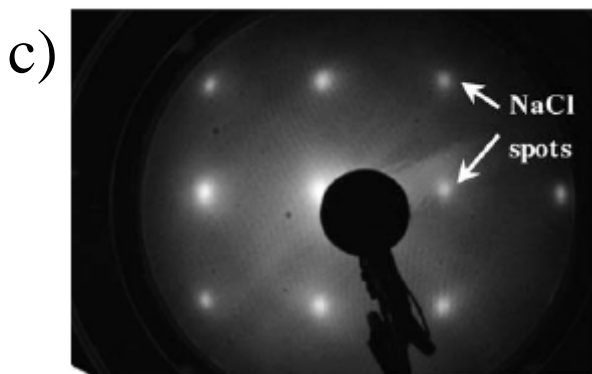
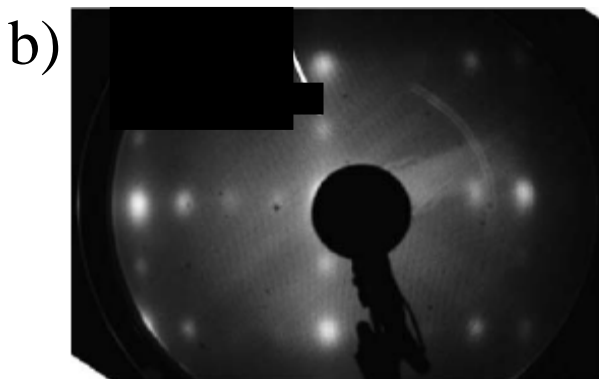
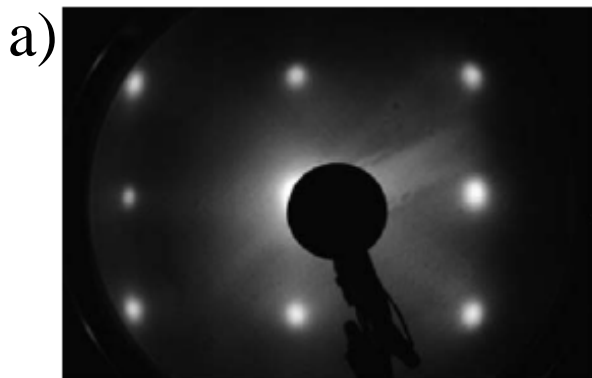


NaCl deposition on Ag single crystal surface

The clean surface of an Ag single crystal was investigated by LEED (fig. (a)). Which is the orientation of the investigated surface?

After deposition of 0.5 ML of NaCl a new LEED pattern of the surface is acquired (fig. (b)). What happens on the surface?

Finally after deposition of 2 ML of NaCl the LEED pattern modifies as in fig. (c). Explain the LEED pattern (Ag has an fcc structure.)



Solution: NaCl deposition on Ag single crystal surface

The Ag single crystal surface investigated by LEED in fig. (a) is the Ag(110).

After deposition of 0.5 ML of NaCl the LEED pattern shows the formation of two kind of domains: the 4x1 (horizontal direction in the LEED pattern) and the 1x2 (vertical direction in the LEED pattern)

Finally after deposition of 2 ML of NaCl the LEED pattern shows that the growth produces a NaCl(100)-(1x1) film.

K. Ait-Mansour *et al.*, Appl. Surf. Sci. **252**, 6368 (2006)

H₂S adsorption on Ir(100).

The adsorption of H₂S on Ir(100) was investigated by LEED. Due to the residual H gas founded in the Ultra High Vacuum chamber the Ir(100) surface naturally reconstructs in the Ir(100)-($a \times b$)-H, as shown in fig.(a). Draw the corresponding pattern in the real space and give a value for a and b .

Fig (b) shows the LEED patterns after exposing the Iridium surface to 5 Langmuir of H₂S at 300 K and (c) after flashing the crystal to 700 K. Give an explication for the evolution of the LEED patterns. Draw the atomic arrangement corresponding to the LEED pattern in fig. (c). Is the answer unique? (Iridium has an fcc structure.) Exposing the Iridium surface to a low coverage of 0.5 L of H₂S at 200 K produces the LEED pattern in fig.(d). Draw the corresponding atomic arrangement.

