

# Diffrazione di raggi X, diffrazione da superfici

Per approfondimenti:

1. **E. Vlieg**  
**X-Ray Diffraction from Surfaces and Interfaces**

<https://onlinelibrary.wiley.com/doi/10.1002/9783527680535.ch10>

2. **Surface Science Reports 10 (1989) 105–188** 105  
North-Holland, Amsterdam

## **SURFACE STRUCTURE DETERMINATION BY X-RAY DIFFRACTION**

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Manuscript received in final form 2 February 1989

# Interazione radiazione-materia

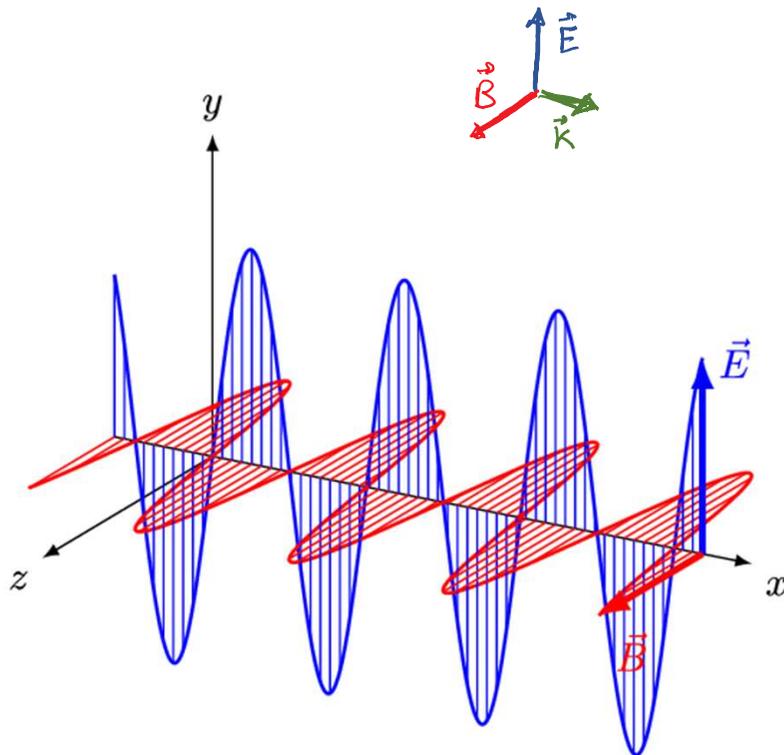
Le equazioni di Maxwell insegnano che un'onda elettromagnetica può sempre essere descritta con un insieme di onde piane, con campi E e B ortogonali tra loro.

$$\vec{E} = \vec{E}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$$\vec{B} = \vec{B}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$\vec{k}$  è il vettore d'onda, la sua direzione è la direzione di propagazione

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

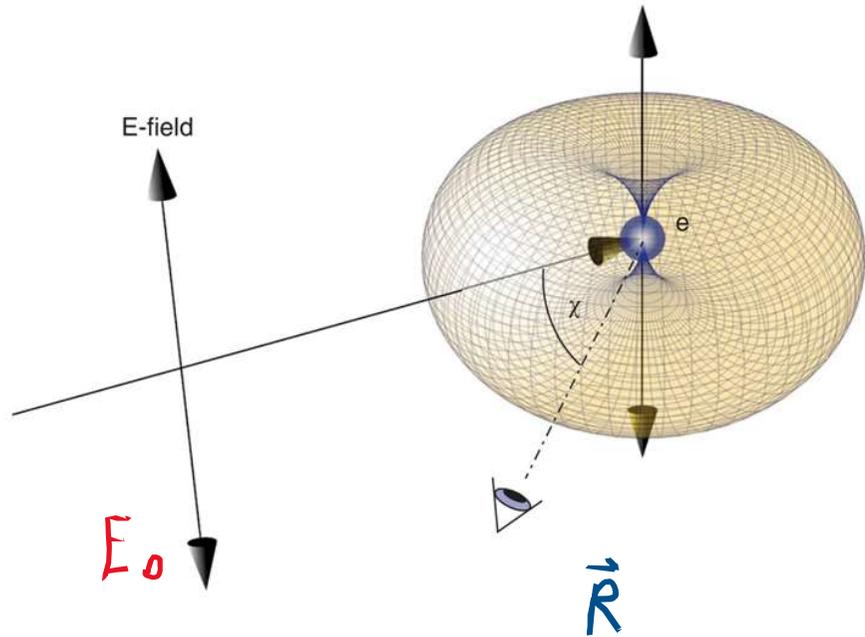


$$B_0 = \frac{E_0}{c}$$

energia fotone

$$E_\gamma = h\nu$$

$$E_\gamma (\text{eV}) = \frac{12398}{\lambda (\text{\AA})}$$



Scattering Thomson  
 $e^-$  immerso nel campo  
 e.m. diventa un'antenna

$$\vec{E}(\vec{R}) \propto \hat{x}$$

$$\vec{B}(\vec{R}) \propto \hat{y}$$

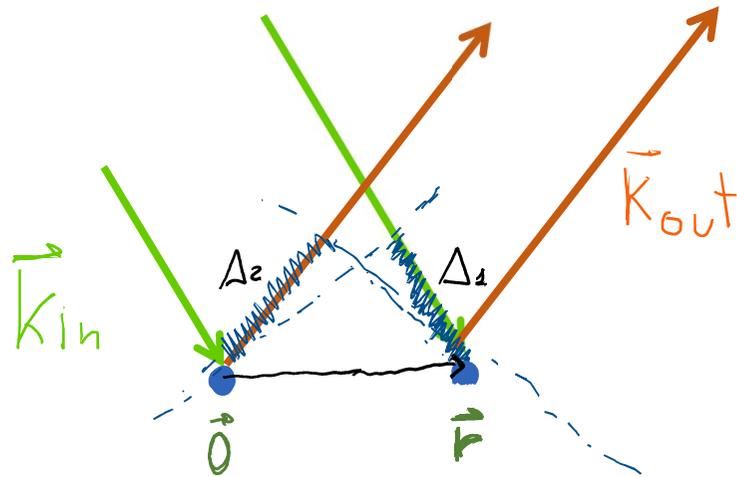
$$E(\vec{R}) = E_{ce} e^{i(\vec{k}_e \cdot \vec{R})}$$

Nota: qui per semplicità  $t=0$   
 Ad un  $t$  qualsiasi:  
 $e^{i(\vec{k} \cdot \vec{R} - \omega t)}$

$$E_{el} = E_0 \frac{e^2 M_0}{4\pi m R} P^{1/2} \quad P = \cos^2 \chi$$

Supponiamo ora che l'e<sup>-</sup> si trovi in  $\vec{r}$  anziché in  $\vec{0}$ . Voglio esprimere il campo in  $\vec{R}$ .

$\cdot \vec{R}$



Rispetto a prima, ho una differenza tra il percorso onde incidente - e<sup>-</sup> - onde uscente

Questa differenza di fase è:

$$\Delta_2 - \Delta_1 = \vec{k}_{out} \cdot \vec{r} - \vec{k}_{in} \cdot \vec{r} \\ = \vec{q} \cdot \vec{r}$$

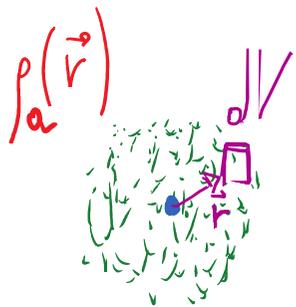
$\vec{q}$  momento scambiato  
 $\vec{q} = \vec{k}_{out} - \vec{k}_{in}$

Il campo in  $\vec{R}$  sarà:

$$\vec{E}(\vec{R}) = \vec{E}_0 e^{i\vec{k}_{out} \cdot \vec{R}} e^{i(\vec{q} \cdot \vec{r})}$$

Il momento scambiato  $\vec{q}$  è la grandezza chiave in un esperimento di diffrazione.

Il risultato precedente ci aiuta ad esprimere il campo creato da una certa densità di  $e^-$ , ad esempio da un atomo.



Un elemento di volume  $dV$ , posto in  $\vec{r}$ , contiene  $\rho_A(\vec{r}) \cdot dV$  elettroni. Il contributo da questo volume dato al campo in  $\vec{R}$  sarà:

$$dE = E_0 e^{i\vec{k} \cdot \vec{R}} \cdot \rho_A(\vec{r}) dV \cdot e^{i\vec{q} \cdot \vec{r}}$$

Integrando  $dE$  sul volume, il campo generato dall'atomo diventa  $E = E_0 e^{i\vec{k} \cdot \vec{R}}$  con:

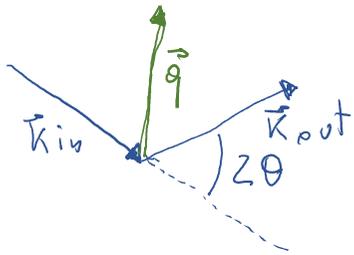
$$\Rightarrow E_0 = \int E_0 \rho_A(\vec{r}) e^{i\vec{q} \cdot \vec{r}} dV = E_0 \frac{e^2}{mc^2 R} P^{1/2} \int \rho_A(\vec{r}) e^{i\vec{q} \cdot \vec{r}} dV$$

$$f_0(\vec{q}) = \int \rho_e(\vec{r}) e^{i\vec{q} \cdot \vec{r}} dV$$

FATTORE d: FORMA ATOMICA

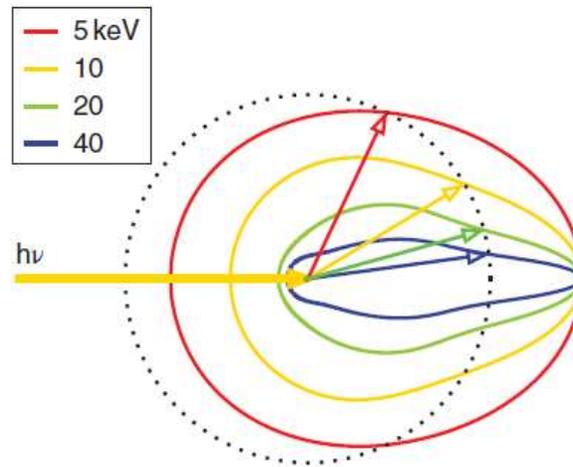
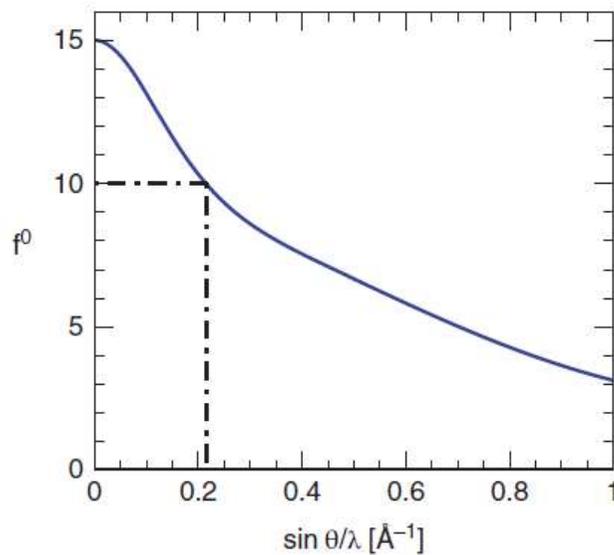
Per semplificare,  $\rho_A(\vec{r})$  viene solitamente descritto come reale,  $\rho_A(r)$ .

Di conseguenza  $f_0(\vec{q})$  sarà anche dipendente da  $q$ :  $f_0(q)$ .

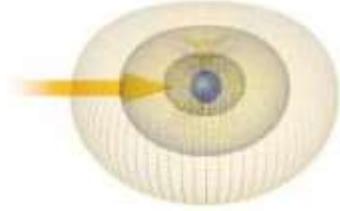


Definendo l'angolo di scattering  $2\theta$  come in figura, si

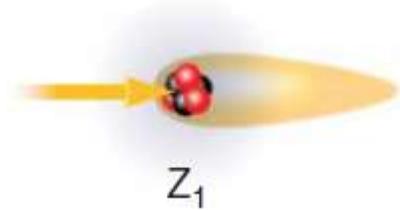
ha  $q = 2k \sin\theta = 4\pi \frac{\sin\theta}{\lambda}$ , ovvero  $q$  è una funzione di  $\frac{\sin\theta}{\lambda}$



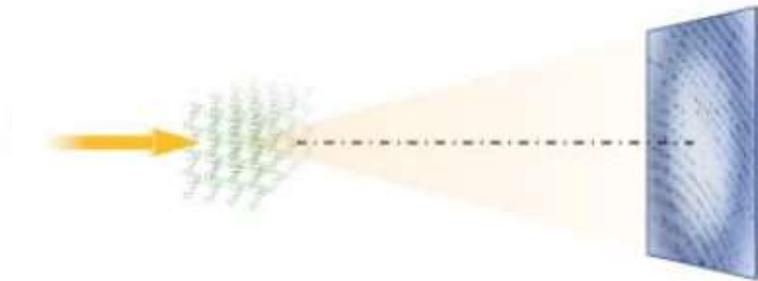
Per fenomeni di interferenza tra i vari contributi di  $\rho_A(r)$  al campo, si trova che  $f_0(q)$  ha una forma affusolata, tanto più accentuata quanto maggiore è  $h\nu$  del campo incidente.



