

Surface Sensitivity & Surface Specificity




The problems of sensitivity and detection limits are common to all forms of spectroscopy. In its simplest form, the question of sensitivity boils down to whether it is possible to detect the desired signal above the noise level.

In virtually all surface studies (especially those on single crystal substrates) sensitivity is a major problem. Consider the case of a sample with a surface of size 1 cm^2 - this will have ca. 10^{15} atoms in the surface layer. In order to detect the presence of impurity atoms present at the 1 % level, a technique must be sensitive to ca. 10^{13} atoms.

Contrast this with a spectroscopic technique used to analyze a 1 cm^3 bulk liquid sample i.e. a sample of ca. 10^{22} molecules. The detection of 10^{13} molecules in this sample would require 1 ppb (one *part-per-billion*) sensitivity - very few techniques can provide anything like this level of sensitivity

This is one reason why common spectroscopic techniques such as NMR (detection limit ca. 10^{19} molecules) cannot be used for surface studies, except on samples with very high surface areas.



Assuming that a technique of sufficient sensitivity can be found, another major problem that needs to be addressed in surface spectroscopy is distinguishing between signals from the surface and the bulk of the sample.

In principle, there are two ways around this problem :

To ensure that the surface signal is distinguishable (shifted) from the comparable bulk signal, and that the detection system has sufficient dynamic range to detect very small signals in the presence of neighboring large signals.

To ensure that the bulk signal is small compared to the surface signal i.e. that the vast majority of detected signal comes from the surface region of the sample.

It is the latter approach which is used by the majority of surface spectroscopic techniques - such techniques can then be said to be *surface sensitive*.

Classification as Scattering Techniques

Table 3.1 Particle Scattering Techniques

<u>Probe</u>		<u>Response</u>
Electrons (E_0, k_0, \dots spin s)		Electrons (E, k, \dots spin s)
Radiation (ω_0, k_0, \dots polarisation)	<u>Sample</u>	Radiation (ω, k, \dots polarisation)
Atoms (E_0, k_0, Z)		Atoms (E, k, Z')
Ions ($E_0, k_0, \pm Z$)		Ions ($E, k, \pm Z'$)

Surface Structure:

	LEED	RHEED	EXAFS NEXAFS	SEXAFS	STM	AFM
Long range order	+	+	-	-	+	+
Short range order	-	-	+	+	+	+
Composition information	-	·	+	+	·	-
Samples	Met	All	All	All	Met	All
Sampling depth (ML)	2-5	5->10	>50	2-10	1	1
Spatial resolution (μm)	10^{-5*}	1			10^{-5}	10^{-4}
Quantification	+	·	-	-	+	+
Theoretical Description	+	·	·	·	·	+
Destructive	?	?	?	?	-	-
Versatility	+	·	+	+	+	+
Ease of use	+/-*	+	-	-	·	+
Popularity	+	-	-	-	+	+

* with dynamical LEED calculations

Surface composition:

	XPS	AES	RAIRS	HREELS	ISS	SSIMS	TPD
Elemental information	+	+	?	+	+	+	·
Chemical information	+	?	+	+	-	+	·
Order information	+ ^o	·	·	·	-	?	-
Samples	Met	Met	All	Met	All	All	All
Sampling depth (ML)	3-10	3-10	>5	1	1	2-3	
Spatial resolution (μm)	5	10 ⁻³	10 ³	10 ³	10 ³	1	
Theoretical Description	+	·	+	·	·	·	+
Isotope sensitivity	-	-	+	+	+	+	+
Quantification	+	+	-	-	·	-	·
Sensitivity (% ML)	0.1	0.1	1	0.1	1	10 ⁻³	0.1
Destructive	-	?	-	-	?	?	+
Versatility	+	·	+	+	·	+	·
Ease of use	+	+	+	·	·	·	+
Popularity	+	+	+	·	·	+	+

^o Photoelectron diffraction



Microscopy

STM (Scanning Tunneling Microscopy)

AFM (Atomic Force Microscopy)

SEM (Scanning Electron Microscopy)

TEM (Transmission Electron Microscopy)(bulk)



Absorption

NEXAFS (Near Edge X-ray Absorption Fine Structure)- also called

XANES (X-ray Absorption Near Edge Spectroscopy)

EXAFS (Extended X-ray Absorption Fine Structure)(bulk)



Electron Spectroscopies

- XPS (X-ray Photoelectron Spectroscopy)
- UPS (Ultraviolet Photoelectron Spectroscopy)
- Auger

Diffraction



- LEED (Low-Energy Electron Diffraction)
- RHEED (Reflection High-Energy Electron Diffraction)
- XRD (X-Ray Diffraction)(bulk)



Desorption

- TDS (Thermal Desorption Spectroscopy)
- PSD (Photon Stimulated Desorption)
- ESD (Electron Stimulated Desorption)
- ESDIAD (Electron Stimulated Desorption Ion Angular Detection)



Vibrational Spectroscopies

IR (Infra Red)

HREELS (High-Resolution Electron Energy
Loss Spectroscopy)

Low Energy Electron Diffraction

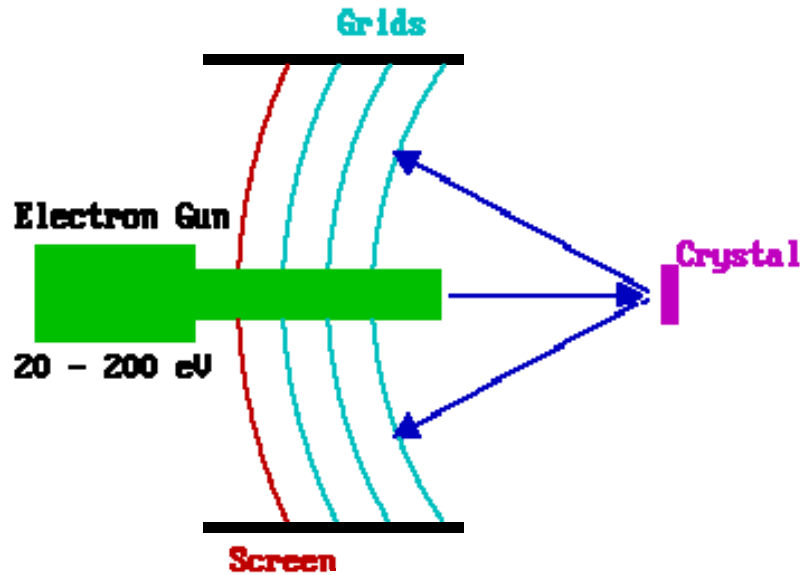
LEED is the principal technique for the determination of surface structures : it may be used in one of two ways:

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.

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.



The LEED experiment uses a beam of electrons of a 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. A typical experimental set-up is shown below.



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.

Basic Theory of LEED

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 localised 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 :

Wavelength, $\lambda = h / p$ (where p - electron momentum)

$$p = m.v = (2mE_k)^{1/2} = (2m.e.V)^{1/2}$$

where

m - mass of electron [kg]

v - velocity [m s⁻¹]

E_k - kinetic energy

e - electronic charge

V - acceleration voltage

General Diffraction Ideas

5000 eV photon (x-ray):

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

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

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

$$= 2.5 \text{ \AA}$$



20 eV electron:

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

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

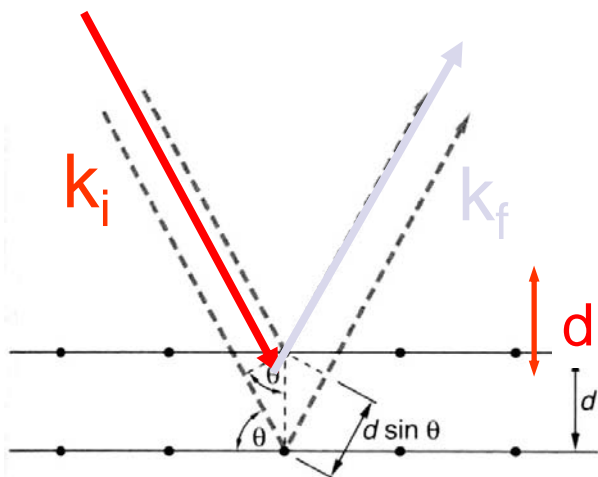
$$\lambda = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{2.42 \times 10^{-24} \text{ kg} \cdot \text{m} \cdot \text{s}^{-1}} \quad (\text{J} = \text{kg} \cdot \text{s}^{-2} \cdot \text{m}^2)$$
$$= 2.74 \times 10^{-10} \text{ m} = 2.7 \text{ \AA}$$