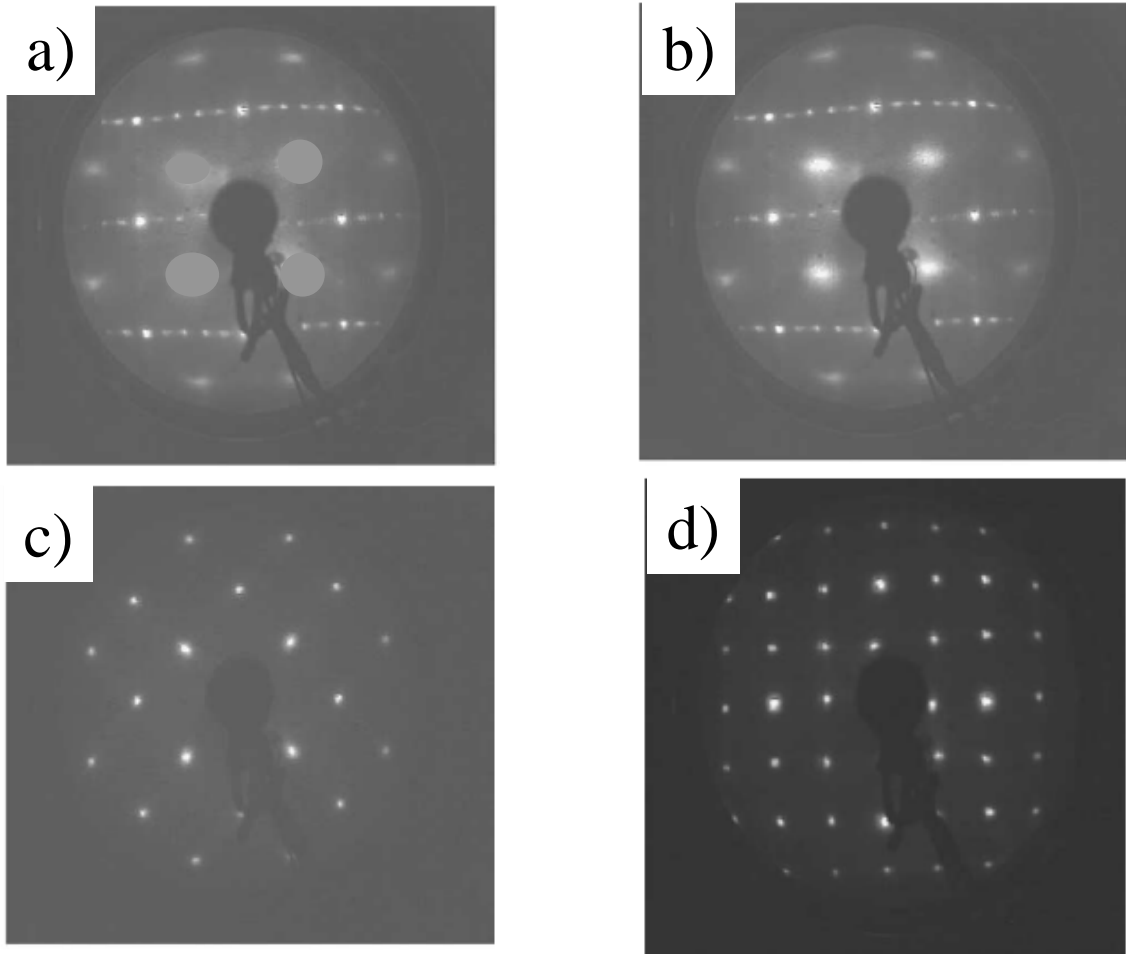
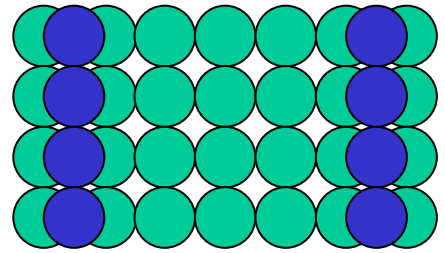