Scattering da un elettrone



Scattering da un atomo



Scattering da un cristallo

Diffrazione di raggi X

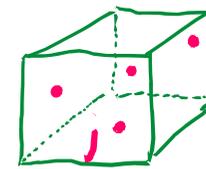
Se ho N atomi, il campo diffuso sarà la somma dei contributi di ognuno, sempre pesata per la differenza di fase:

$$E \propto E_{ee} \sum_{i=0}^{N-1} f_i(\vec{q}) e^{i\vec{q} \cdot \vec{r}_i}$$

Se gli atomi appartengono ad un reticolo cristallino, l'interferenza tra i contributi di ognuno danno origine ad un pattern di diffrazione

Se il cristallo è descritto da una cella primitiva con base, scrivo prima il contributo della singola cella:

$$E_{\text{cella}} \propto E_{ee} \sum_{j=0}^{\bar{N}-1} f_j(\vec{q}) e^{i(\vec{q} \cdot \vec{r}_j)}$$



$\bar{N}$  atomi/cella

$$= F(\vec{q})$$

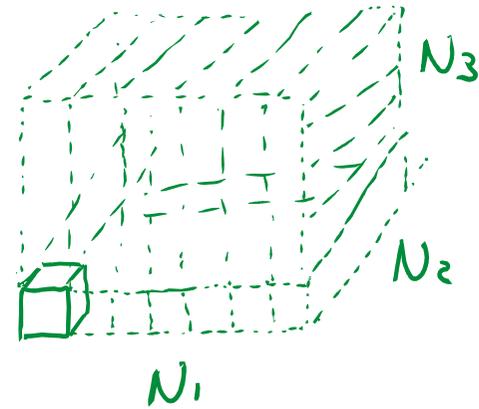
**Fattore di Struttura**

Se il cristallo è costituito da  $N_1 \times N_2 \times N_3$  celle:

$$E_{cr}(\vec{q}) \propto F(\vec{q}) \cdot \sum_{\vec{R}_j} e^{i\vec{q} \cdot \vec{R}_j}$$

con  $\vec{R}_j$  coordinata delle celle all'interno

del cristallo:  $\vec{R}_j = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$



$$n_i = 0, \dots, N_i - 1$$

$\vec{a}_i$  vettori delle celle

La somma

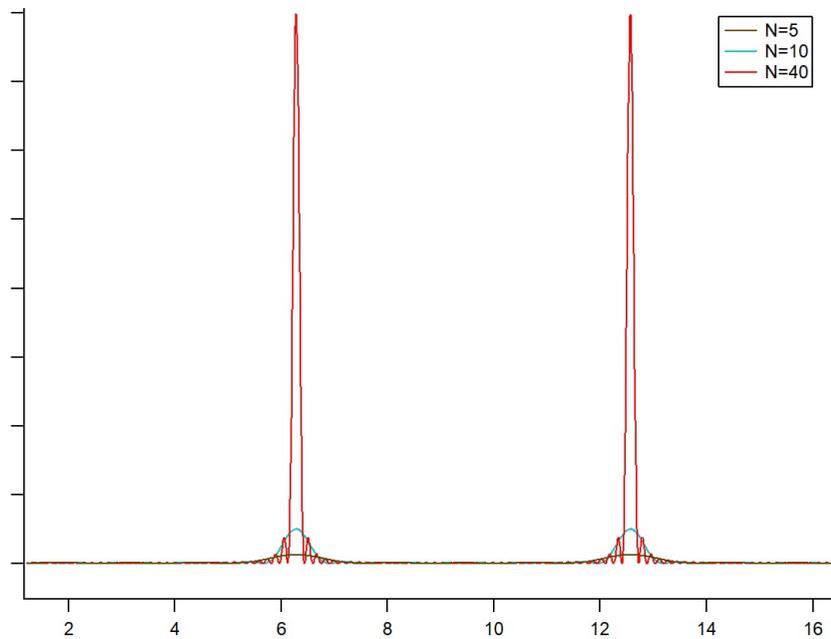
$$\sum_{\vec{R}_j} e^{i \vec{q} \cdot \vec{R}_j} = \sum_{j_1=0}^{N_1-1} \sum_{j_2=0}^{N_2-1} \sum_{j_3=0}^{N_3-1} e^{i \vec{q} \cdot (j_1 \vec{a}_1 + j_2 \vec{a}_2 + j_3 \vec{a}_3)}$$

si può dimostrare che diventa:

$$= \frac{\sin \frac{1}{2} N_1 \vec{q} \cdot \vec{a}_1}{\sin \frac{1}{2} \vec{q} \cdot \vec{a}_1} \frac{\sin \frac{1}{2} N_2 \vec{q} \cdot \vec{a}_2}{\sin \frac{1}{2} \vec{q} \cdot \vec{a}_2} \frac{\sin \frac{1}{2} N_3 \vec{q} \cdot \vec{a}_3}{\sin \frac{1}{2} \vec{q} \cdot \vec{a}_3}$$

L'intensità diffratta da un cristallo sarà perciò:

$$I(\vec{q}) \propto |F(\vec{q})|^2 \cdot \frac{\sin^2\left(\frac{1}{2} N_1 \vec{q} \cdot \vec{a}_1\right)}{\sin^2\left(\frac{1}{2} \vec{q} \cdot \vec{a}_1\right)} \frac{\sin^2\left(\frac{1}{2} N_2 \vec{q} \cdot \vec{a}_2\right)}{\sin^2\left(\frac{1}{2} \vec{q} \cdot \vec{a}_2\right)} \frac{\sin^2\left(\frac{1}{2} N_3 \vec{q} \cdot \vec{a}_3\right)}{\sin^2\left(\frac{1}{2} \vec{q} \cdot \vec{a}_3\right)}$$



$$y = \frac{\sin^2\left(\frac{1}{2} N x\right)}{\sin^2\left(\frac{1}{2} x\right)}$$

- per  $N \gg 1$ ,  $\neq 0$  se  $x = 2\pi n$
- $\text{FWHM} \propto \frac{1}{N}$

L'intensità diffratta dal cristallo sarà quindi non  
nulla, e poi  $I(\vec{q}) \propto |F(\vec{q})|^2$  se il vettore scambiato  
soddisfa:

$$q_x \cdot a_1 = 2\pi h$$

$$q_y \cdot a_2 = 2\pi k$$

$$q_z \cdot a_3 = 2\pi l$$

$h, l, k$  interi

L'insieme di punti  $\vec{q}$  che soddisfano le relazioni precedenti formano un reticolo, definito nello spazio  $\vec{k}$ , detto **reticolo reciproco**.

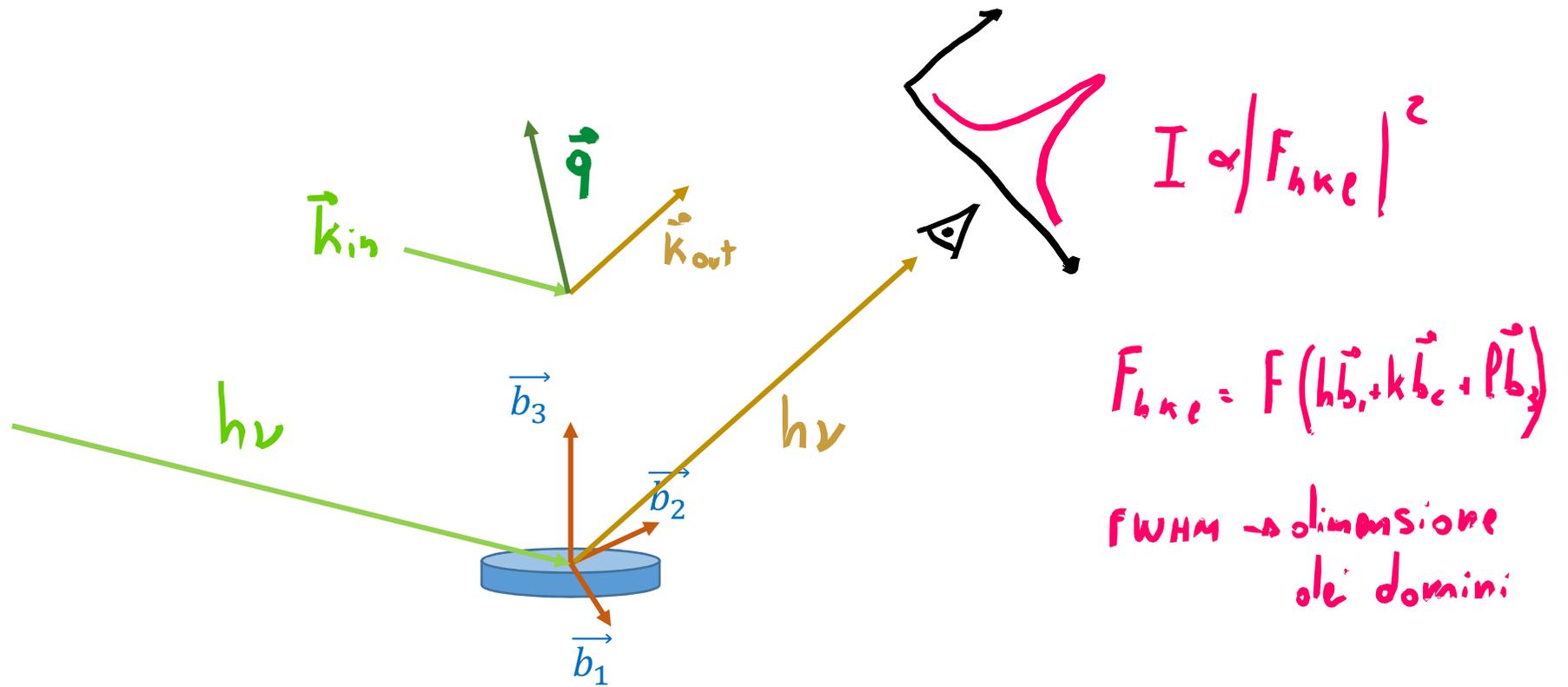
Ogni reticolo cristallino, identificato da una cella di vettori  $\vec{a}_1, \vec{a}_2, \vec{a}_3$ , ha associato un reticolo reciproco la cui cella è:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