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

Bragg Scattering vs. LEED Equation

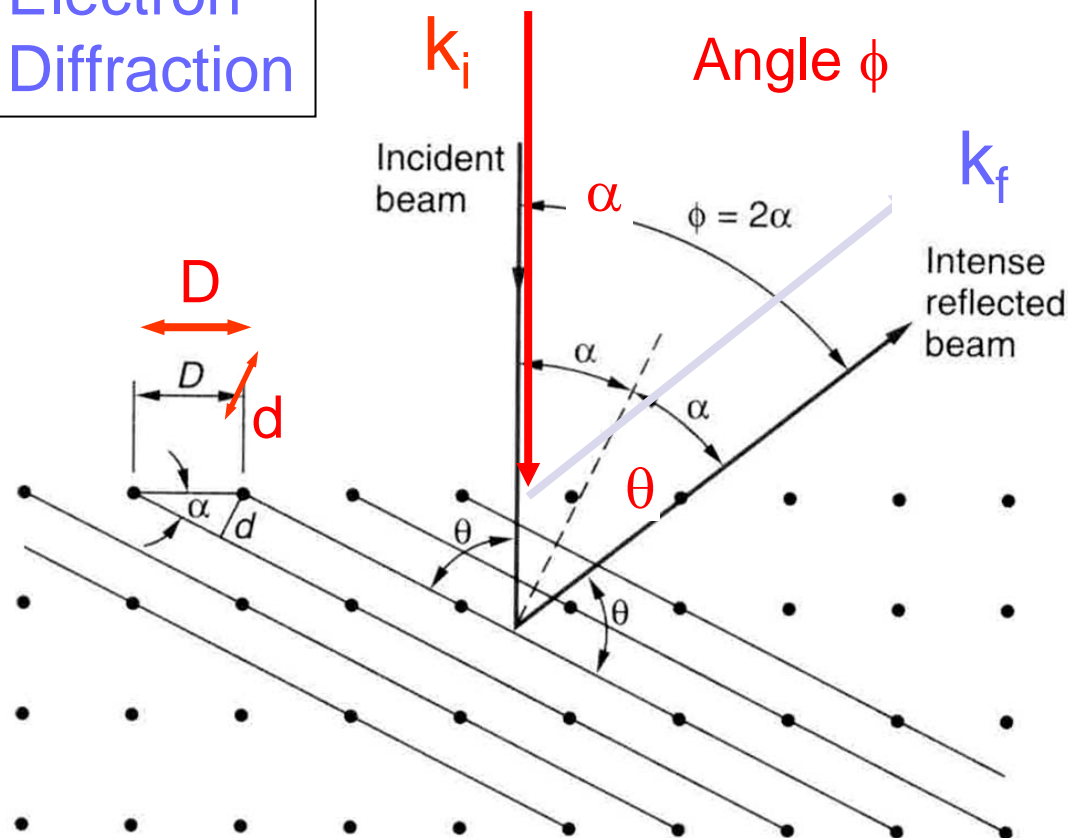
Derive LEED equation using [Bragg's Law](#) for X-ray diffraction, where appropriate angles are substituted and λ is for the [electron](#) wavelength

X-ray Diffraction

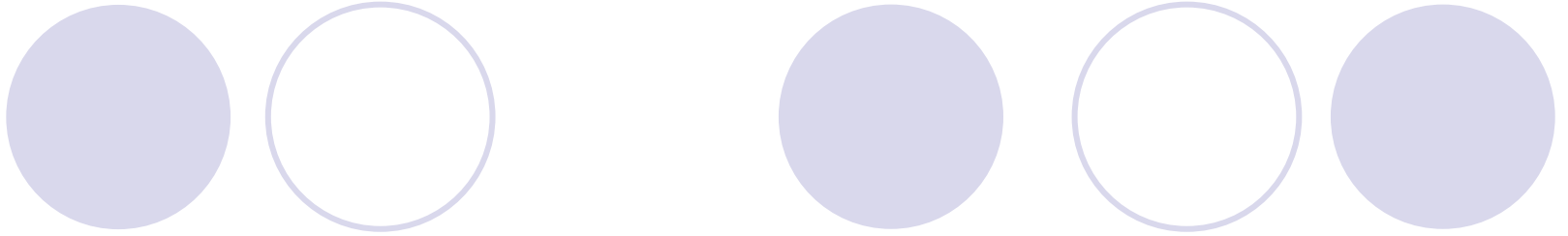


$$n\lambda_{\text{xray}} = 2d \sin \theta$$

Electron Diffraction



$$n\lambda_{\text{elec}} = D \sin \phi$$



If you consider the backscattering of a wavefront from two adjacent atoms at a well-defined angle, θ , to the surface normal, then it is clear that there is a "path difference" (d) in the distance the radiation has to travel from the scattering centers to a distant detector (which is effectively at infinity) - this path difference is best illustrated by considering two "ray paths" such as the right-hand pair of green traces in the above diagram.

The size of this path difference is $a \sin \theta$ and this must be equal to an integral number of wavelengths for constructive interference to occur when the scattered beams eventually meet and interfere at the detector i.e.

$$d = a \sin \theta = n \cdot \lambda$$

where :

λ - wavelength

n - integer (..-1, 0, 1, 2,..)



For two isolated scattering centers the diffracted intensity varies slowly between zero (complete destructive interference ; $d = (n + \frac{1}{2})\lambda$) and its maximum value (complete constructive interference ; $d = n.\lambda$) - with a large periodic array of scatterers, however, the diffracted intensity is only significant when the "Bragg condition"

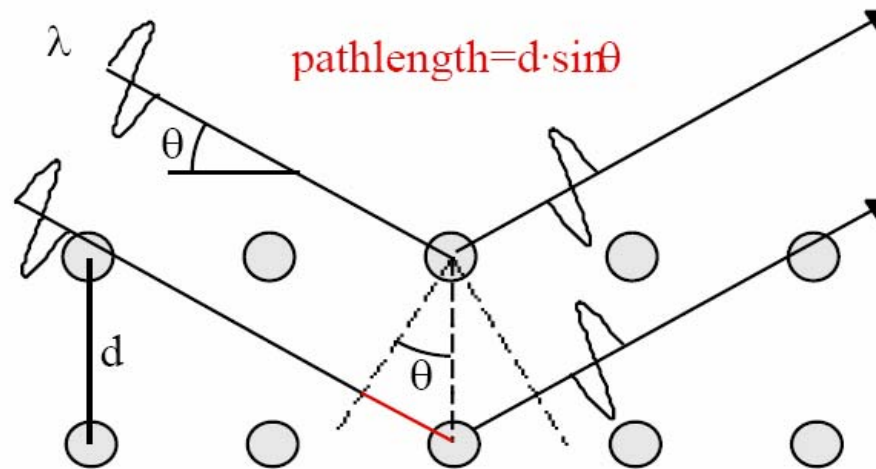
$$a \sin \theta = n.\lambda$$

is satisfied exactly.



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 $\sim 10\text{-}50 \text{ \AA}$ into surface



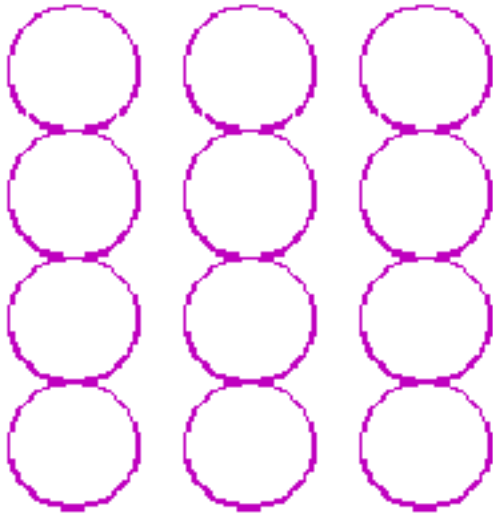
$$n\lambda = 2d \sin \theta$$

Bragg Equation

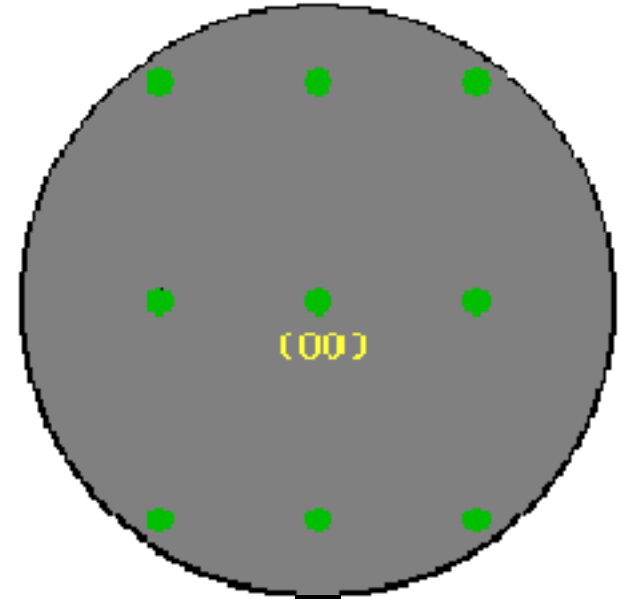
$$n \left(\frac{h}{\sqrt{2meV}} \right) = 2d \sin \theta$$

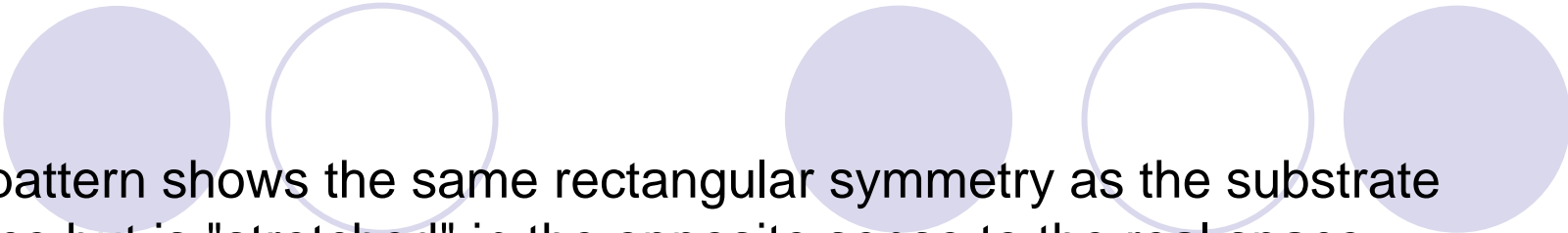
As an example we can look at the LEED pattern from an $fcc(110)$ surface. In the diagram below the surface atomic structure is shown on the left in plan view. The primary electron beam would then be incident normally on this surface as if fired from your current viewpoint and the diffracted beams would be scattered from the surface back towards yourself. The diffraction pattern on the right illustrates how these diffracted beams would impact upon the fluorescent screen.