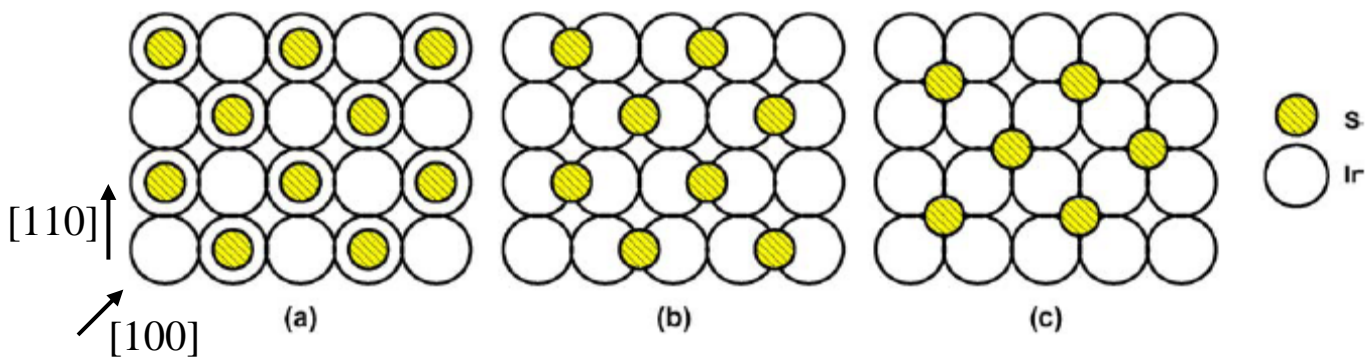
Fig. (a) The LEED patterns of the clean Ir(100)-($a \times b$)-H surface. (b) The LEED patterns obtained after exposing the clean Ir(100)-($a \times b$)-H surface to 5 L H₂S at 300 K and (c) after flashing the crystal to 700 K. $E_p = 136$ eV. (d) The LEED pattern after exposing the clean Iridium surface to 0.5 L of H₂S at 200 K

Solution: H₂S adsorption on Ir(100).

The surface reconstruct in the
Ir(100)-(1 x 5)-H

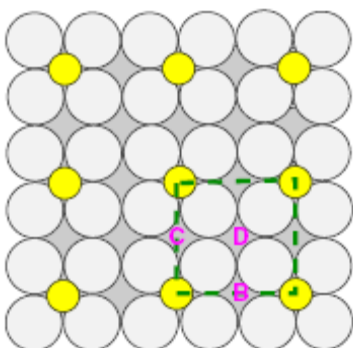


The Sulphur partially lifts the (1 x 5) reconstruction at 300 K, while annealing to 700 K results in the complete lifting of the reconstruction. The LEED pattern in fig. (c) corresponds to a c(2x2) arrangement of the S adsorbed atoms. Three different atomic configurations are possible on the simple basis of the LEED pattern (see below)..



Top view of 0.5 ML c(2 x 2)-S trial structures: (a) atop, (b) bridge and (c) hollow adsorption sites.

The LEED pattern in fig (d) correspond to a p(2x2) structure as shown in the figure below



Growth of Pd on Au(100)

The clean surface of an Au(100) single crystal was investigated by LEED and RHEED (fig. 1). Clearly the surface is reconstructed. Why? Can you draw the corresponding real pattern?

Can you explain why the RHEED patterns along the [011] and [001] directions are different?

After deposition of 1.0 ML of Pd new LEED and RHEED patterns are acquired (see fig. 2). Which is the structure of the Pd layer?

How many atomic planes contribute to the RHEED signal? Using the data shown in Fig 1 and 2, how can you calculate the ratio between the in-plane lattice parameter of Au and Pd?

(Au has an fcc structure.)