**Nota:** La cella di Wigner Seitz del reticolo reciproco è chiamata zona di Brillouin.

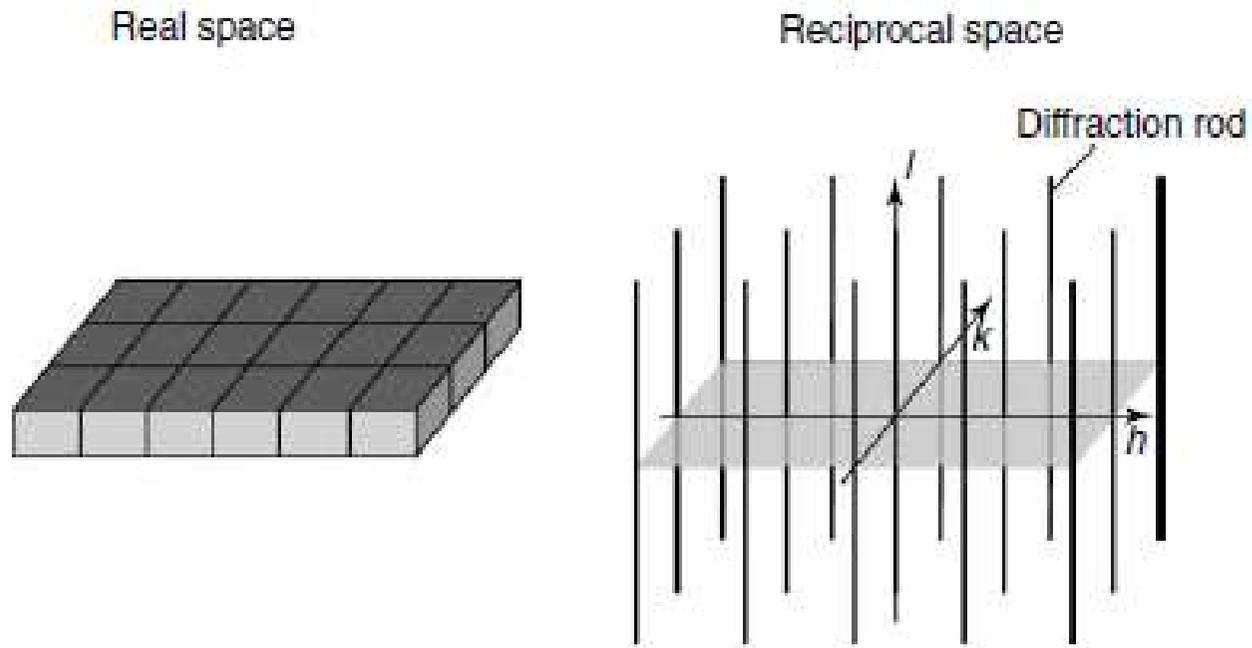


Ho un picco se  $\vec{q} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$

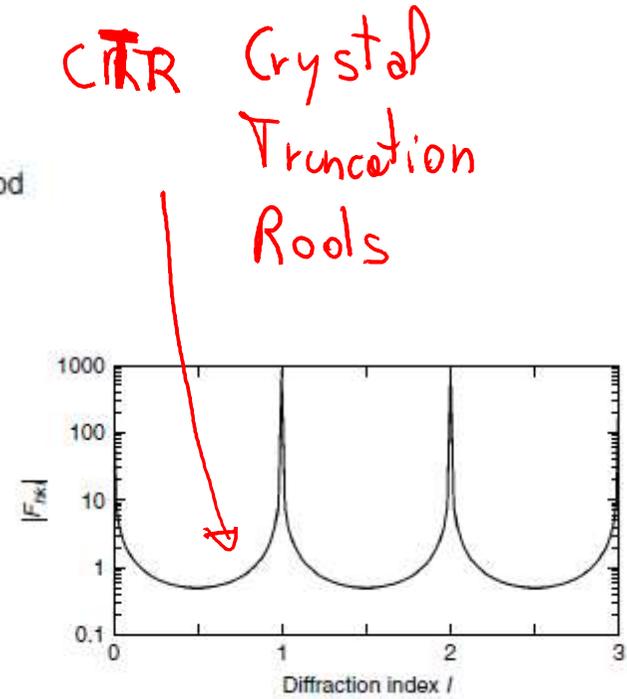
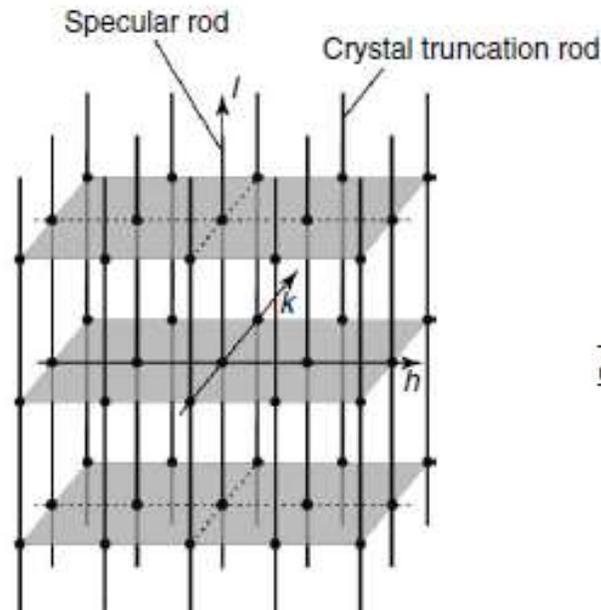
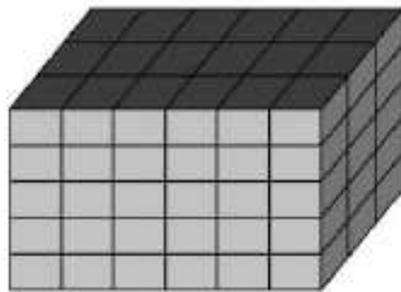
ovvero, se il momento scambiato  $\vec{q}$  corrisponde ad un vettore del reticolo reciproco del sistema.

Se considero la diffrazione da un sistema 2D, le condizioni di diffrazione si applicano solo su  $x$  e  $y$ . La condizione su  $z$  scompare:

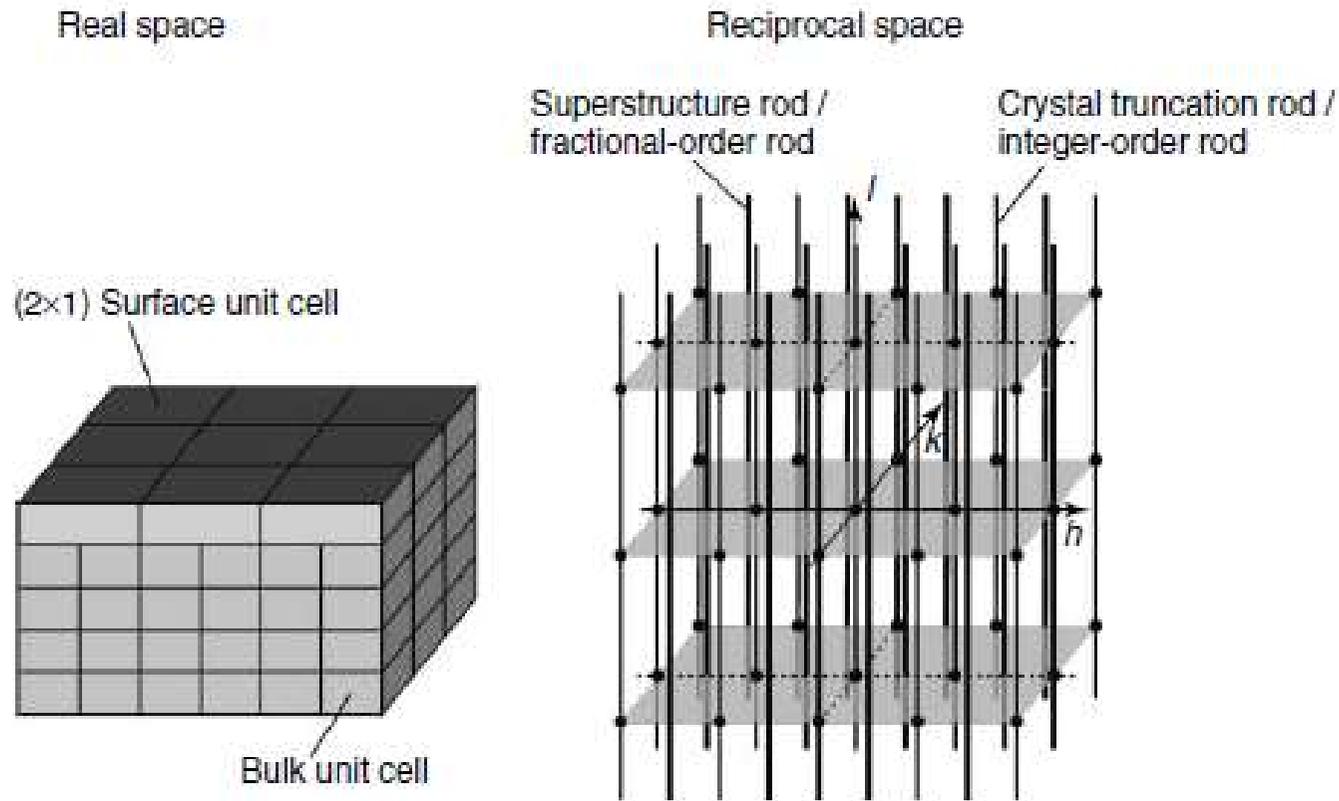
il reticolo reciproco di un sistema 2D è un insieme di rod.



!! Un Sistema reale sarà sempre 3D. Posso vederlo come la somma di bulk + superficie.  
La presenza della superficie fa sì che oltre ai picchi di diffrazione di bulk ci sia intensità diffratta anche lungo le rod.



Se ho una ricostruzione della superficie, compariranno delle rod in corrispondenza di ordini frazionari.



IP modello con cui abbiamo definito  $f(\vec{q})$  è troppo semplice -  
Stiamo trascurando effetti di risonanza che ci sono se  $\hbar\omega$  è vicina ad una soglia di  
assorbimento -

Si introducano le correzioni e  $f_0$  e si scrive il fattore di  
forma come;

$$f(\vec{q}) = f_0(\vec{q}) + f'_1(\vec{q}) + i f''$$

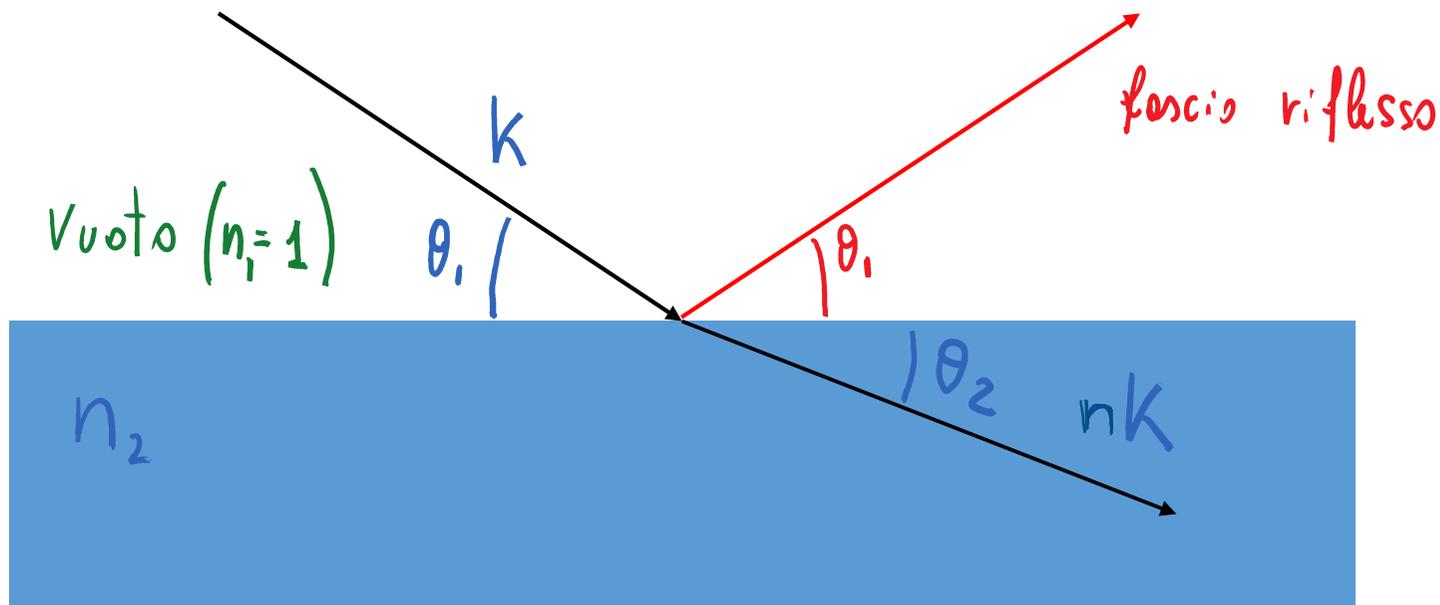
Nella regione dei raggi X l'indice di rifrazione è:

$$n(\lambda) = 1 - \frac{r_0}{2\pi} \lambda^2 \sum_i N_i f_i(0)$$

$N_i$  : # atomi di specie  $i$  per unità di volume

!!  
•  $n = n_R + i n_I = 1 - \delta + i\beta$

•  $\delta \approx 10^{-3} - 10^{-6} \Rightarrow n \bar{e}$  molto vicino a 1



$$\frac{\cos \theta_1}{\cos \theta_2} = (1 - \delta) < 1 \quad \text{Legge di Snell}$$

C'è un'angolo  $\theta_1 = \theta_c$  al di sotto del quale ho riflessione totale

$$\theta_c = \cos^{-1}(1 - \delta)$$

Ne] vuoto:

$$E(z) = E_0 e^{ikz}$$

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

Ne] mezzo:

$$E(z) = E_0 e^{in_k z}$$

$$n = n_R + i n_I$$

$$= E_0 e^{-n_I k z} e^{i n_R k z}$$

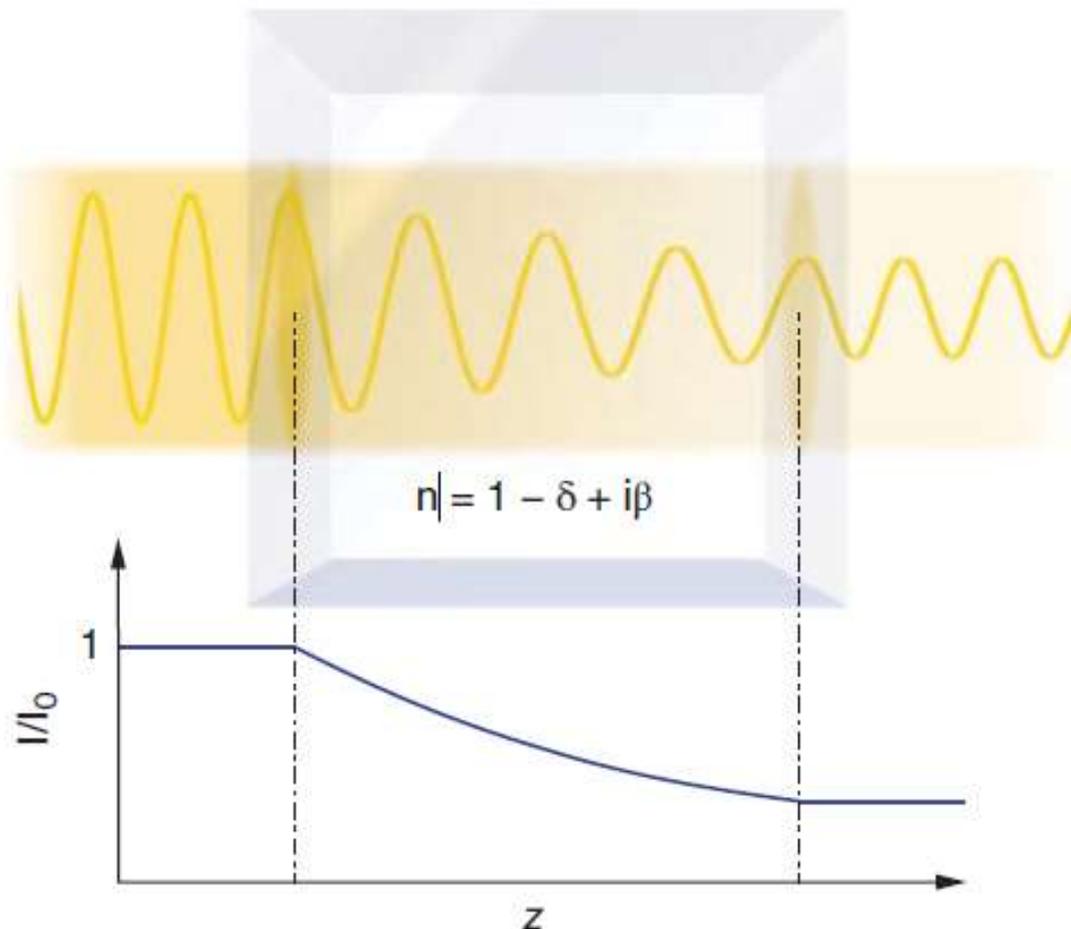
L'intensità va come  $|E|^2$

$$\frac{I}{I_0} = e^{-\mu z}$$

**Equazione di Beer-Lambert**

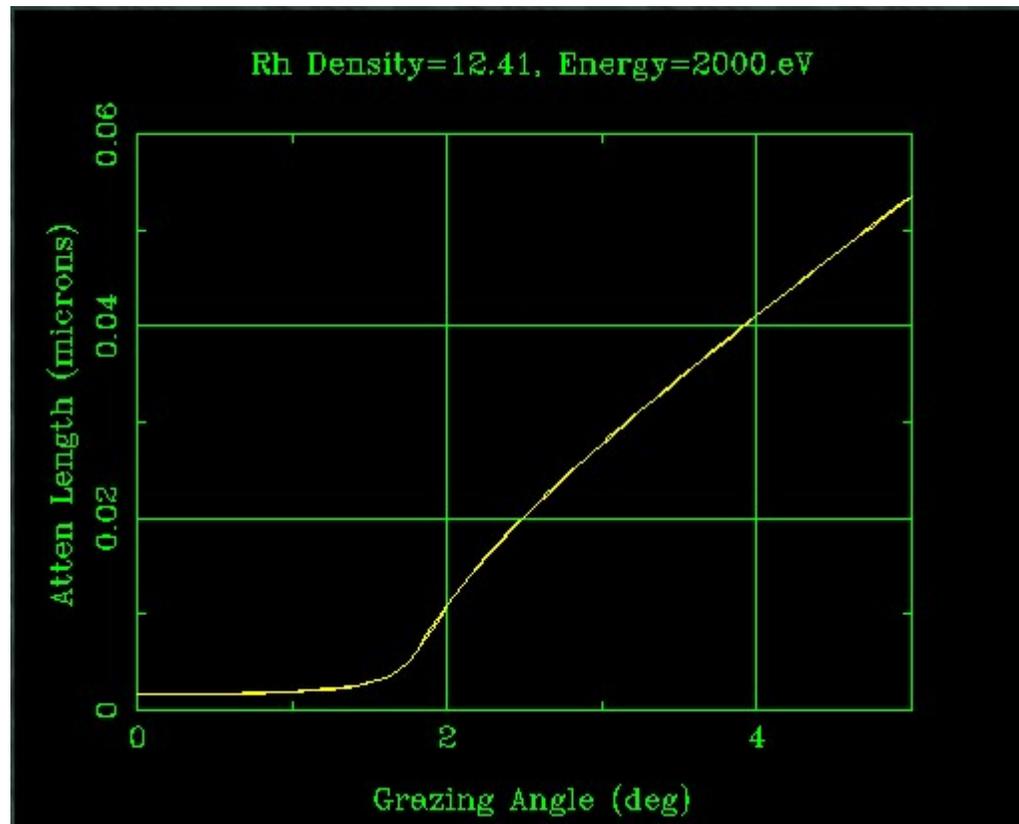
$$\mu = 2 n_I k$$

coefficiente  
di assorbimento



Si può verificare che la lunghezza di penetrazione nel mezzo è:

$$\Lambda = \frac{\lambda}{4\pi \text{Im} \sqrt{\alpha^2 - \alpha_c^2 - 2i\beta}}$$



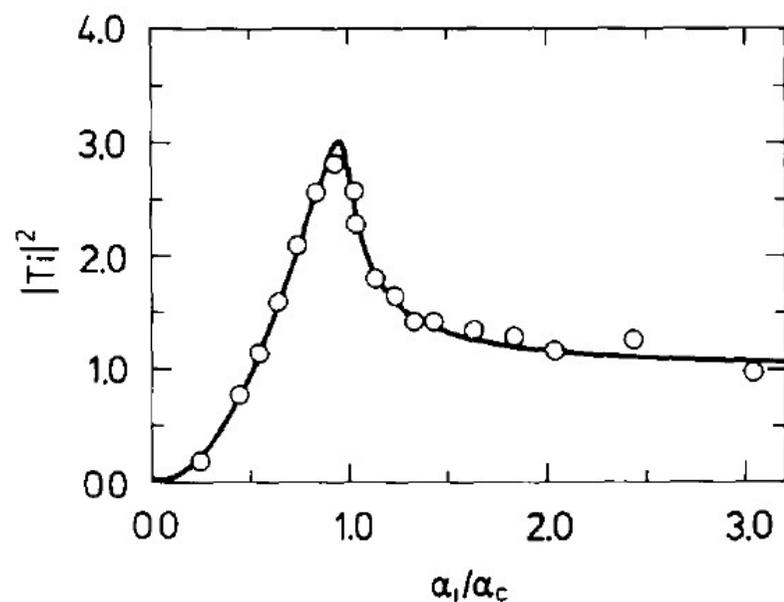
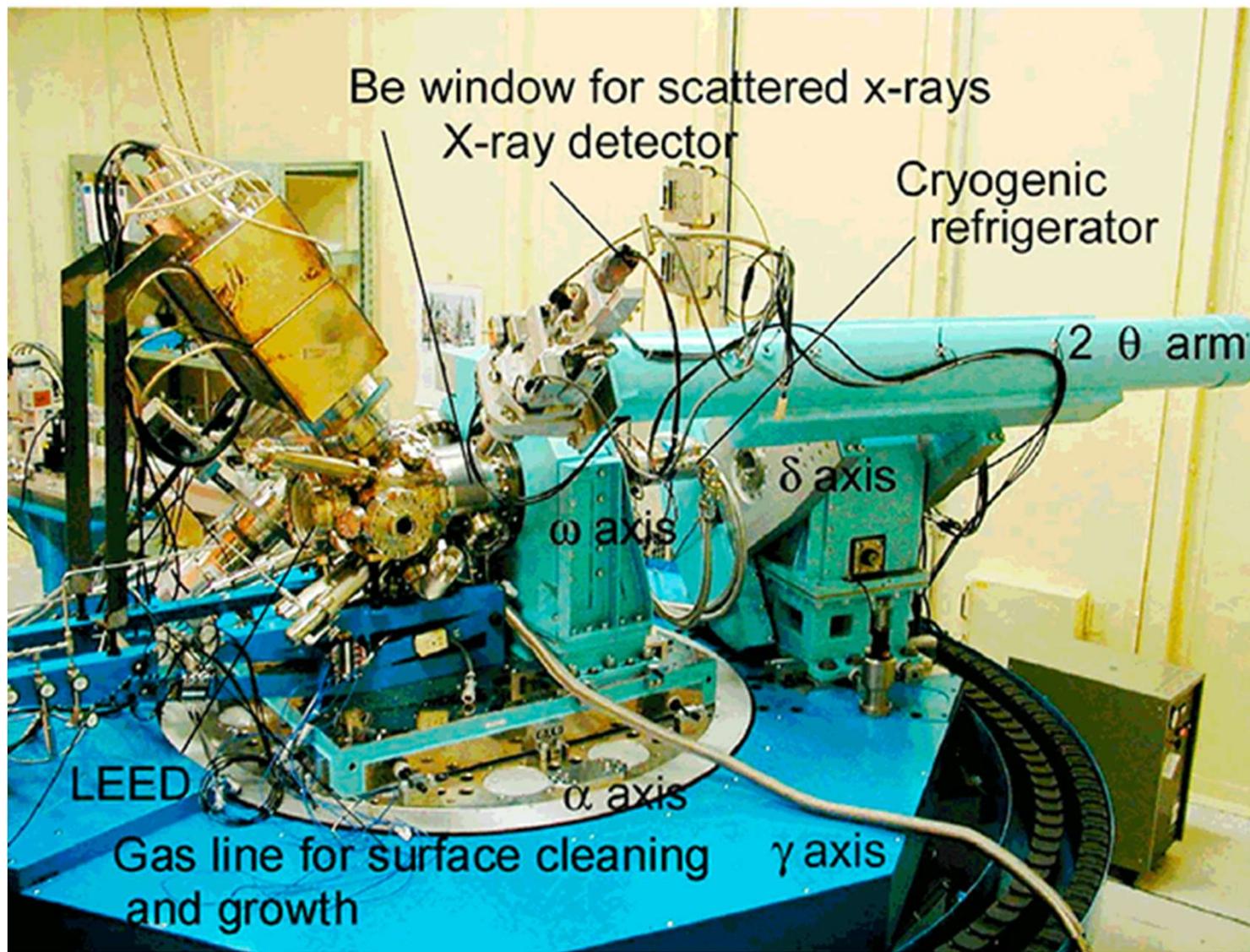


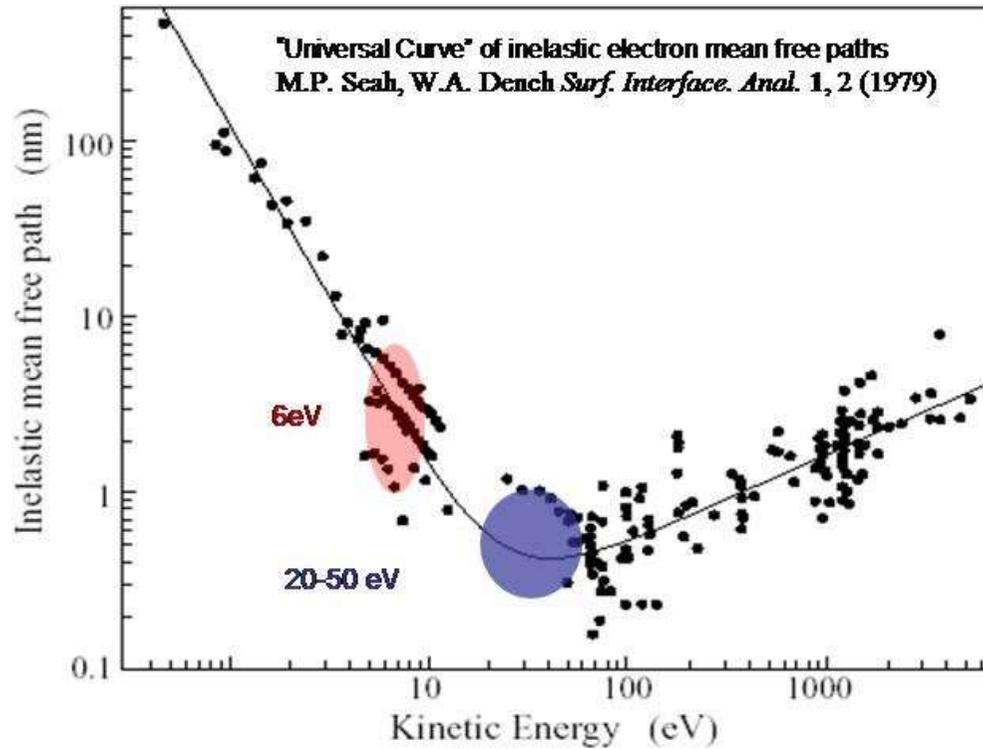
Fig. 6. Transmission coefficient  $|T_i|^2$  as a function of incidence angle  $\alpha_i$ . The curve is shown for an InSb(111) surface and a wavelength  $\lambda = 1.2 \text{ \AA}$ , the critical angle is  $\alpha_c = 0.25^\circ$ . The experimental points are from the  $(4/3,0)$  reflection of the InSb( $\bar{1}\bar{1}\bar{1}$ ) $3 \times 3$  surface normalized to the correct scale. The intensity of a superlattice reflection is a measure of the intensity of the evanescent wave and hence of the transmission coefficient. From ref. [25].