Real Space - $fcc(110)$ surface



Diffraction Pattern





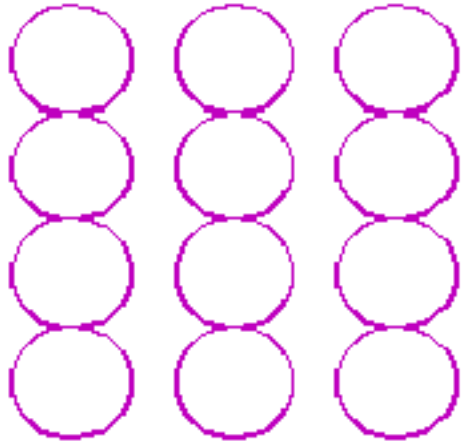
The pattern shows the same rectangular symmetry as the substrate surface but is "stretched" in the opposite sense to the real space structure due to the reciprocal dependence upon the lattice parameter.

The pattern is also centrosymmetric about the (00) beam - this is the central spot in the diffraction pattern corresponding to the beam that is diffracted back exactly normal to the surface (i.e. the $n = 0$ case in our 1-D model).

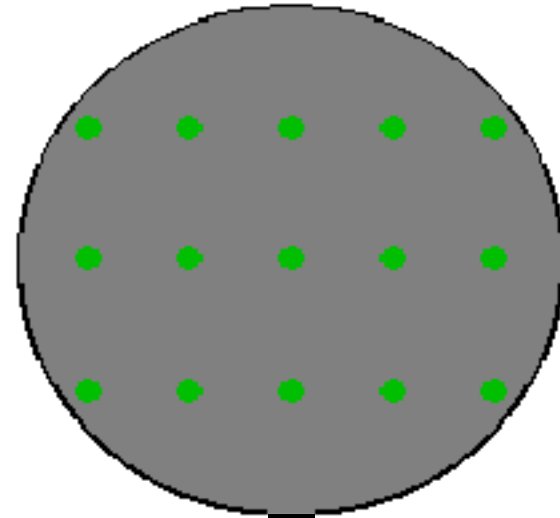
The above illustration of the diffraction pattern shows only the "first-order" beams i.e. it is representative of the diffraction pattern visible at low energies when only for $n = 1$ is the angle of diffraction, θ , sufficiently small for the diffracted beam to be incident on the display screen.

The diagram below shows the diffraction pattern that might be expected if the energy of the incident electrons is doubled - some of the second order spots are now visible and the pattern as a whole has apparently contracted in towards the central (00) spot.

Real Space - fcc(110) surface

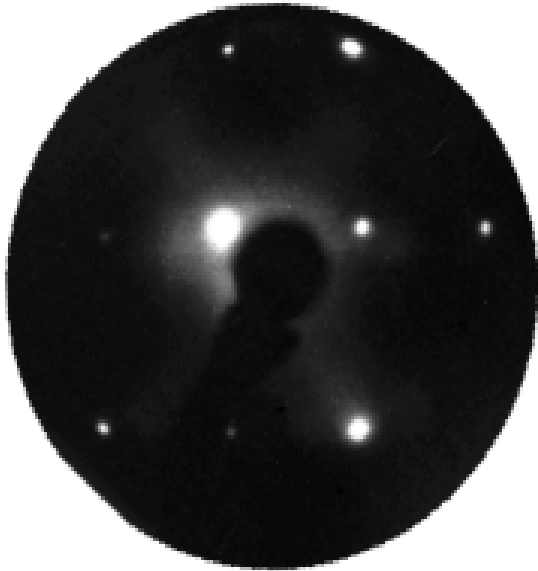


Diffraction Pattern



LEED Patterns from Cu(110)

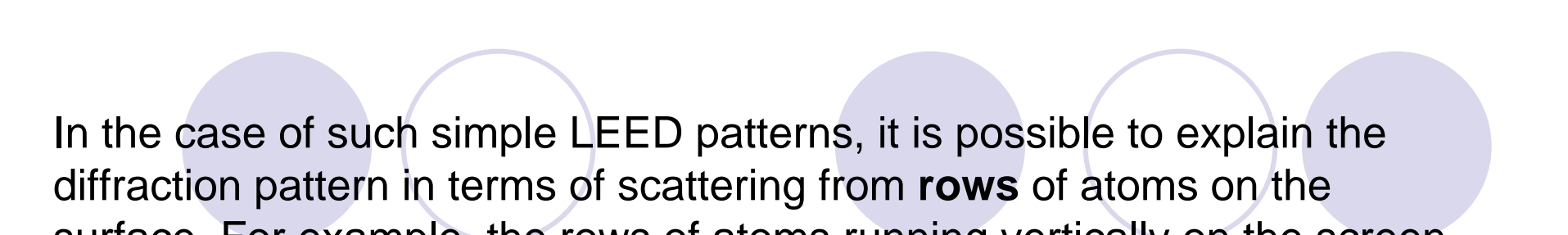
Cu(110)



90 eV



140 eV



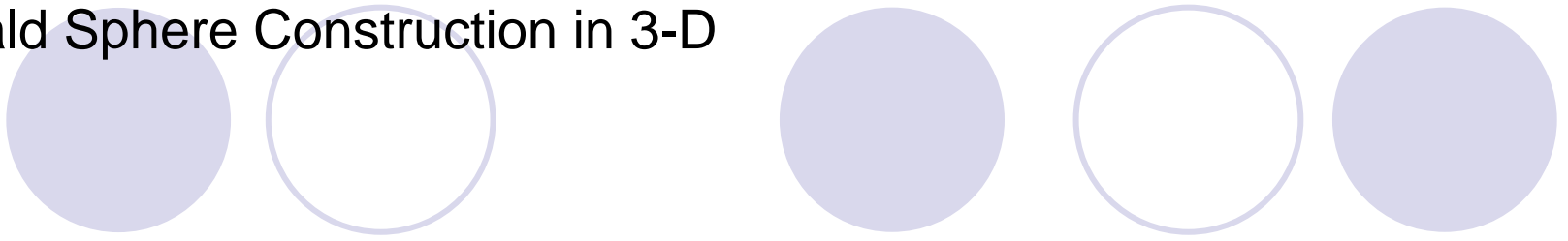
In the case of such simple LEED patterns, it is possible to explain the diffraction pattern in terms of scattering from **rows** of atoms on the surface. For example, the rows of atoms running vertically on the screen would give rise to a set of diffracted beams in the horizontal plane, perpendicular to the rows, thus leading to the row of spots running in a line horizontally across the diffraction pattern through the (00) spot.

The further the rows are apart, then the closer in are the diffracted beams to the central (00) beam. This is, however, a far from satisfactory method of explaining LEED patterns from surfaces.

A much better method of looking at LEED diffraction patterns involves using the concept of reciprocal space : more specifically , it can be readily shown that –

" The observed LEED pattern is a (scaled) representation of the *reciprocal net* of the pseudo-2D surface structure "

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

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

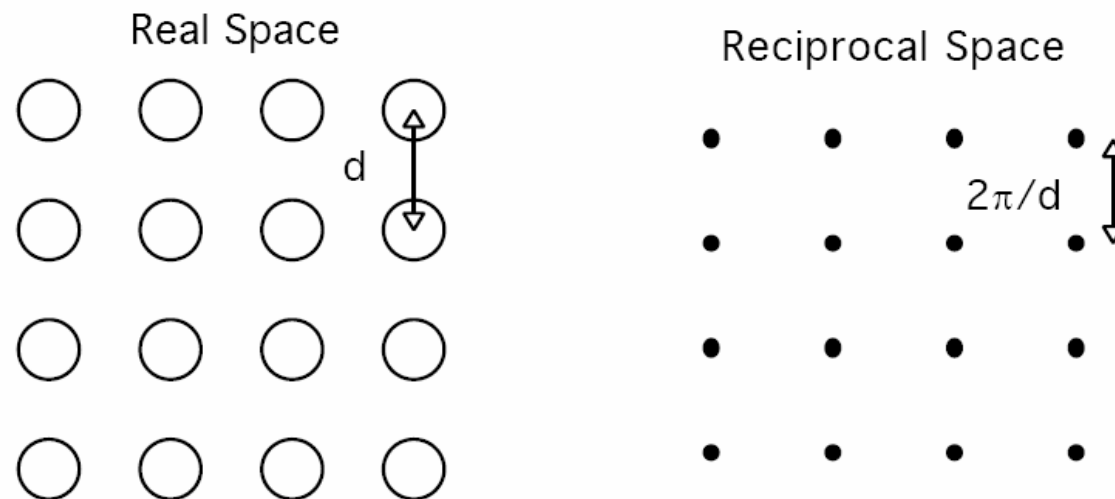
During scattering (diffraction):

- 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 .