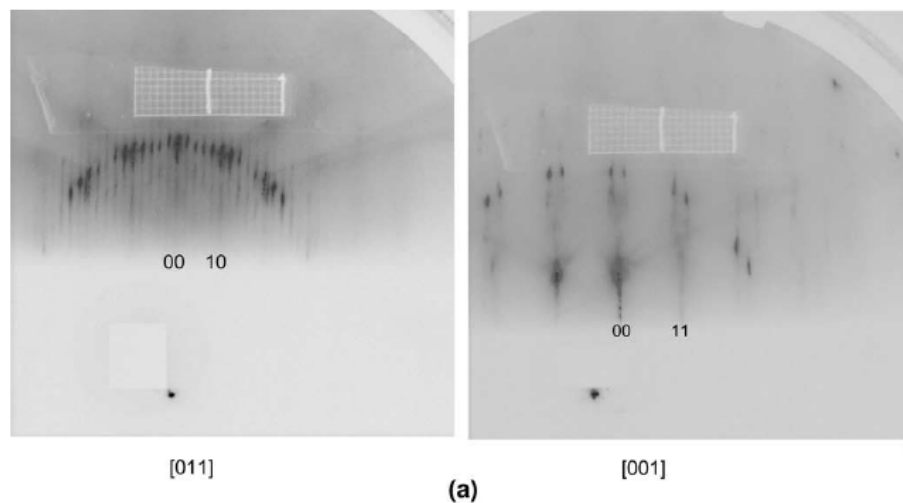
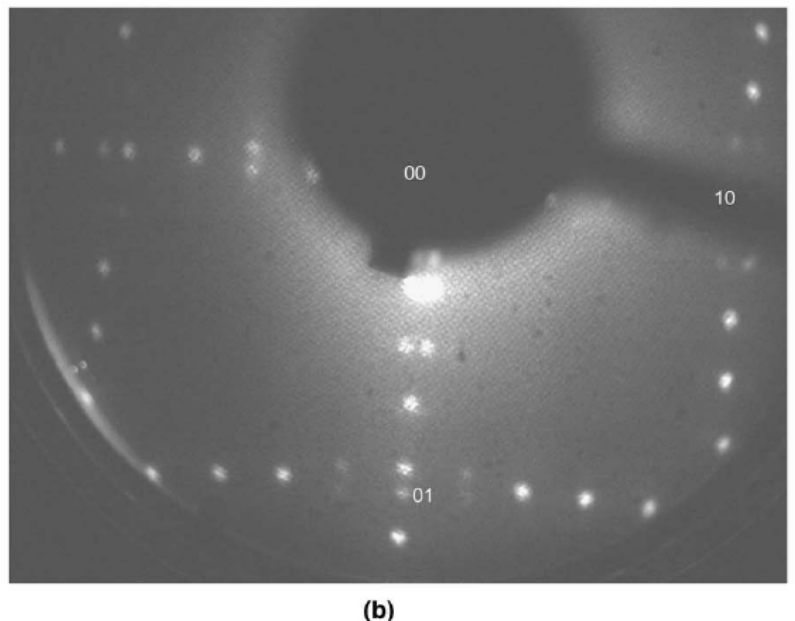
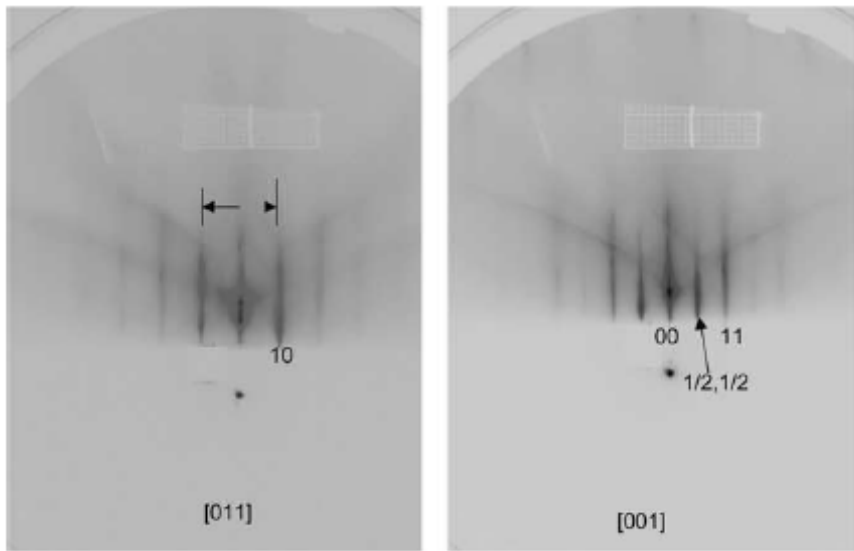
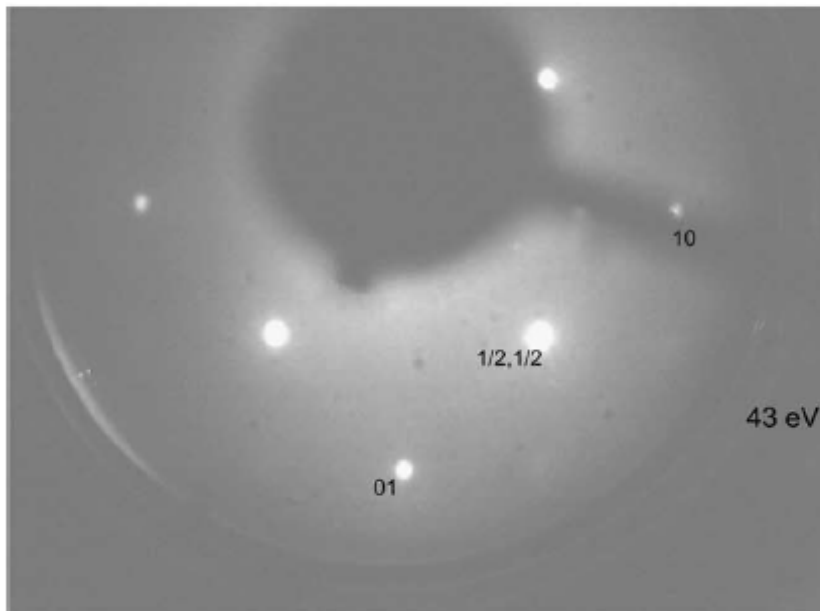