[http://www.spring8.or.jp/wkg/BL13XU/instrument/img/BL13XU\\_exp3.gif](http://www.spring8.or.jp/wkg/BL13XU/instrument/img/BL13XU_exp3.gif)

Il libero cammino medio degli **elettroni** nel mezzo è invece molto inferiore

## Cammino libero medio degli elettroni nella materia



$$\lambda = \frac{143}{E^2} + 0.054 \cdot \sqrt{E}$$

$$I = I_0 e^{-\frac{d}{\lambda}}$$

$E \ll$  : l'energia non è sufficiente a eccitare  
 plasmoni ( $E_p \sim 10-20 \text{ eV}$ ) moto collettivo  $e^- \sim$  liberi  
 fononi ( $E_{\text{fonon}} \sim 0.1-5 \text{ eV}$ ) moto collettivo nuclei reticolo

# LEED: Low Energy Electron Diffraction

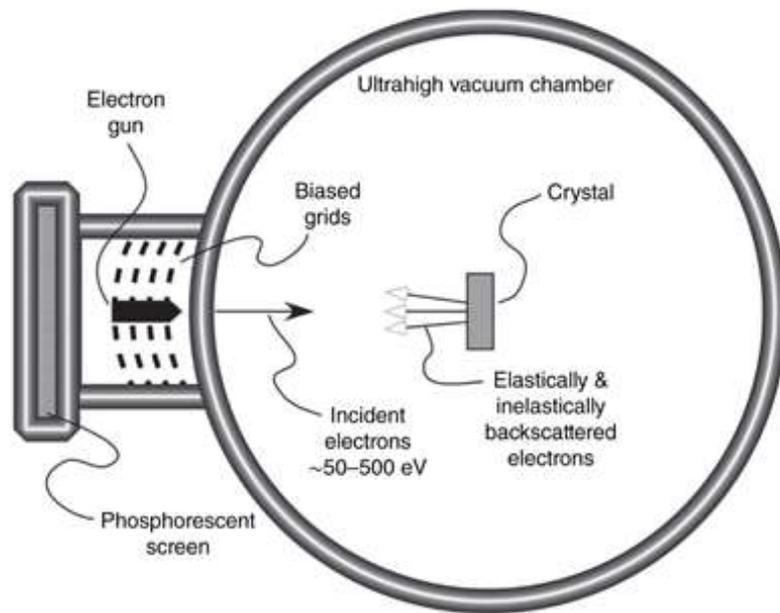
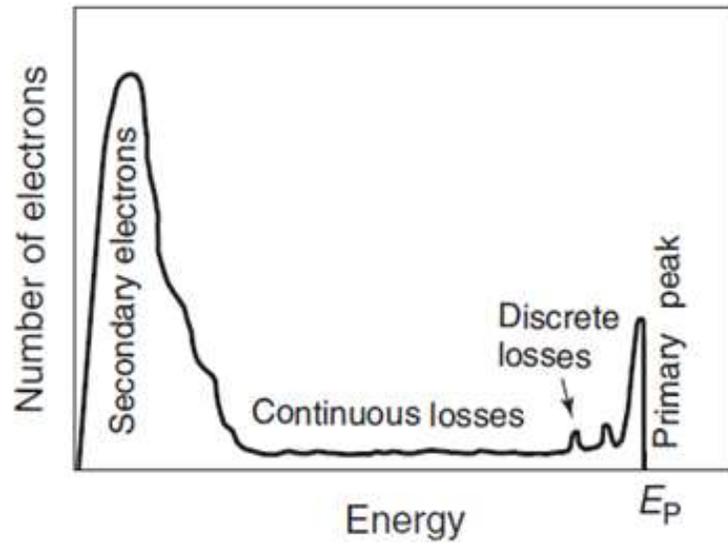
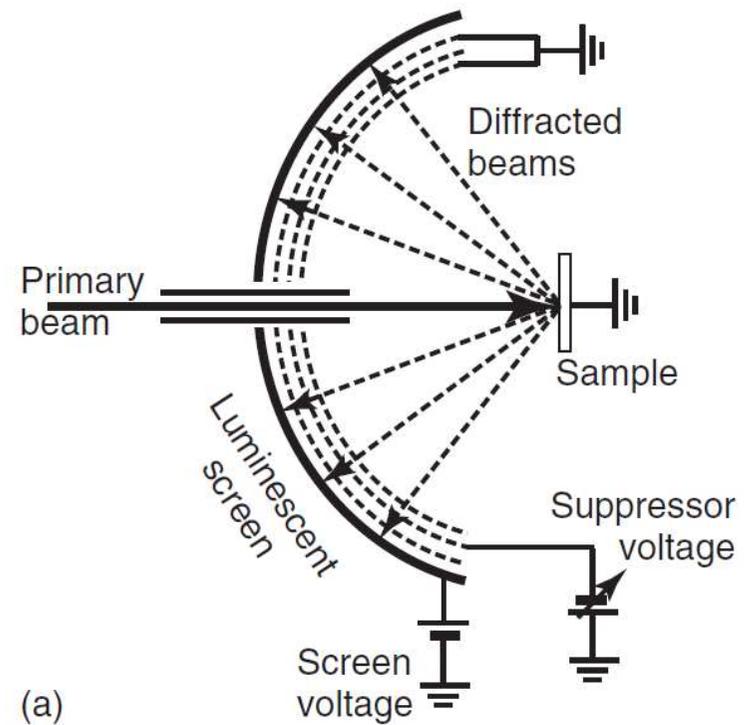


Figure 2.12 Schematic drawing of a LEED chamber.

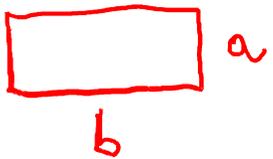
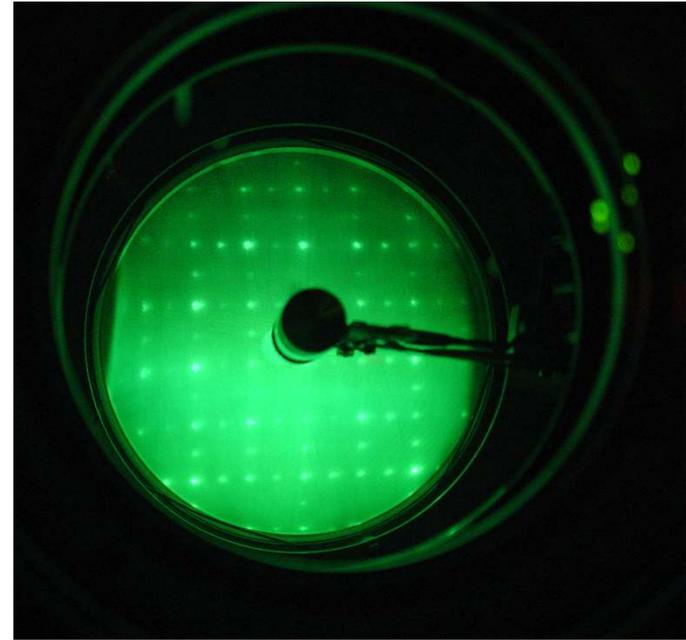
Surface Science: Foundations of Catalysis and Nanoscience, Fourth Edition.  
 Kurt W. Kolasinski.  
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(a)

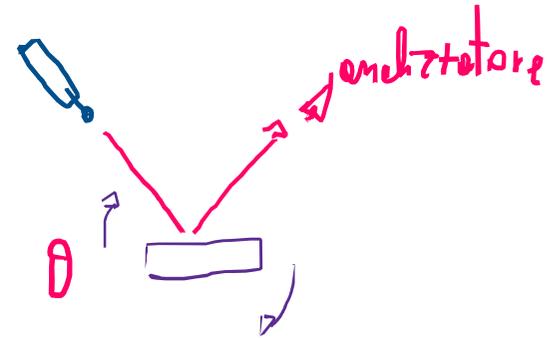
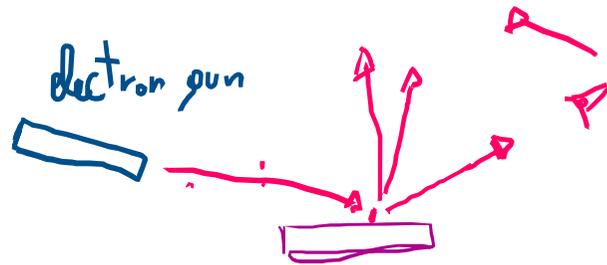
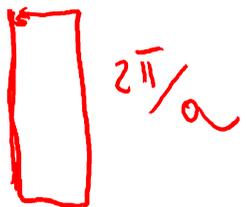


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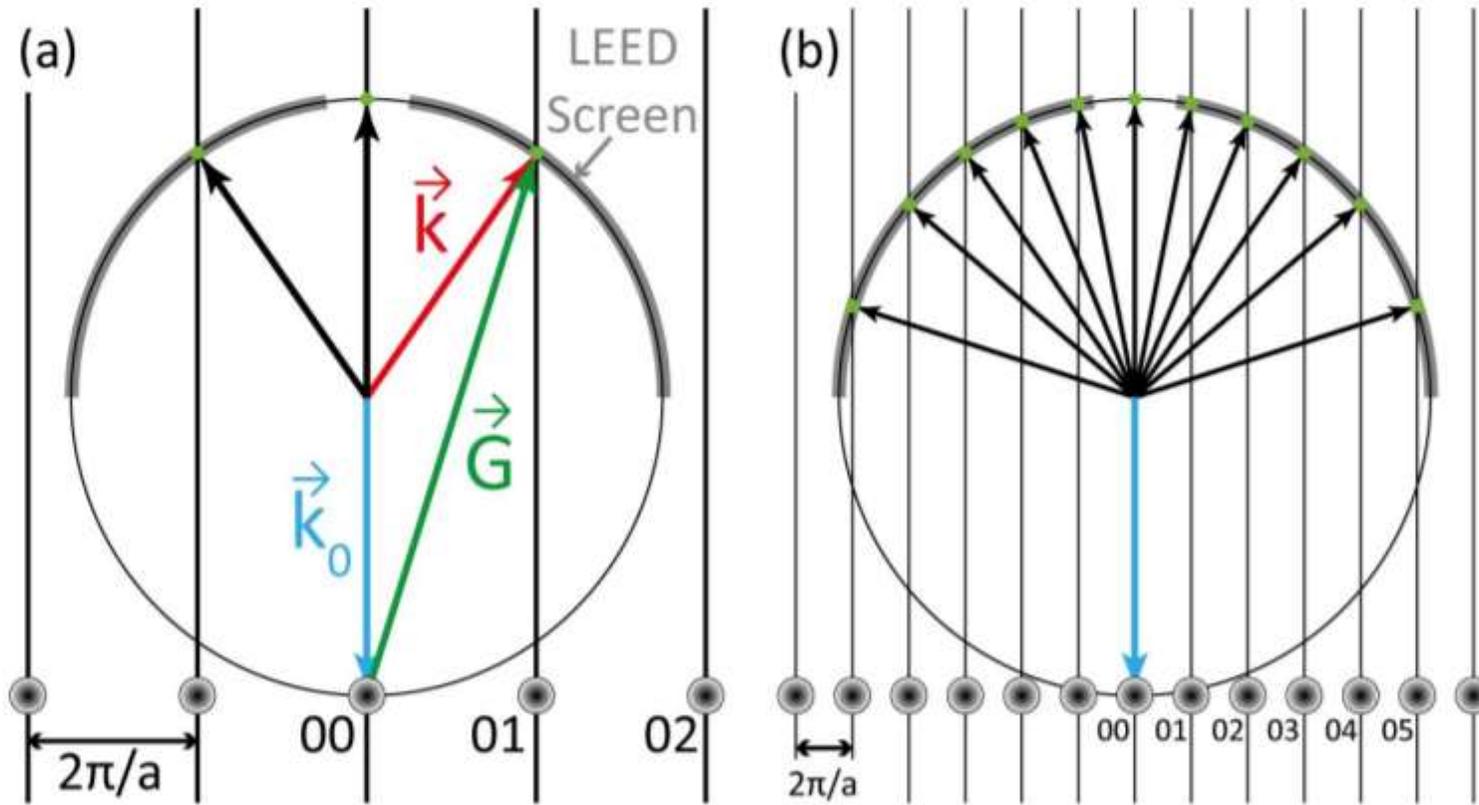