The reciprocal space lattice is a set of imaginary points constructed in such a way that the direction of a vector from one point to another coincides with the direction of a normal to the real space planes and the separation of those points (absolute value of the vector) is equal to the reciprocal of the real interplanar distance.

It is convenient to let the reciprocal lattice vector be 2π times the reciprocal of the interplanar distance. This convention converts the units from periods per unit length to radians per unit length. Radians per centimeter (cm^{-1}) are widely used units. It simplifies comparison of different periodic phenomena. For instance k , the wavevector, has an absolute value of $2\pi/\lambda$. If we choose the above convention, we are able to compare the two values directly. Henceforth this convention will be used. All it does is expand the size of the reciprocal lattice.

How can one construct a reciprocal lattice from a direct one?

Pick some point as an origin, then:

- a) from this origin, lay out the normal to every family of parallel planes in the direct lattice;
- b) set the length of each normal equal to 2π times the reciprocal of the interplanar spacing for its particular set of planes;
- c) place a point at the end of each normal.

Real vs. (Reciprocal, Diffraction, or k) Space

Real Space (i.e. spacing of surface atoms in nm)



k-Space (i.e. spacing of diffraction spots in nm^{-1})

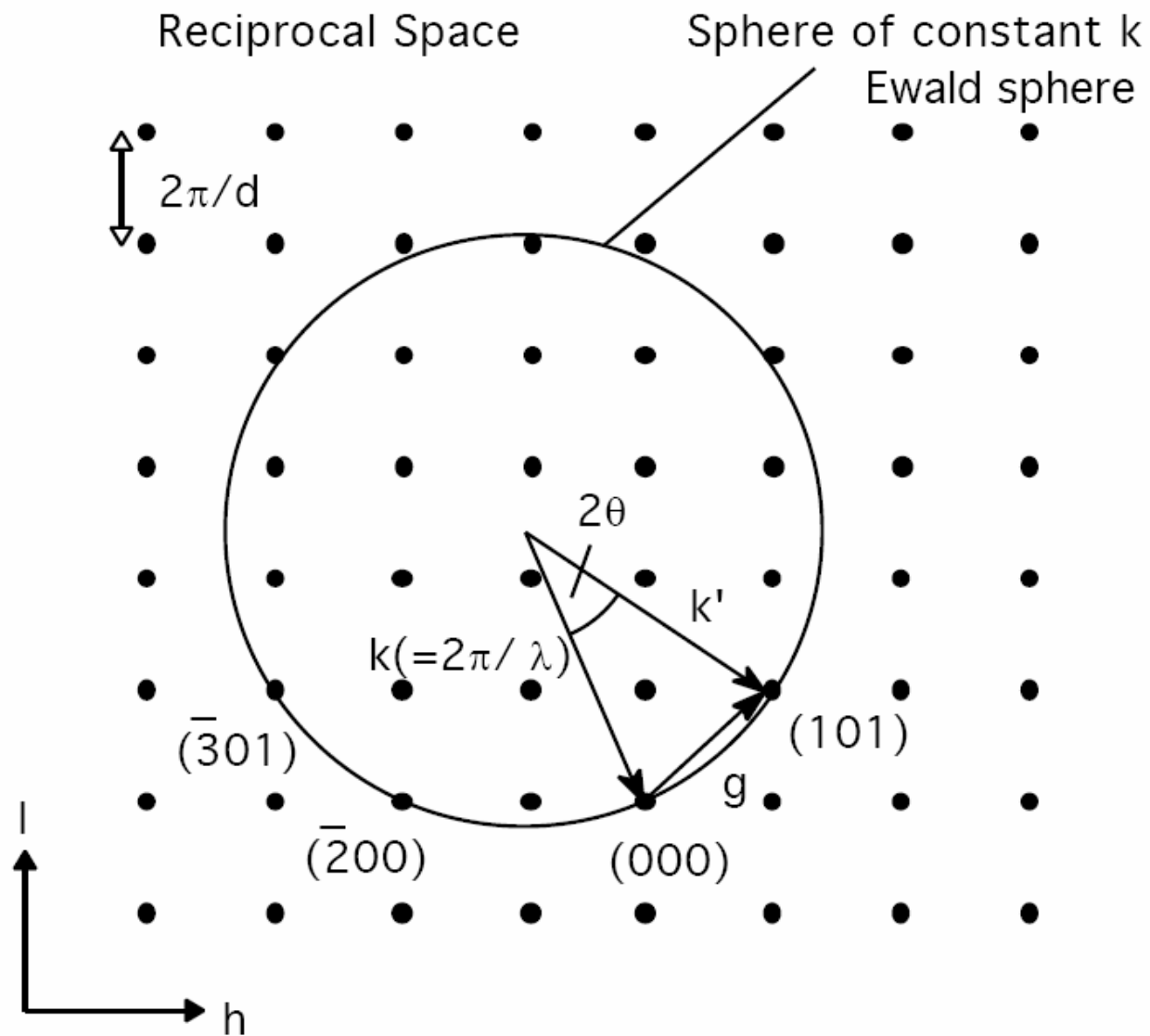


$$G = \frac{2\pi}{a}$$

larger real-space



smaller k-space



- (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

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

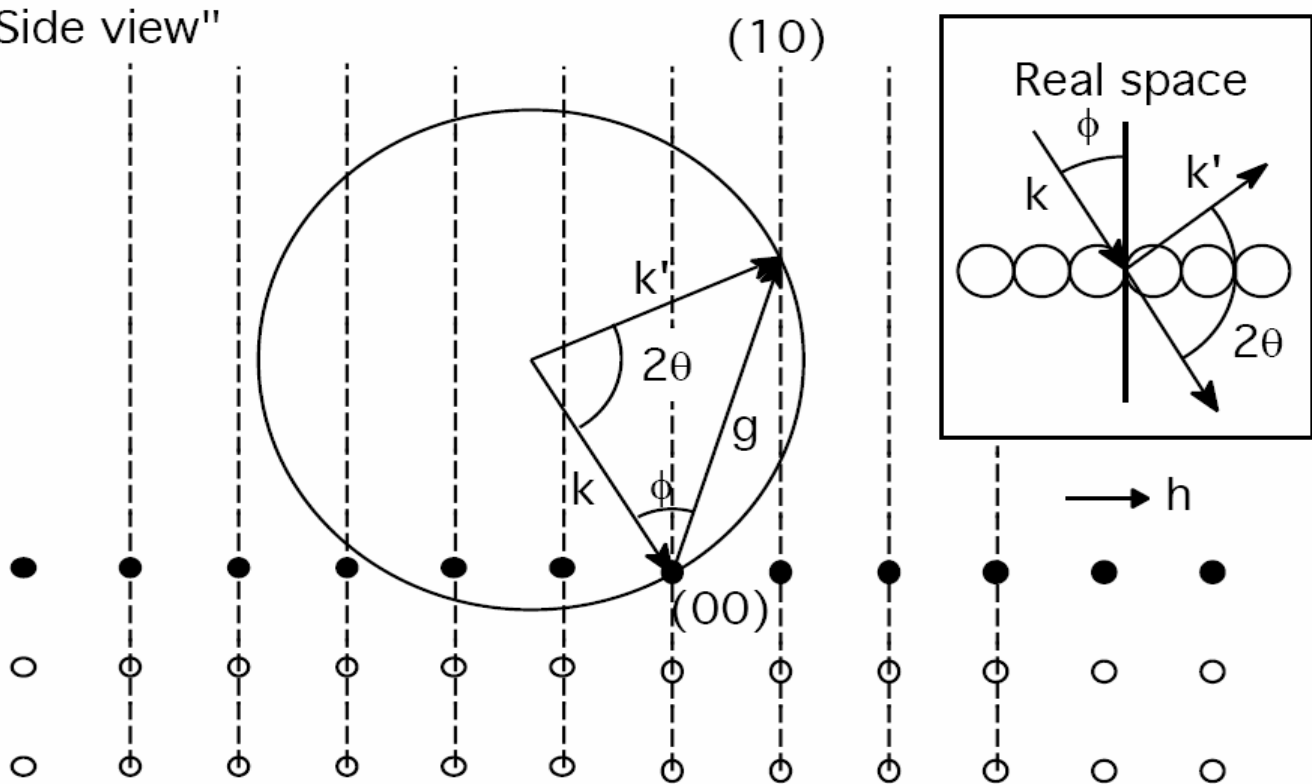
where \vec{g} is the scattering vector.