Fig. 1. (a) RHEED patterns (40 KeV, 3° incidence angle) for a clean Au(100) after argon ion sputtering and annealing under UHV conditions and (b) Au(100) LEED pattern (43 eV).





(a)



(b)

Fig. 2. (a) RHEED and (b) LEED patterns for Au(100) electrode covered with 1ML Pd

Solution: Growth of Pd on Au(100)

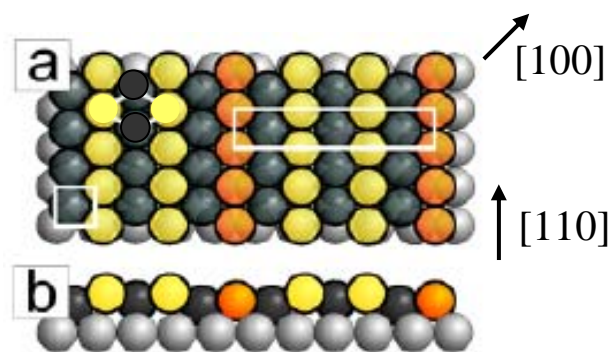
The Au(100) surface shows the (5x1) reconstruction in two mutually orthogonal domains along the [011] and the [01 -1] directions (Fig 1). The reconstruction can be seen as channels, 1 atom wide and with a separation of 5 atoms, running along the [011] and the [01 -1] directions. The RHEED is sensible to the surface profile perpendicular to the electron beam, meaning that it can not see the periodicity of the channels (domains) running parallelly to the electron beam direction. Consequently the RHEED pattern along the [011] direction clearly shows the $5n$ symmetry of the (5x1) rows parallel to the beam direction, while the RHEED pattern along the [001] direction is a mean of the signal due to the scattering of both kind of domains resulting in broader and less resolved peaks.

After deposition of 1 ML of Pd the both the LEED and RHEED patterns suggest a c(2x2) surface structure. This implies that the Pd deposition remove the surface reconstruction of the Au(100) and that the Pd grows in register with the Au(100) surface.

The depth sensitivity D of the RHEED is given by $D = \lambda \cos(90 - \alpha)$ with $\alpha = 3^\circ$. Taking $\lambda = 10$ nm, one obtains $D = 0.5$ nm, meaning that only the topmost two-three layers are investigated by RHEED.

The in-plane lattice parameters, \mathbf{a}_{011} and \mathbf{a}_{001} , perpendicular to the incident directions of electron beam at [011] and [001] directions respectively, can be precisely determined by measuring the reciprocal lattice rod spacing between the (0 0) and (1 0) and (1 1) beams in RHEED. Thus the change of in-plane lattice parameters, \mathbf{a}_{011} and \mathbf{a}_{001} , with various Pd coverage can be determined by the RHEED pattern analysis. The analysis shows no change in the RHEED peak position meaning that the Pd forms a pseudomorphic flat layer.