↓ reciproco

$2\pi/b$



# SFERA di EWALD



$E_1$

$E_2$

La superficie (110) dell'oro spontaneamente ricostruisce 1x2

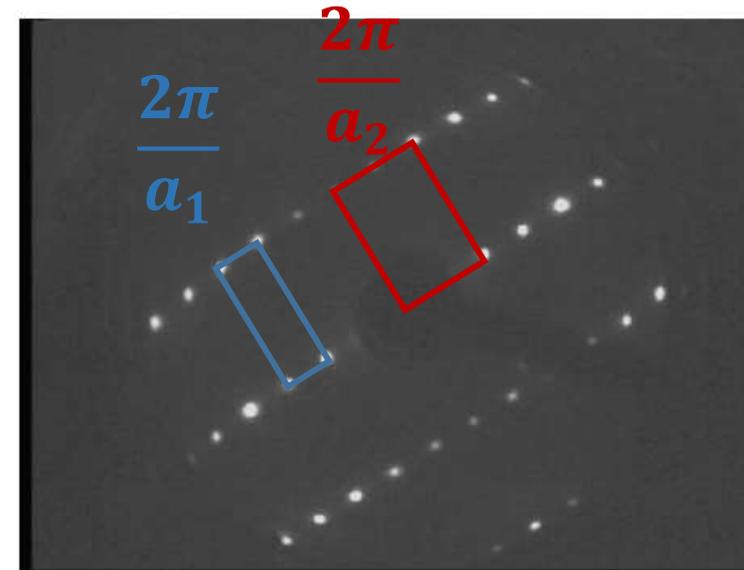
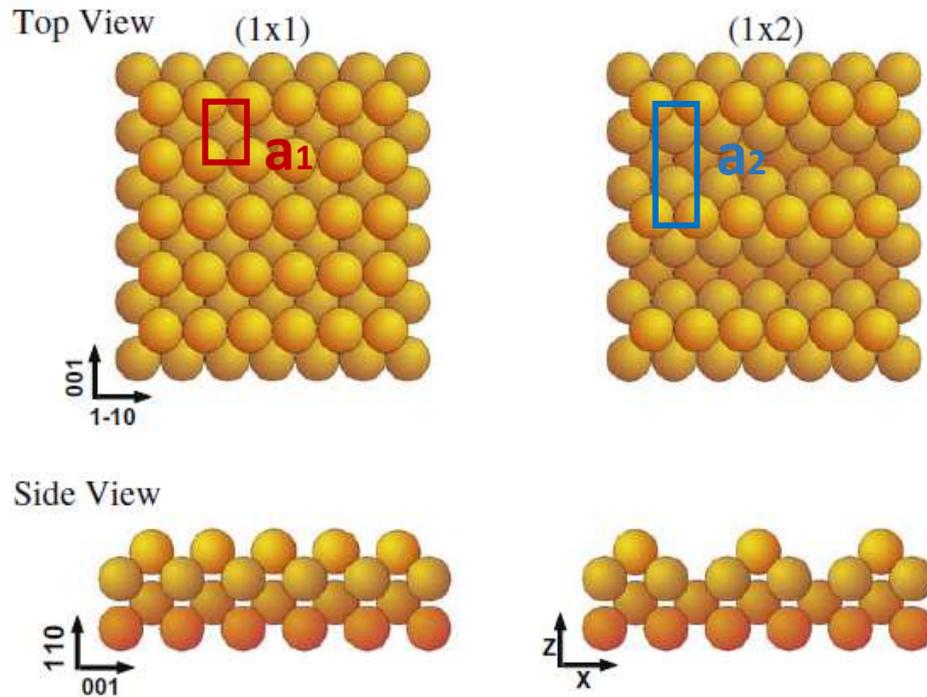
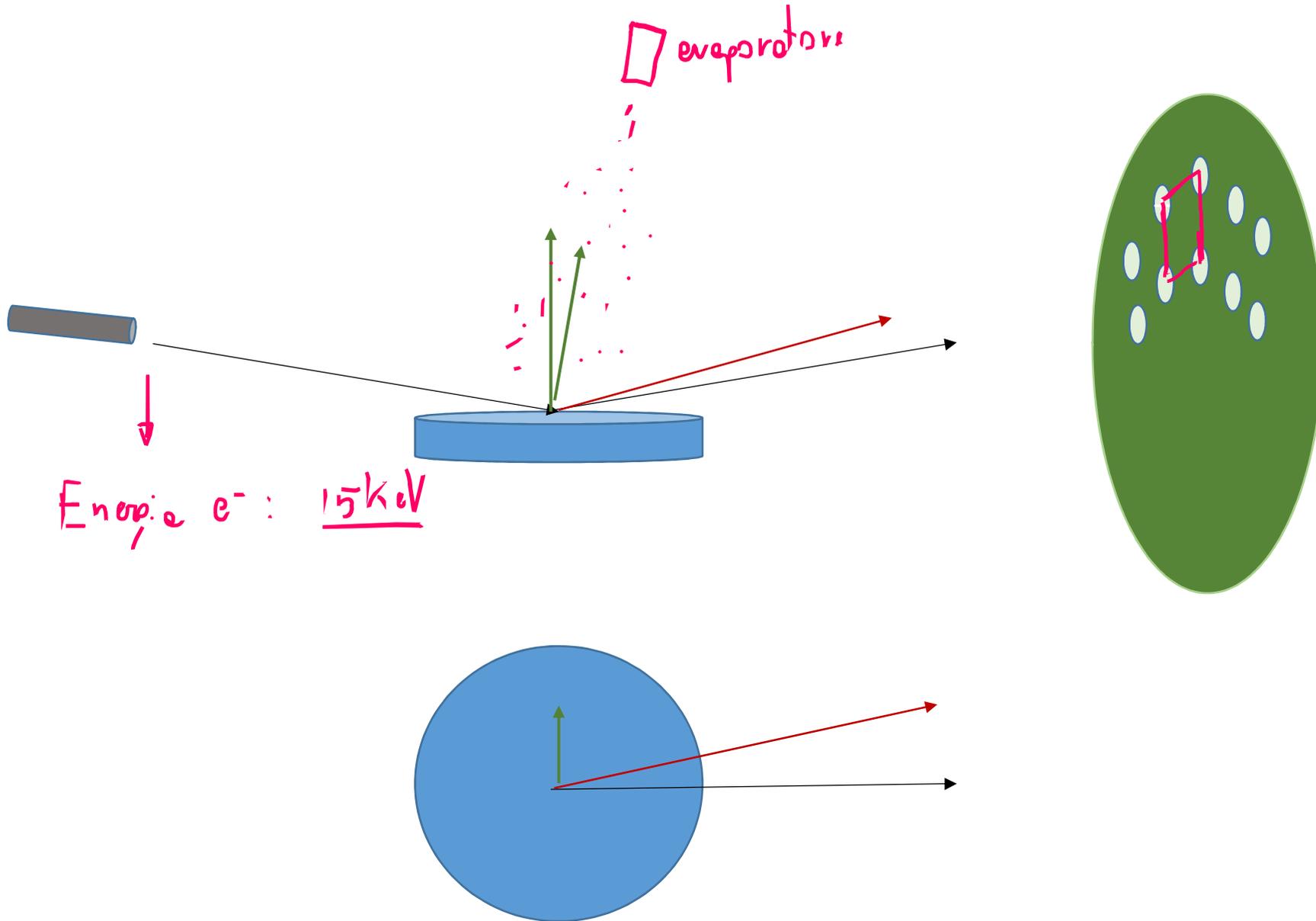
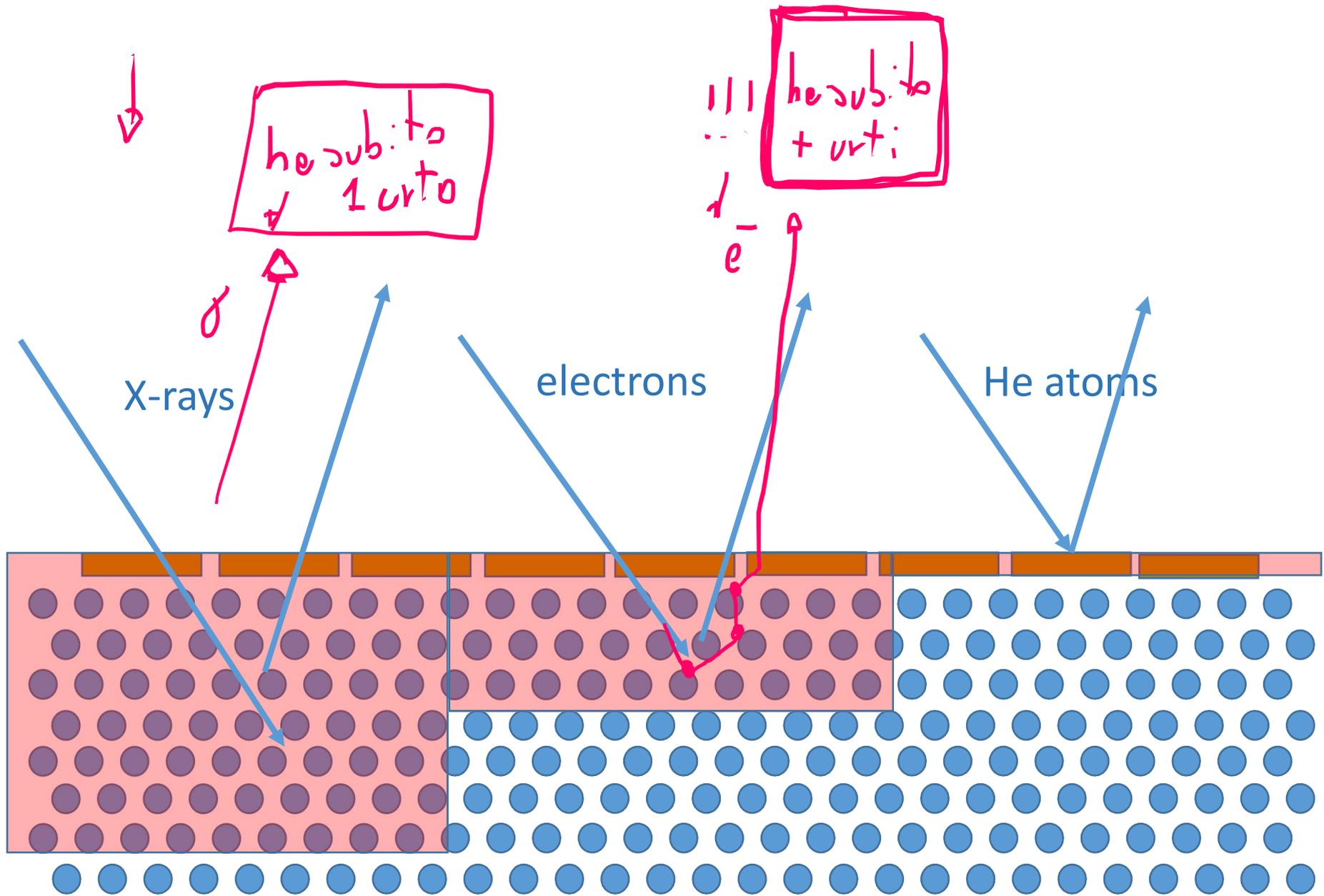


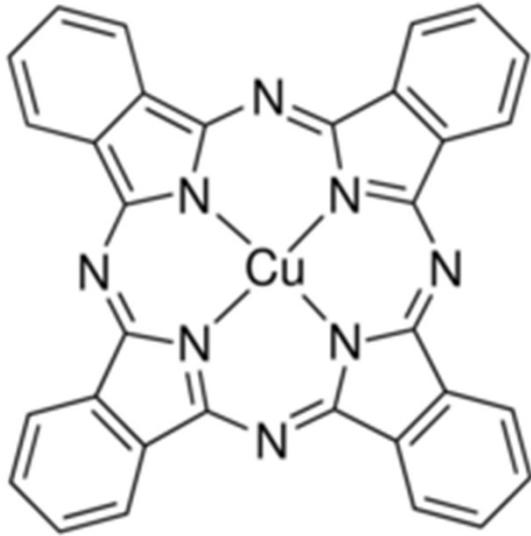
Fig. 2. LEED pattern at 130 eV

# RHEED – Reflection High-Energy Electron Diffraction

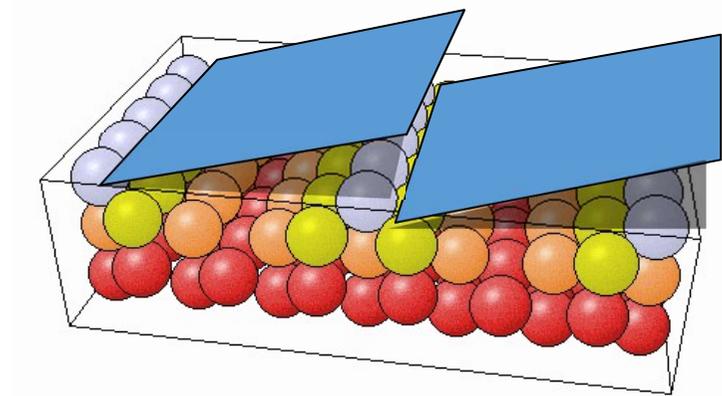
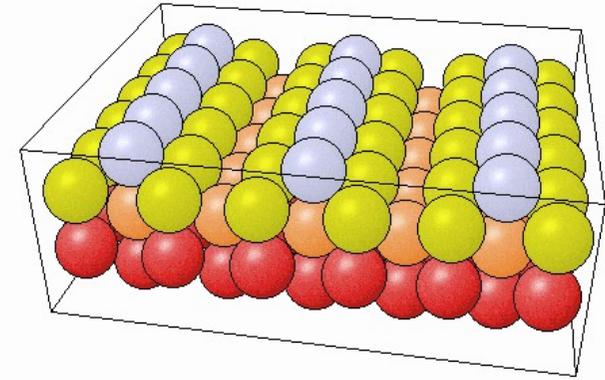