- (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

Ewald Sphere Construction in 2-D

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

"Side view"



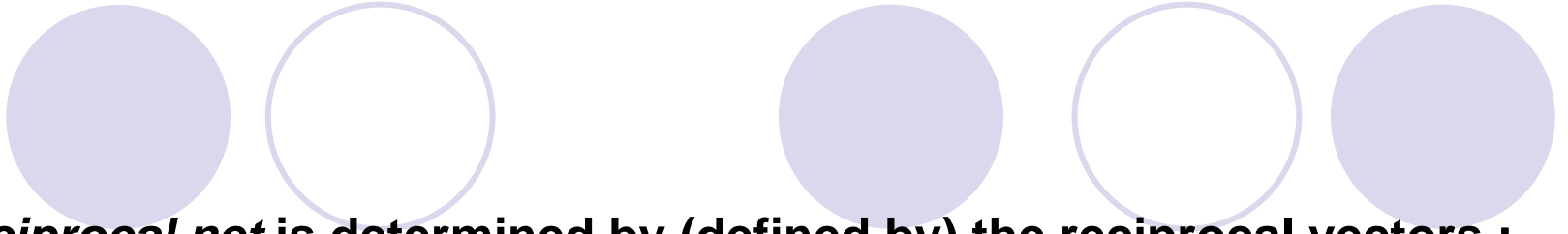
Ewald Sphere Construction for LEED



- In LEED, electron beam incident along surface normal

- $2d$ becomes d in Bragg equation $d \cdot \sin\theta = \sqrt{h^2 + k^2} \cdot \lambda$

Solving for θ by geometry using Ewald sphere construction:



The *reciprocal net* is determined by (defined by) the reciprocal vectors :

a_1^* & a_2^* (for the substrate) and b_1^* & b_2^* (for the adsorbate)

Initially we will consider just the substrate. The reciprocal vectors are related to the real space unit cell vectors by the scalar product relations:

$$a_1 \cdot a_2^* = a_1^* \cdot a_2 = 0$$

and

$$a_1 \cdot a_1^* = a_2 \cdot a_2^* = 1$$

a_1 is perpendicular to a_2^* , and a_2 is perpendicular to a_1^*

there is an inverse relationship between the lengths of a_1 and a_1^* (and a_2 and a_2^*) of the form :

$$|a_1| = 1 / (|a_1^*| \cos A)$$

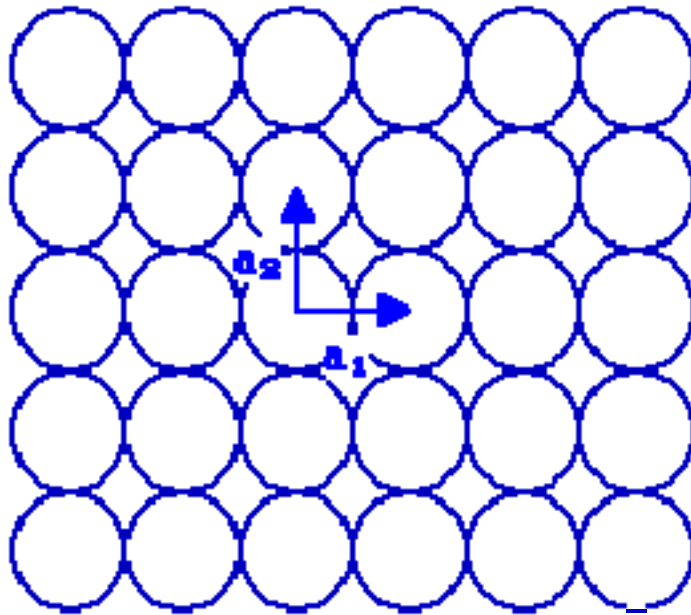
where A is the angle between the vectors a_1 and a_1^* .

Note : when $A = 0$ degrees ($\cos A = 1$) this simplifies to a simple reciprocal relationship between the lengths a_1 and a_1^* .

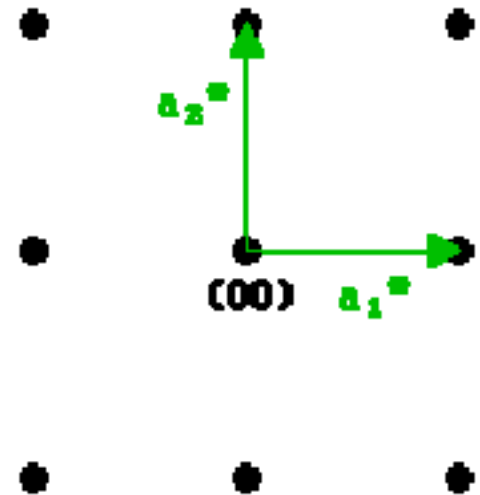
Exactly analogous relations hold for the real space and reciprocal vectors of the adsorbate overlayer structure : b_1 , b_1^* , b_2 and b_2^* .

To a first approximation, the LEED pattern for a given surface structure may be obtained by superimposing the reciprocal net of the adsorbate overlayer (generated from b_1^* and b_2^*) on the reciprocal net of the substrate (generated from a_1^* and a_2^*)

The diagram below shows an *fcc*(100) surface (again in plan view) and its corresponding diffraction pattern (i.e. the reciprocal net) .



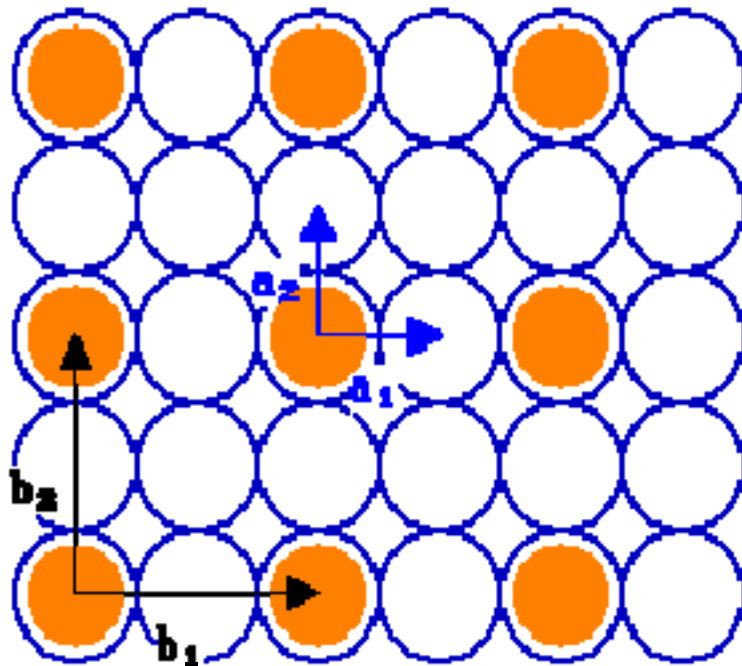
Diffraction Pattern



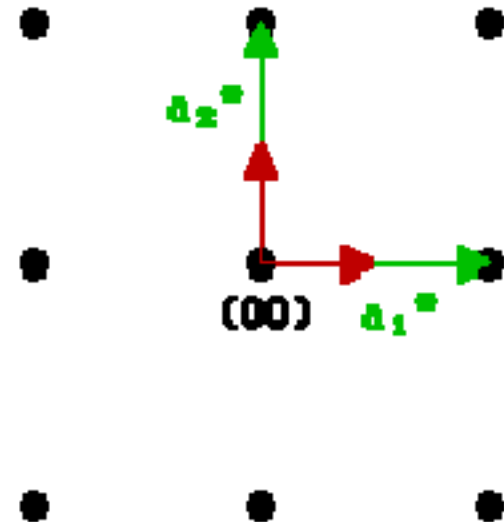
We can demonstrate how these reciprocal vectors can be determined by working through the problem in a parallel fashion for the two vectors :

	a_1^* must be perpendicular to a_2	a_2^* must be perpendicular to a_1
\Rightarrow	a_1^* is parallel to a_1	a_2^* is parallel to a_2
\Rightarrow	The angle, A , between a_1 & a_1^* is zero	The angle, A , between a_2 & a_2^* is zero
\Rightarrow	Hence, $ a_1^* = 1 / a_1 $	Hence, $ a_2^* = 1 / a_2 $
\Rightarrow	If we let $ a_1 = 1$ unit, then $ a_1^* = 1$ unit.	$ a_2 = a_1 = 1$ unit, therefore $ a_2^* = 1$ unit.

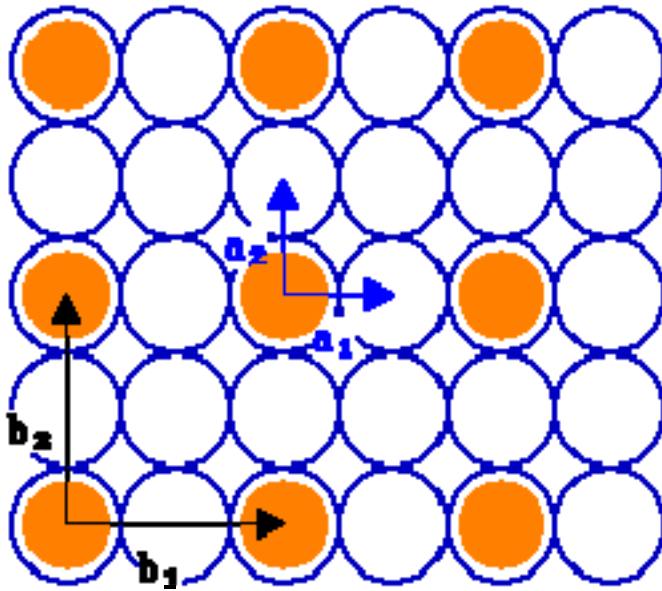
Let us now add in an adsorbate overlayer - a primitive (2 x 2) structure with the adsorbed species shown bonded in on-top sites - and apply the same logic as just used above to determine the reciprocal vectors, \mathbf{b}_1^* and \mathbf{b}_2^* , for this overlayer.