FIG. 1 Model of Au(100)-(5x1) in (a) the top and (b) the side view. The unit meshes of the bulk layer (quadratic), and the overall (5x1) unit mesh are also given.



Monitoring the film growth by RHEED: in-phase vs out-of-phase patterns

RHEED is a technique largely used to monitor the layer by layer growth of thin films. This can be understood calculating the intensity of the specular peak of the RHEED diffraction pattern in the case of a one-dimensional model.

a) Let assume that the sample surface is a flat chain of N atoms, with lattice size a . Which is the intensity of the specular peak?

b) At a coverage of 0.5 ML we assume the surface described by a step function in such a way that the surface height is 0 if $i < N/2$ and h if $i > N/2$. Which is the intensity of the specular peak?

c) In the case of a two-dimensional surface with two exposed layer it can be seen that the intensity of the specular peak is given by:

$$I = N^2 [1 - 2(1 - \cos(\delta K h))\theta(1 - \theta)]$$

where θ is the fractional coverage of the second layer.

Which is the behavior of I as a function of θ ? At which coverage I presents the minimum and the maximum?

d) What happens if we chose experimental conditions for in-phase (constructive) interference and, on the contrary, for out-of-phase (destructive) interference?

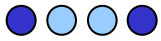
e) You want to study the growth of Ag on Ag(100) by RHEED. Which is the incidence angle α you have to choose in order to have the best sensibility for investigating the crystallographic structure of the surface and for monitoring the film growth. (Ag has an fcc structure with $a = 0.409$ nm and your RHEED has an energy of 40 KeV) ?

Solution: Monitoring the film growth by RHEED: in-phase vs out-of-phase patterns

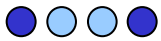
- a) The diffracted amplitude is given by $\Psi = \sum_i e^{i\delta\mathbf{K} \cdot \mathbf{R}_i}$ where $\delta\mathbf{K} = \mathbf{K}_i - \mathbf{K}_f$ and $\mathbf{R}_i = a \mathbf{i}$ pointing in the x direction. Because we are interested in the specular peak $\delta\mathbf{K} = \delta\mathbf{K}_z = 2K\cos\alpha$ meaning that $\delta\mathbf{K}$ and \mathbf{R} are orthogonal. The intensity $I = \Psi^2 = N^2$.
- b) The diffracted amplitude is given by $\Psi = N/2 (1 + e^{i\delta\mathbf{K} \cdot h})$ and $I = \Psi^2$.
- c) The specular intensity presents a maximum for $\theta = 0, 1$ and a minimum for $\theta = 1/2$. Of course, once the second layer has been completely filled, you can repeat the same procedure for the third layer, and so on, which gives the oscillatory behavior of I as a function of the coverage
- d) For in-phase conditions $\delta\mathbf{K} \cdot h = 2\pi n$ I becomes independent on θ . With this experimental conditions we can get information on the atomic crystallographic structure but not on the surface roughness.
For out-of-phase conditions $\delta\mathbf{K} \cdot h = (2n+1)\pi$ the intensity of the specular peak is a function of the coverage θ .
- e) To monitor the Ag growth you have to choose out-of-phase conditions. The out-of-phase conditions is given by $\delta\mathbf{K} \cdot h = 2K\cos\alpha \cdot h = \pi, 3\pi, \dots$ meaning $\cos\alpha = \lambda/4h$. For 40 KeV $\lambda = 0.006$ nm. For Ag(100) $h = a/2 = 0.205$ nm. This implies $\alpha = 89.6^\circ$ or 88.7° while the in-phase conditions, useful for studying the crystallographic order of the surface, is obtained for $\alpha = 89.2^\circ$
Note the high angular resolution you need to find the right experimental conditions

Hydrogen adsorption on Rh(110).