## The CuPc/Au(110) system

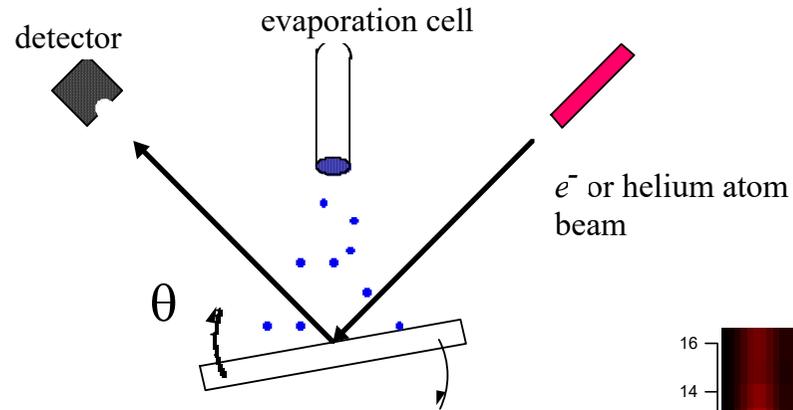


Planar shape  
High thermal stability  
High chemical stability



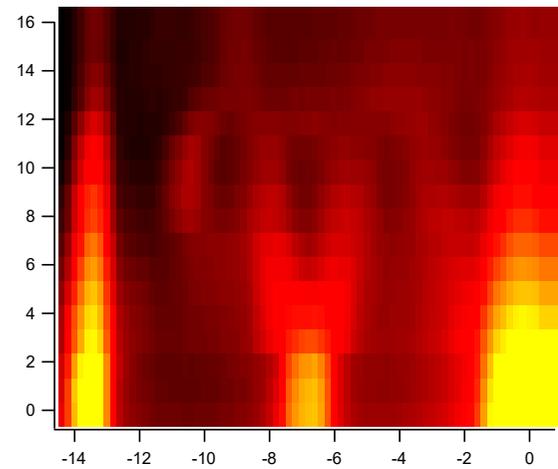
## The CuPc/Au(110) system

## Cu-Pc/Au(110) growth



Electron diffraction

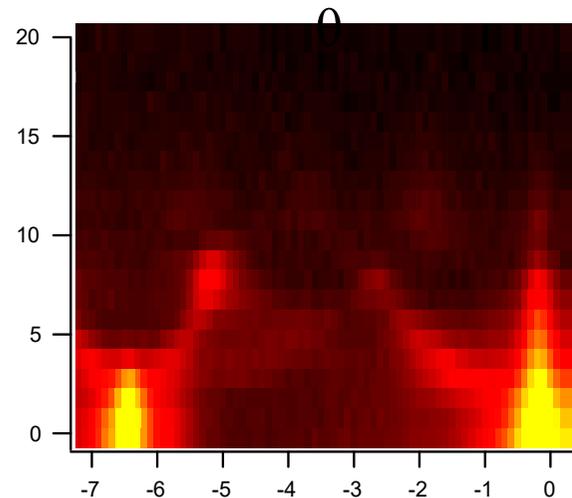
He atom diffraction



× 3 phase

× 5 phase

× 2 substrate phase



× 7 phase

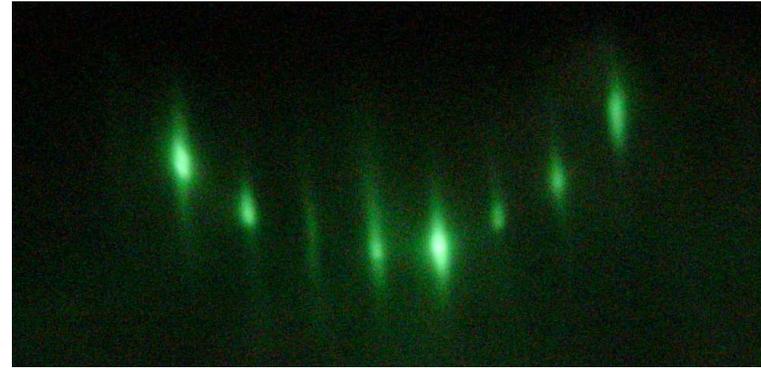
× 5 phase

× 2 substrate phase

## The CuPc/Au(110) system

## RHEED growth evolution

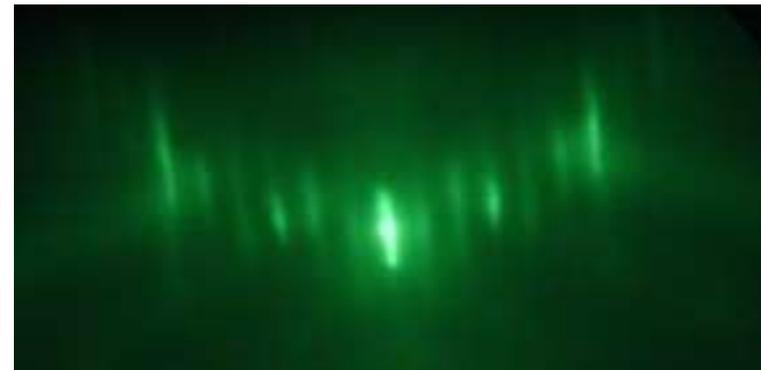
**Au(110) 1x2 missing row**



**Cu-Pc / Au x5 phase**

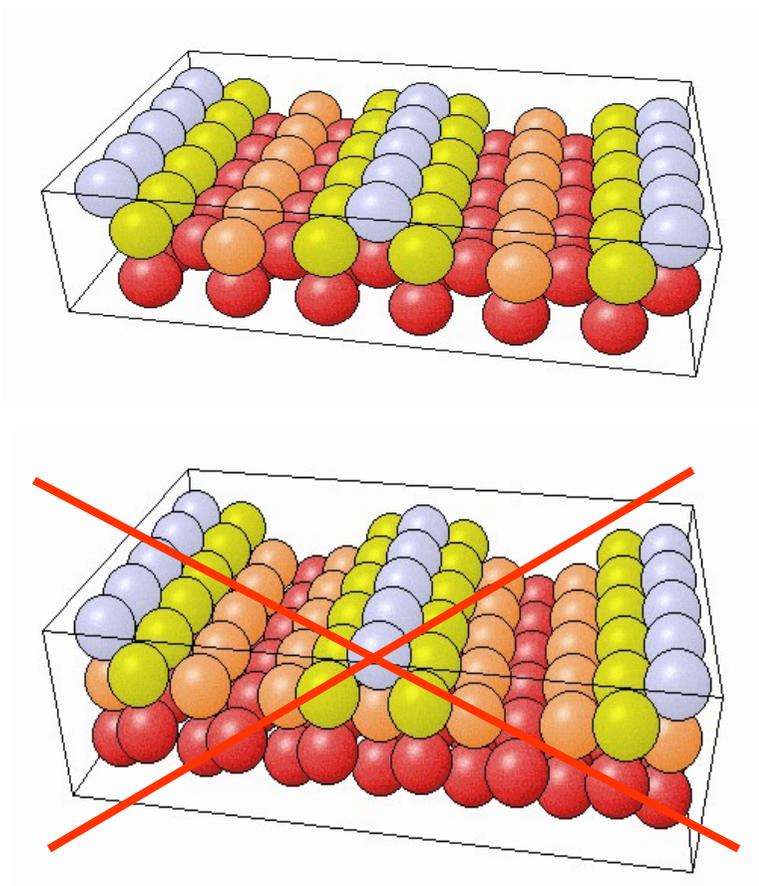


**Cu-Pc / Au x3 phase**

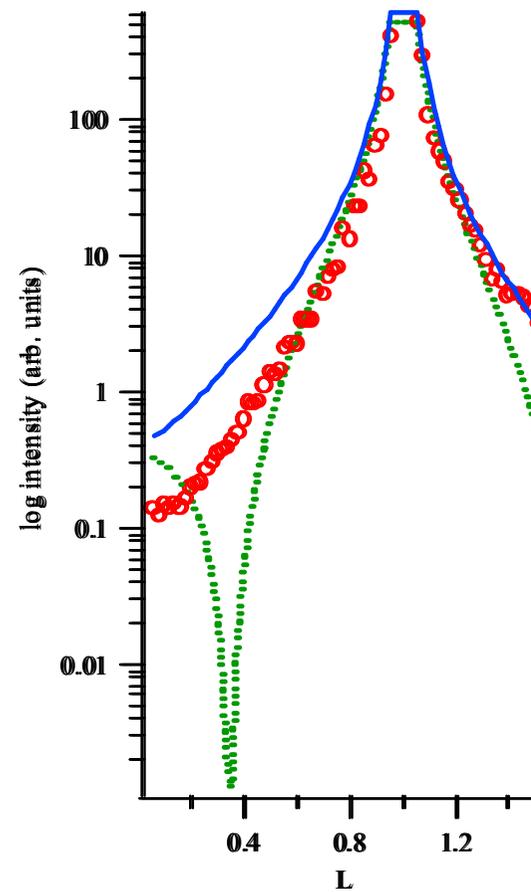


# The CuPc/Au(110) system

# Au(110) cell structure: out of plane X-ray diffraction

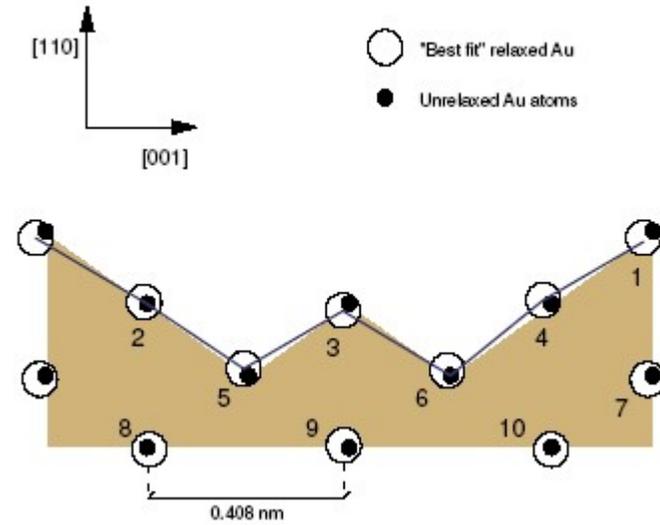
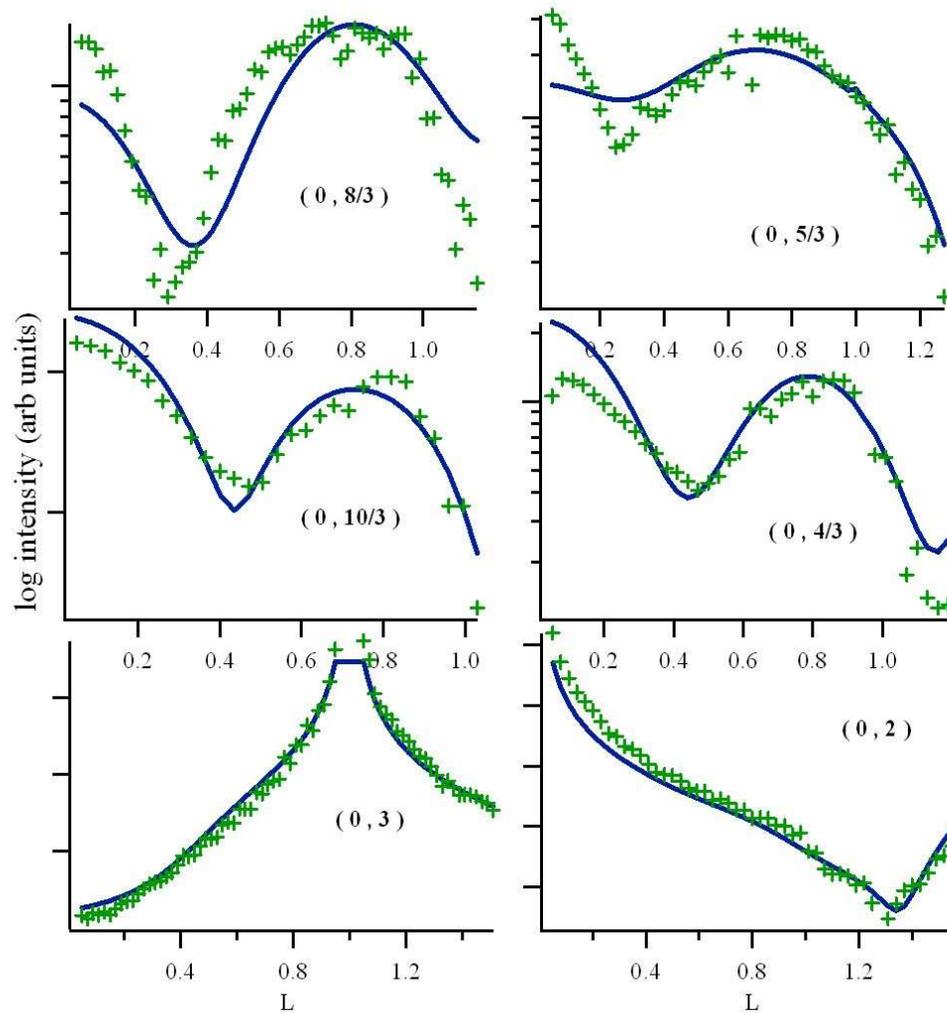


(0, 3) rodscan



# The CuPc/Au(110) system

# X-ray diffraction: $\times 3$ phase rodscans



Shallow  $\times 3$  reconstruction

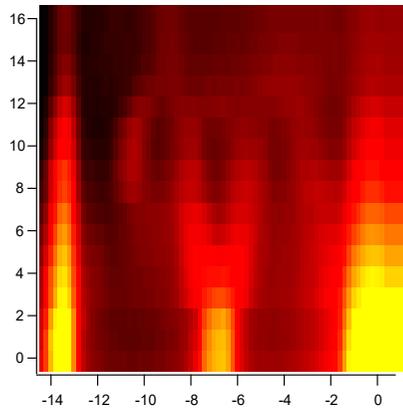
The cell is asymmetric



Asymmetric molecule orientation

# The CuPc/Au(110) system

# The $\times 5$ phase

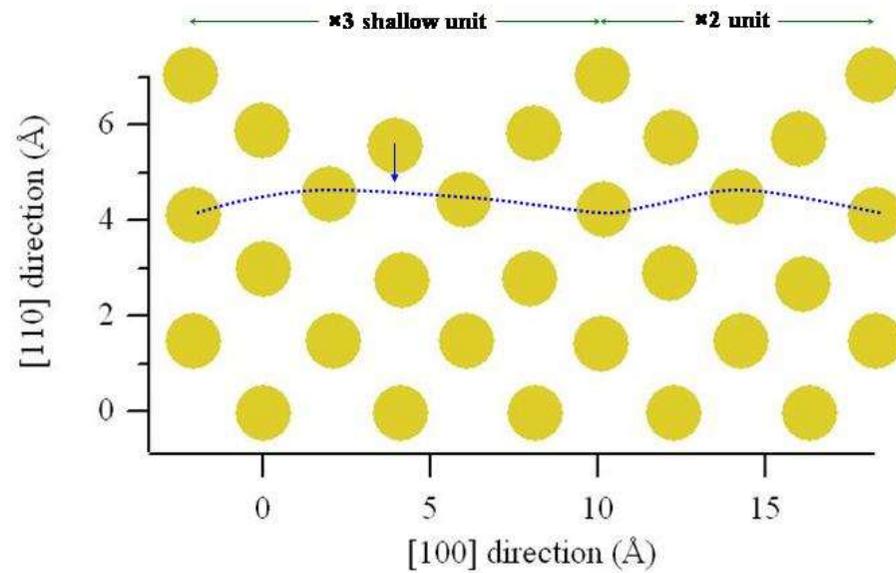
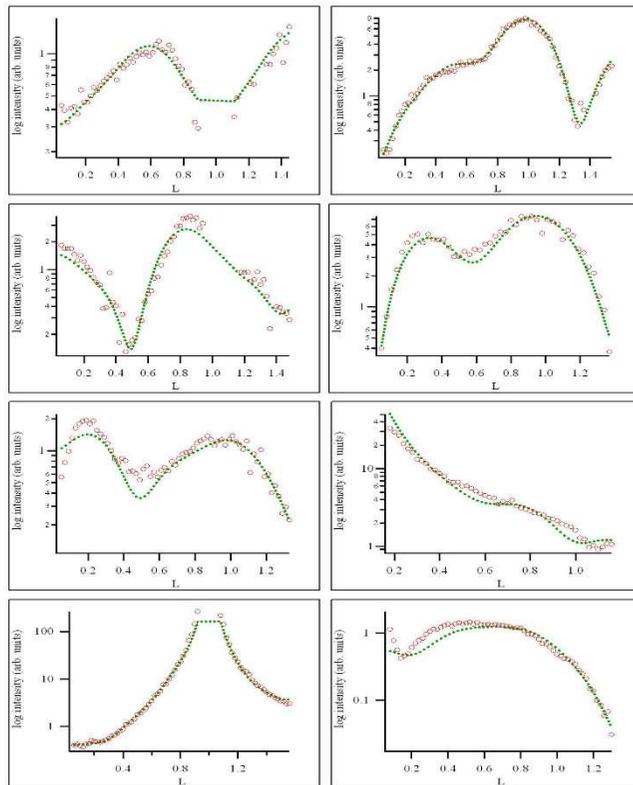