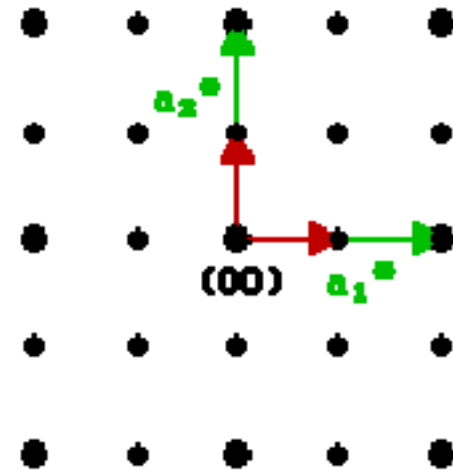
Diffraction Pattern



All we have to do now is to generate the reciprocal net for the adsorbate using \mathbf{b}_1^* and \mathbf{b}_2^* (shown in red).



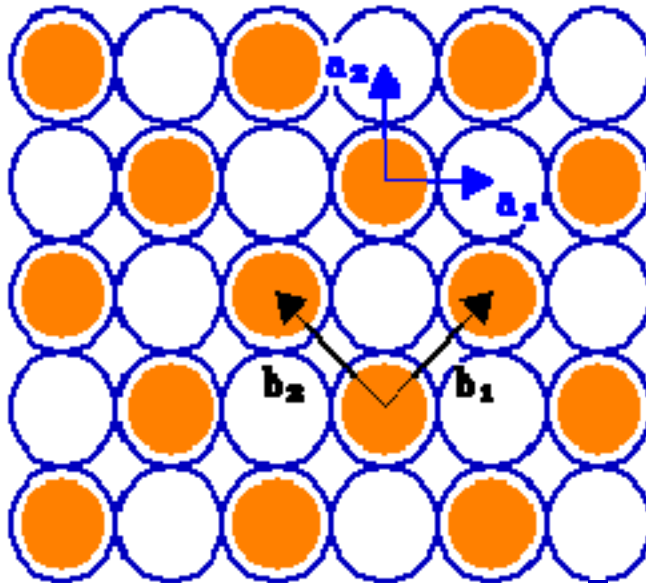
Diffraction Pattern



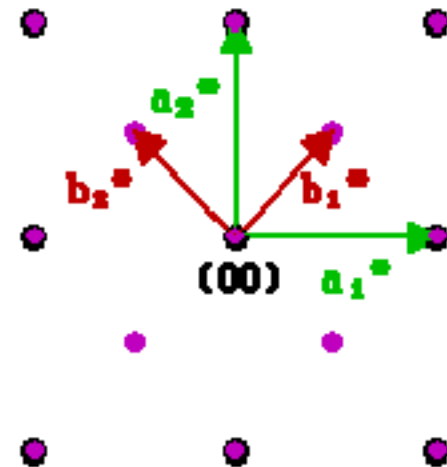
We can demonstrate how these reciprocal vectors can be determined by working through the problem in a parallel fashion for the two vectors :

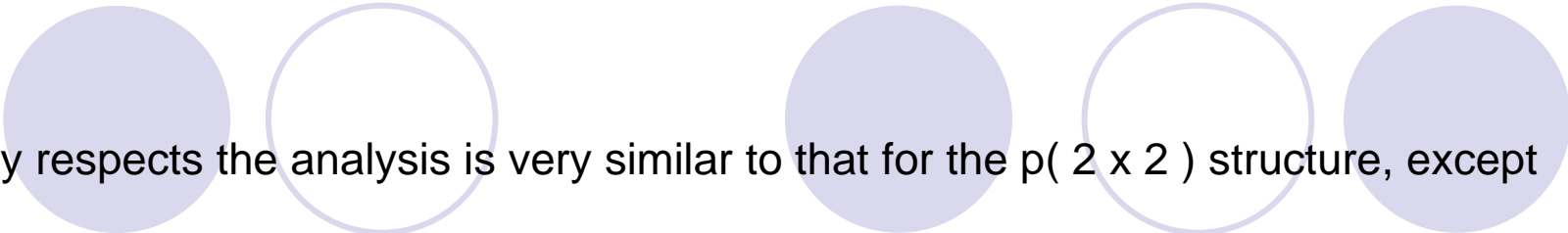
	\mathbf{b}_1^* must be perpendicular to \mathbf{b}_2	\mathbf{b}_2^* must be perpendicular to \mathbf{b}_1
\Rightarrow	\mathbf{b}_1^* is parallel to \mathbf{b}_1	\mathbf{b}_2^* is parallel to \mathbf{b}_2
\Rightarrow	The angle, B , between \mathbf{b}_1 & \mathbf{b}_1^* is zero	The angle, B , between \mathbf{b}_2 & \mathbf{b}_2^* is zero
\Rightarrow	Hence, $\mathbf{b}_1^* = 1 / \mathbf{b}_1$	Hence, $\mathbf{b}_2^* = 1 / \mathbf{b}_2$
\Rightarrow	$\mathbf{b}_1 = 2 \mathbf{a}_1 = 2$ units; \Rightarrow $\mathbf{b}_1^* = 1/2$ unit.	$\mathbf{b}_2 = 2 \mathbf{a}_2 = 2$ units; \Rightarrow $\mathbf{b}_2^* = 1/2$ unit.

Let's look at the $c(2 \times 2)$ structure on the same $fcc(100)$ surface. The diagram below shows both a real space $c(2 \times 2)$ structure and the corresponding diffraction pattern:



Diffraction Pattern





In many respects the analysis is very similar to that for the p(2 x 2) structure, except that:

$$| \mathbf{b}_1 | = | \mathbf{b}_2 | = \sqrt{2} \text{ units}$$

consequently

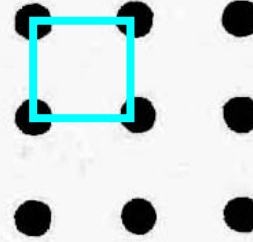
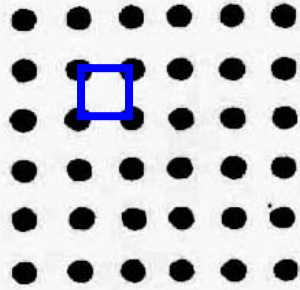
$$| \mathbf{b}_1^* | = | \mathbf{b}_2^* | = 1/ \sqrt{2} \text{ units.}$$

The vectors for the adsorbate overlayer are rotated with respect to those of the substrate by 45° . Note that the c(2 x 2) diffraction pattern can also be obtained from the pattern for the primitive structure by "missing out every alternate adsorbate-derived diffraction spot". This is a common feature of diffraction patterns arising from centered structures.

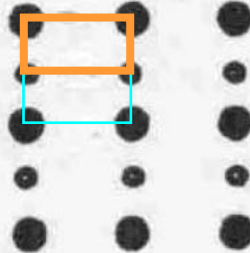
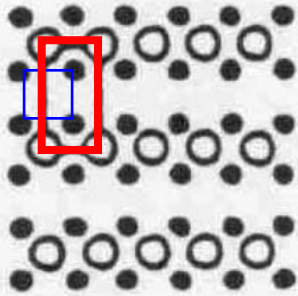
k-Space: Square Lattice Reconstructions

Real space

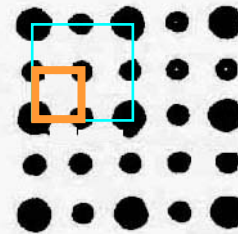
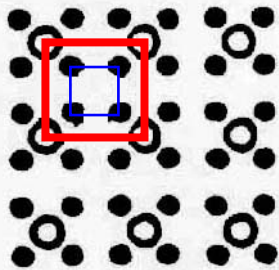
LEED



1x1



2x1

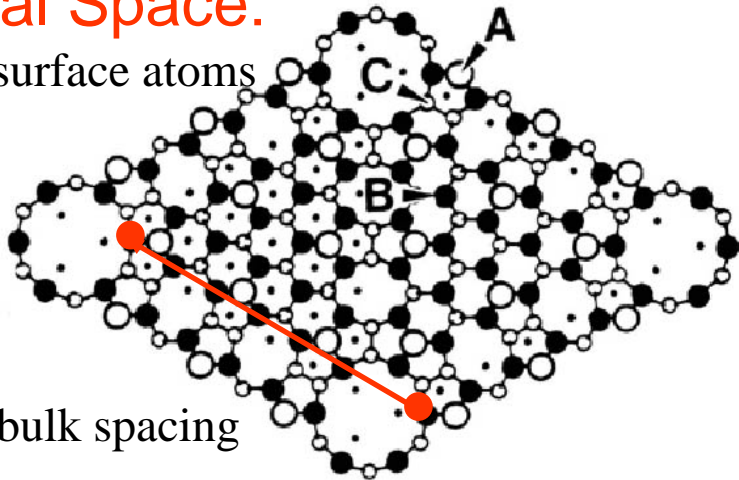


p(2x2)

LEED: Si(111)7x7

Real Space:

