendicular to the surface and directly above a top layer Ni atom (see fig. 2.26 – after Andersson & Pendry, 1980).

For very good calculations, $R_{min}<0.2$. Atomic separations to 0.01 Å resolution can be obtained

Agreement never perfect because ion core potentials not exact. Unaccepatable values >0.6.



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COMMON NAME:                 Ni(100) C(2X2) CO
CLASSIFICATION:               28.6.8.12
DATE OF FIRST PUBLICATION: 28 APR 1981
REFERENCE:
SD KEVAN RF DAVIS DH ROSENBLATT JG
TOBIN MG MASON DA SHIRLEY CH LI SY
TONG PHYS REV LETT VOL 46 1629(1981)
DATE ENTERED IN SCIS:        MAY 1986
SURFACE:
SUBSTRATE      FACE           ADSORBATE      SURFACE PATTERN
Ni             (100)          CO             c(2X2),(1,1/-1,1)
BULK STRUCTURE TEMP           ADS STATE      COVERAGE
FCC                           MOLECULAR      0.5 CO/Ni
STRUCTURE:
REFERENCE UNIT CELL a=3.52    b=3.52        A(a,b)=90
LAYER   ATOM    ATOM POSITIONS      NORMAL LAYER SPACING  ERROR
A1      O       0.0     0.0         1.13
A2      C       0.0     0.0         1.80                  0.04
S1      Ni      0.0     0.0         0
S2      Ni      0.5     0.5         1.76
S3      Ni      0.5     0.0         0
S4      Ni      0.0     0.5         1.76

2D SYMMETRY    THERMAL VIBRATIONS                            R(  )
P4M

SURFACE PREPARATION:
STANDARD PROCEDURES(SEE COMMENTS)

CLEANLINESS:
METHOD OF STRUCTURAL DETERMINATION:
NORMAL PHOTOELECTRON DIFFRACTION:  CONVERGENT MULTIPLE-SCATTERING
CALCULATION.  WAKOH Ni POTENTIAL, α(ALPHA) SCATTERED-WAVE
POTENTIALS FOR CANDO.

EXPERIMENTAL DATA:
NORMAL PHOTOELECTRON DIFFRACTION ON BOTH THE C(1S) AND O(1S)
ADSORBATE CORE LEVELS IN THE PHOTON ENERGY RANGE FROM 300 TO
650eV
STRUCTURES EXAMINED:
CO BOND AXIS NORMAL TO THE SURFACE WITH THE CARBON END DOWN
VARIOUS ADSORPTION SITES(TOP BRIDGE AND HOLLOW SITES)
VARIOUS C-Ni INTERPLANAR DISTANCES AND C-O BOND DISTANCES
BETWEEN 1.6 AND 2.3A IN STEPS OF 0.1A
BULK SPACINGS ASSUMED IN Ni

COMMENTS:
REF. R.F.DAVIS, S.D.KEVAN, D.H.ROSENBLATT, M.G.MASON
J.G.TOBIN, D.A.SHIRLEY  PHYS REV LETT 45,1877(1980)
RESULT IS TOP SITE
SEE FIGURE S42
```

4.4 Summary

Provides information about:

- Symmetry of surface or adsorbate unit cell
- Size of surface or adsorbate unit cell
- Steps, domains
- Temperature dependant phenomena
- Reconstruction and relaxation (dynamical LEED)

Surface sensitive (10-50 Å, 3-10 atomic layers)

Relatively simple, inexpensive instrumentation

Rapid for simple analysis

I(V) or I(θ) curves can be used with theory to measure atomic positions with high accuracy (~0.01 Å)

BUT

Some electron-induced chemistry

Intrusive instrumentation

Domains, reconstruction, relaxation, steps, defects complicate simple patterns

Intensity measurement requires expensive instrumentation

Dynamical LEED calculations not trivial to perform nor perfect

No way to go directly from I(V) or I(θ) curves to structure