A LEED study of the adsorption of H on Rh(110) at 80 K shows the following sequence of LEED patterns as a function of the H coverage θ (only one quadrant of the LEED pattern is shown). Draw the corresponding real space patterns. (Rhodium has an fcc structure. 1ML corresponds to a number of H atoms equal to the number of the Rh(110) surface atoms)



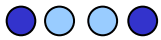
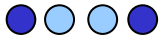
$$\Theta = 0.33 \text{ ML}$$



$$\Theta = 0.5 \text{ ML}$$



$$\Theta = 0.66 \text{ ML}$$



$$\Theta = 1.5 \text{ ML}$$



$$\Theta = 2.0 \text{ ML}$$



Solution: Hydrogen adsorption on Rh(110).

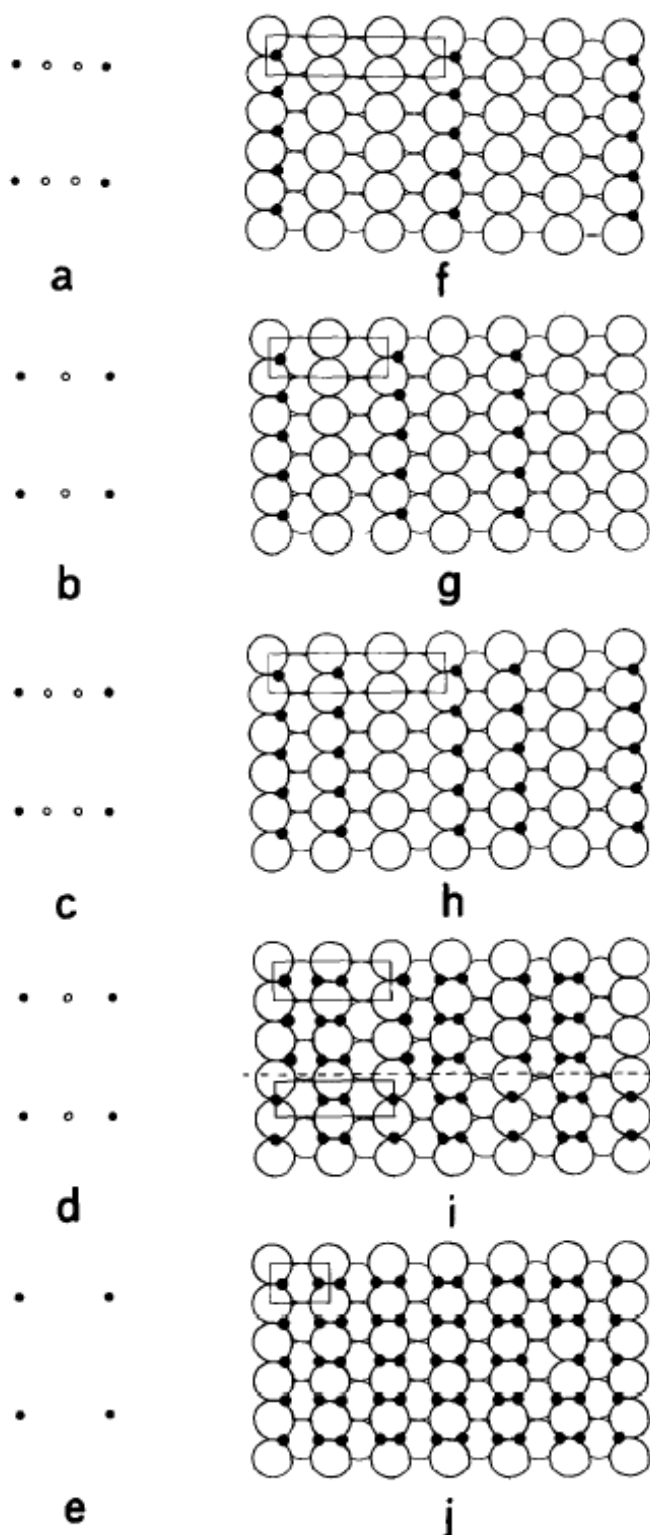


Fig.1. Sequence of the observed lattice gas structures in LEED at $T=80$ K. Left-hand side: drawing of the LEED patterns (electron energy $E=95$ eV). Right-hand side: tentative structure model. (a) and (f): $p1 \times 3$ phase; (b) and (g): $p1 \times 2$ phase; (c) and (h): $1 \times 3-2H$ phase; (d) and (i): $1 \times 2-3H$ phase (two possible locations of the H atoms are indicated); (e) and (j): $1 \times 1-2H$ phase.