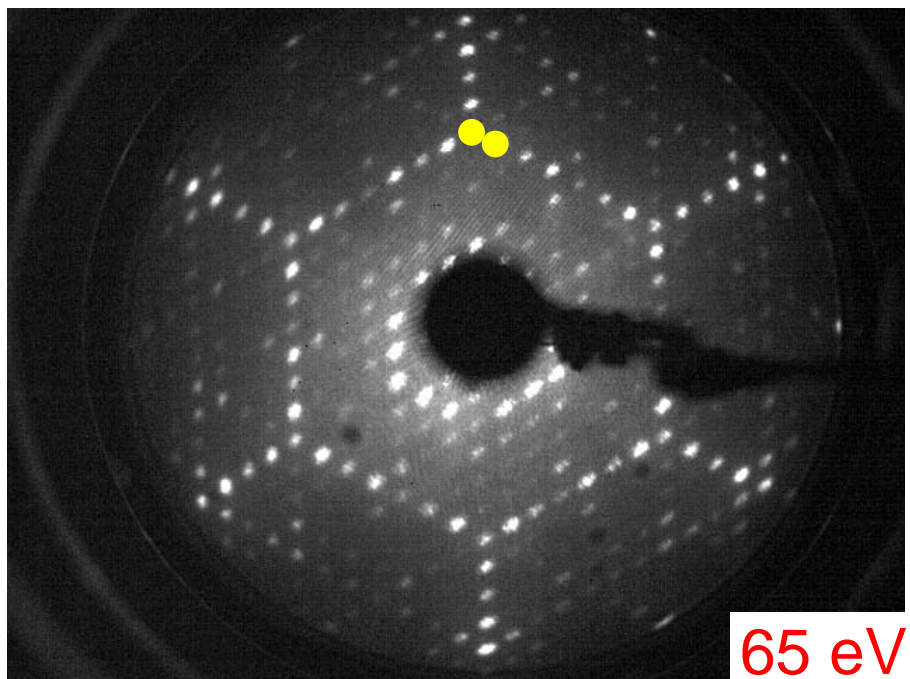
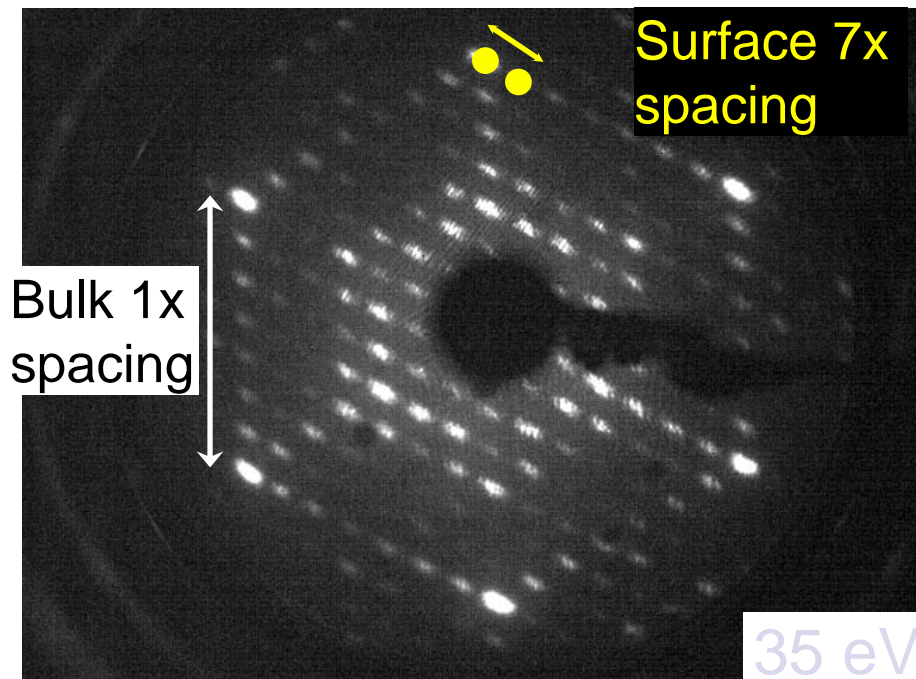
Si surface atoms



7x bulk spacing

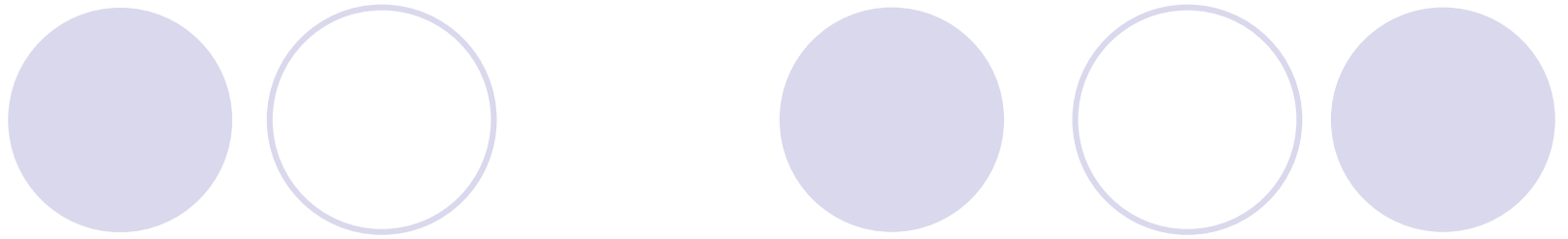
$$n\lambda = D \sin \phi$$

- Larger D spacings give closer LEED spots (smaller ϕ).
- Higher energy electrons give closer spots.



Reflection High Energy Electron Diffraction (RHEED)

- Low Energy Electron Diffraction (LEED) utilizes the inherent surface sensitivity associated with low energy electrons in order to sample the surface structure. As the primary electron energy is increased not only does the surface specificity decrease but two other effects are particularly noticeable:
-
- forward scattering becomes much more important (as opposed to the backward scattering observed in LEED)
- the scattering angle (measured from the incident beam direction) tends towards 180 degrees for back-scattering and 0 degrees for forward scattering.



In LEED, low energy electrons were used to

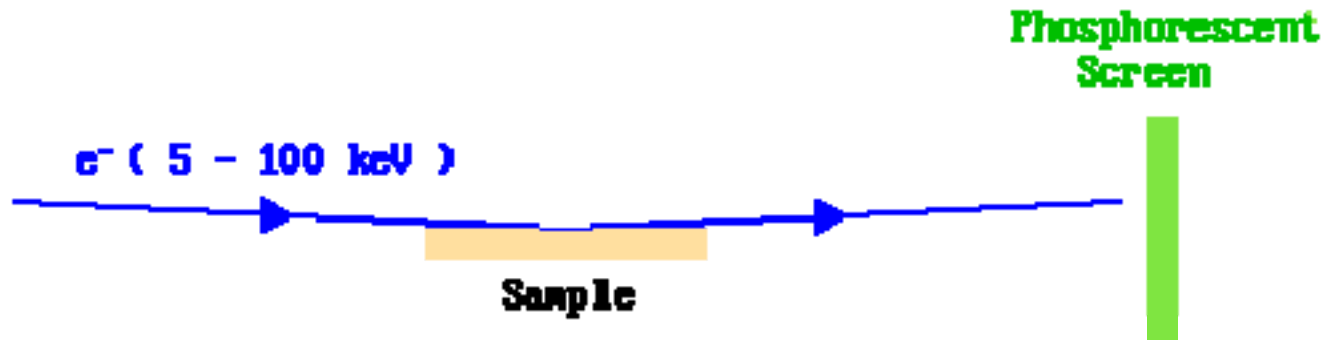
- provide large elastic scattering cross-section for *back*-scattered electrons
- keep the penetration depth of the electrons short

In RHEED, another solution is used

- provide large elastic scattering cross-section for *forward*-scattered electrons
- keep penetration depth small by using grazing incidence



In order to extract surface structural information from the diffraction of high energy electrons, therefore, the technique has to be adapted and the easiest way of doing this is to use a reflection geometry in which the electron beam is incident at a very grazing angle - it is then known as Reflection High Energy Electron Diffraction (RHEED).





The diagram above shows the basic set-up for a RHEED experiment, with the sample viewed edge-on. In practice the display screen is usually a phosphor coating on the inside of a vacuum window (viewport) and the diffraction pattern can be viewed and recorded from the atmospheric side of the window.

The small scattering angles involved are compensated for by using relatively large sample/screen distances.

The sample can be rotated about its normal axis so that the electron beam is incident along specific crystallographic directions on the surface.

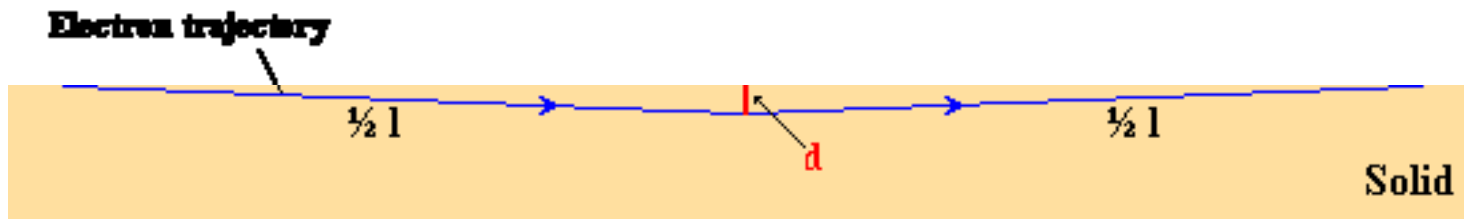
In order to understand the diffraction process we need to consider how the electron beam can interact with the regular array of surface atoms in this experimental geometry. It is worth noting, however, that the use of glancing incidence ensures that, despite the high energy of the electrons, the component of the electron momentum perpendicular to the surface is small. Under these conditions an electron may travel a substantial distance through the solid (in accord with the much longer mean free path of such high energy electrons) without penetrating far into the solid. The technique, consequently, remains surface sensitive.

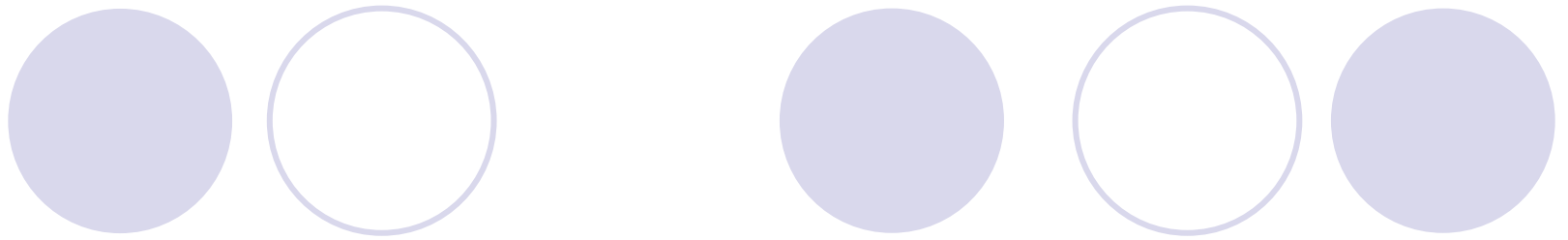
For an incidence angle of 88 degrees

$$d / l = 0.017$$

eg. $d < 0.2 \text{ nm}$ when $l = 10 \text{ nm}$

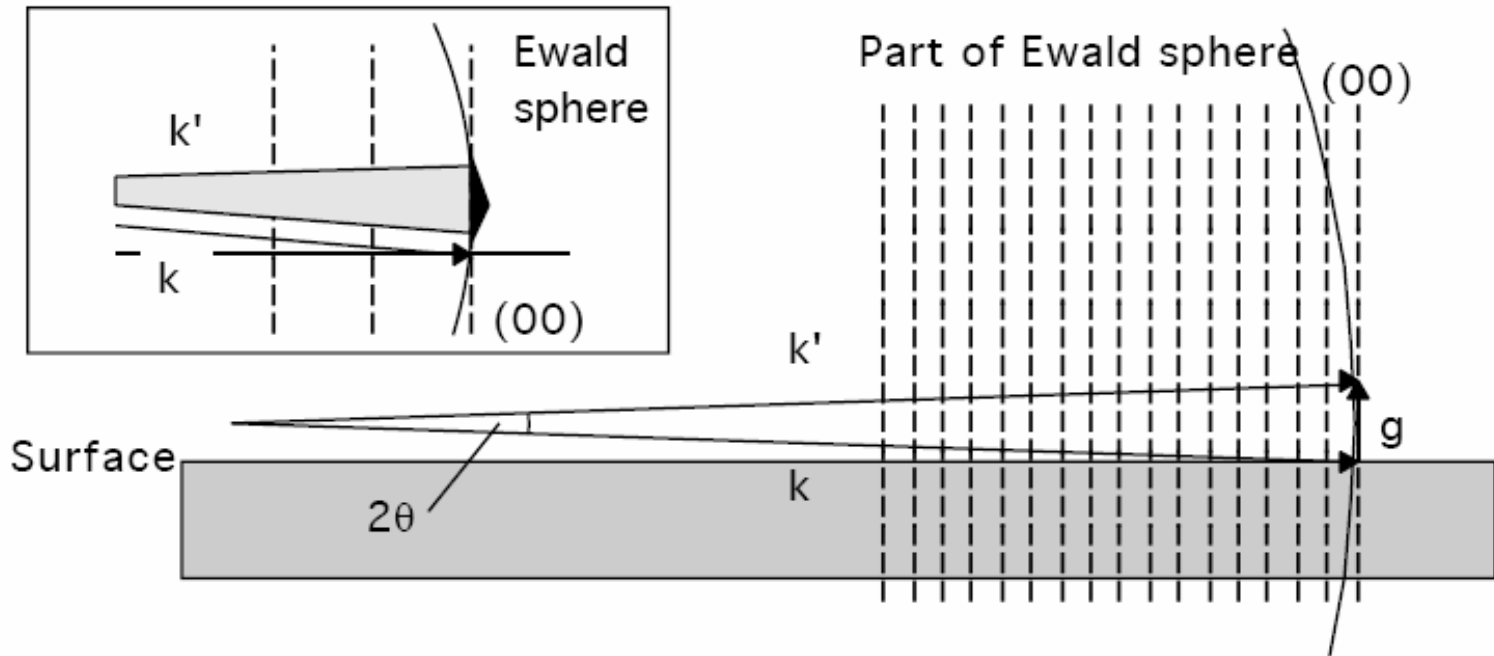
Vacuum





- 2.49 Å

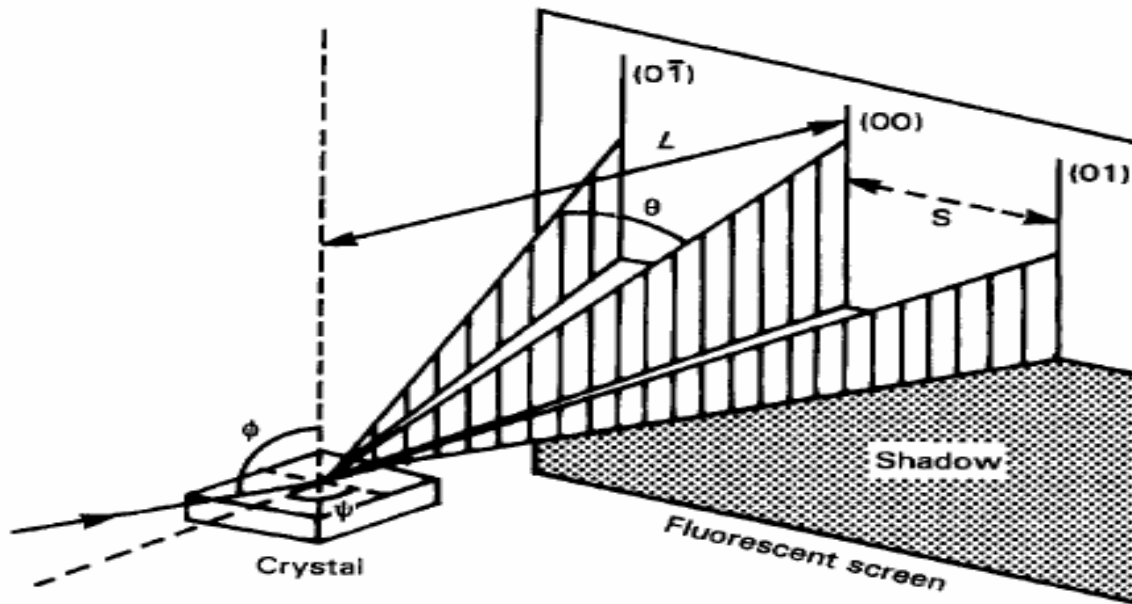
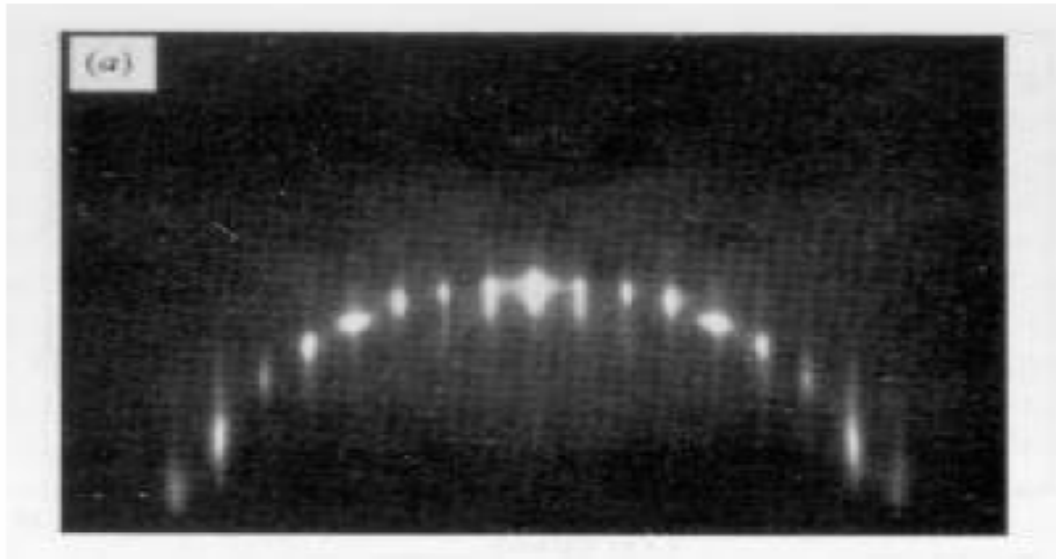
Draw Ewald sphere for an incidence angle of 88° :





- (1) Ewald sphere crosses many lattice rods - many spots separated by small diffraction angle differences
but few near grazing exit angles - usually only see (00) beam and perhaps $(\bar{1}0)$ beam
- (2) Crossing of Ewald sphere with lattice (condition for diffraction) rod very poorly defined - RHEED spots are broadened into "vertical" streaks

Now diffraction out of incidence plane (determined by periodicity orthogonal to incidence plane) becomes important



What, if any, advantages does RHEED offer over LEED ?

- In terms of the quality of the diffraction pattern absolutely none ! - moreover, 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. However ,
- 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).
- 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.
- By using RHEED it is therefore possible to measure, and hence also to control, atomic layer growth rates in Molecular Beam Epitaxy (MBE) growth of electronic device structures - this is by far and away the most important application of the technique.