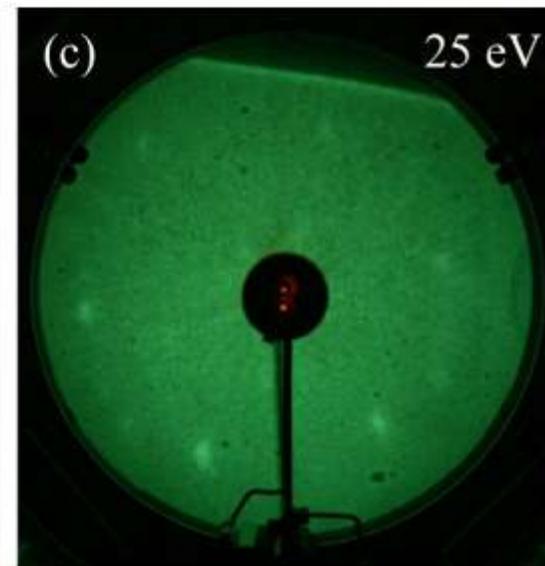
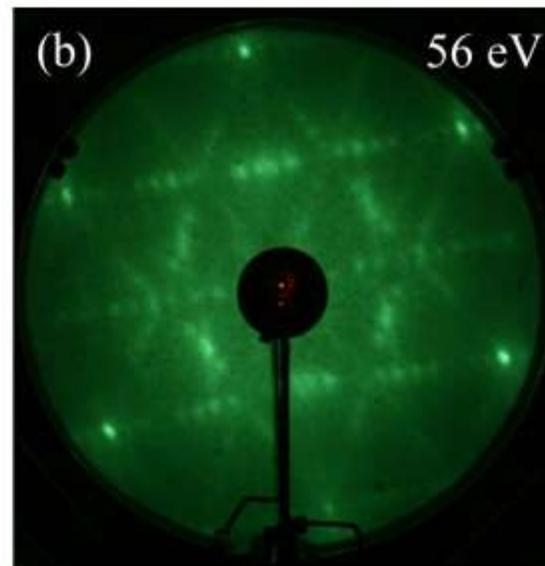
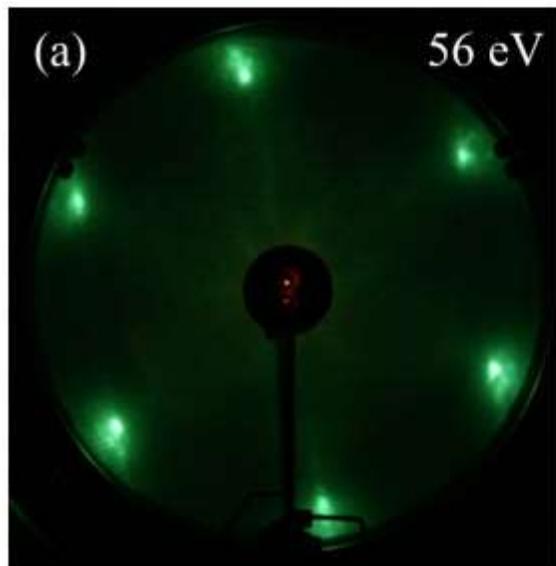
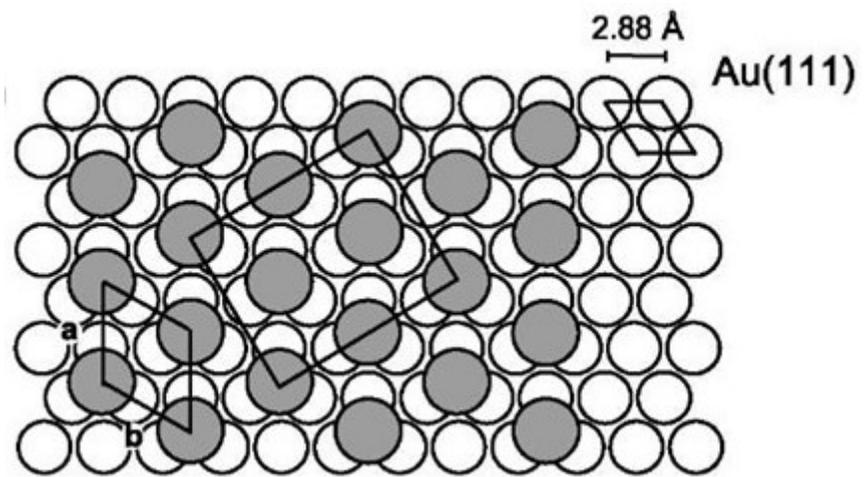
$\times 3$  phase

$\times 5$  phase

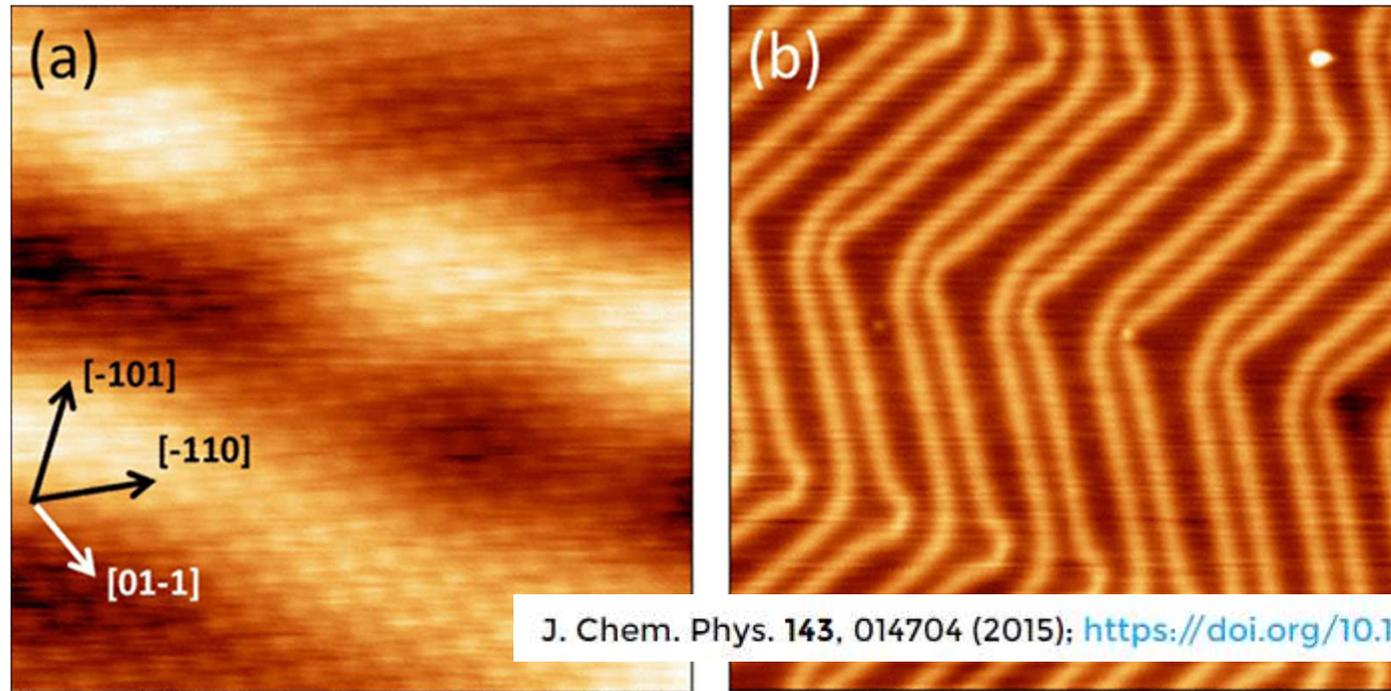
$\times 2$  substrate phase

- Shallow reconstructed  $\times 5$  cell
- Junction of  $\times 3$  and  $\times 2$  cells
- Buckling of the third layer



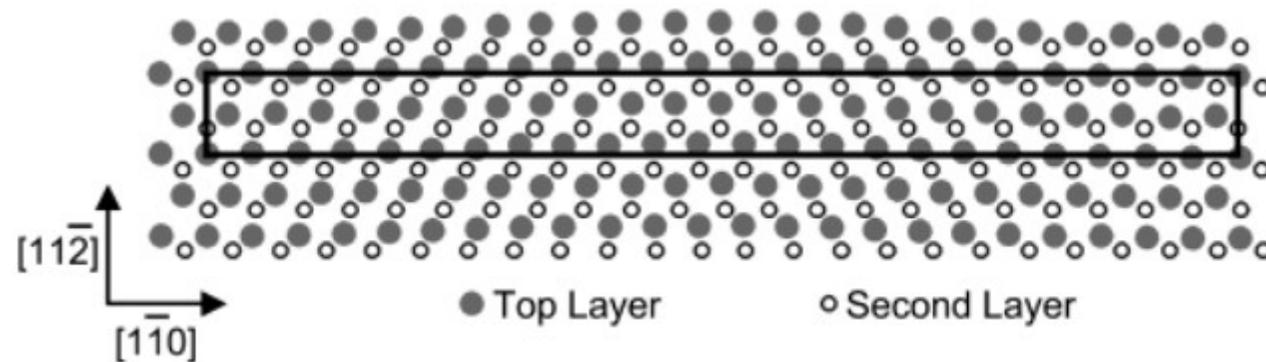


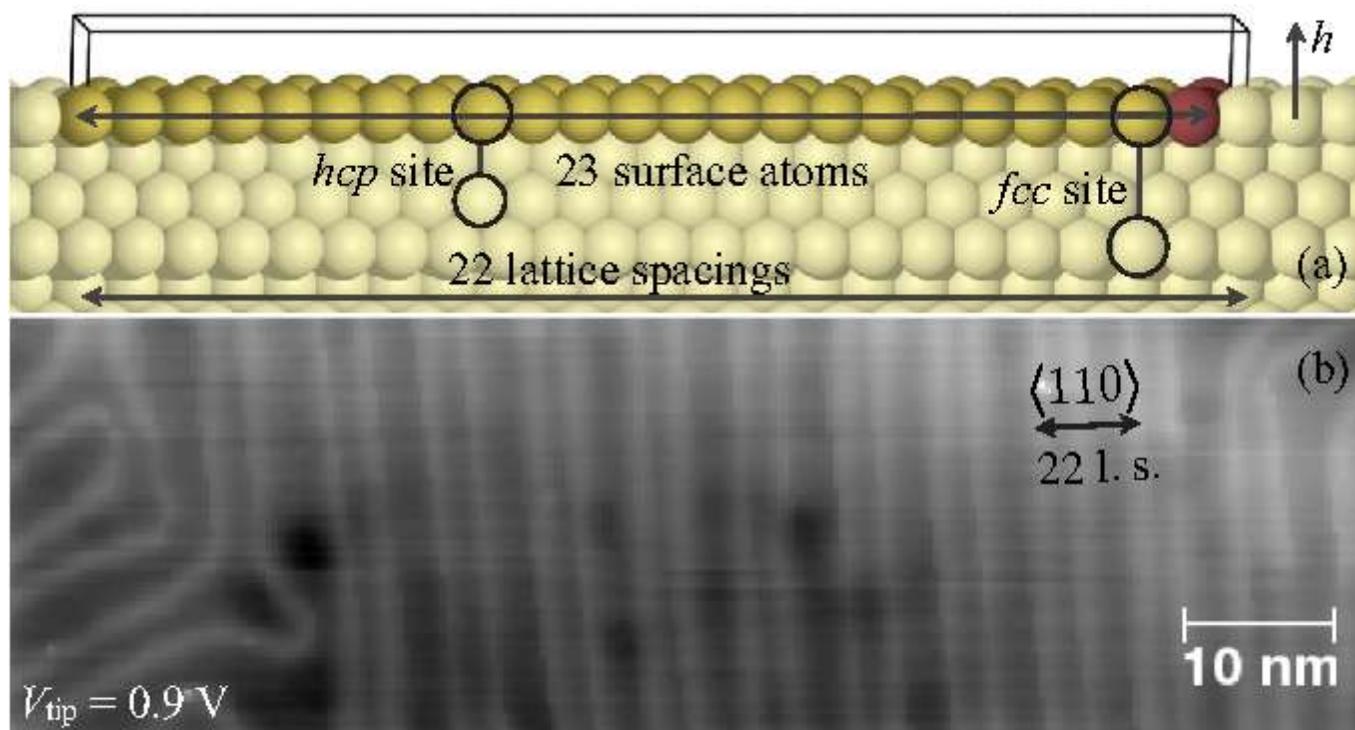
# La ricostruzione herringbone di Au(111)



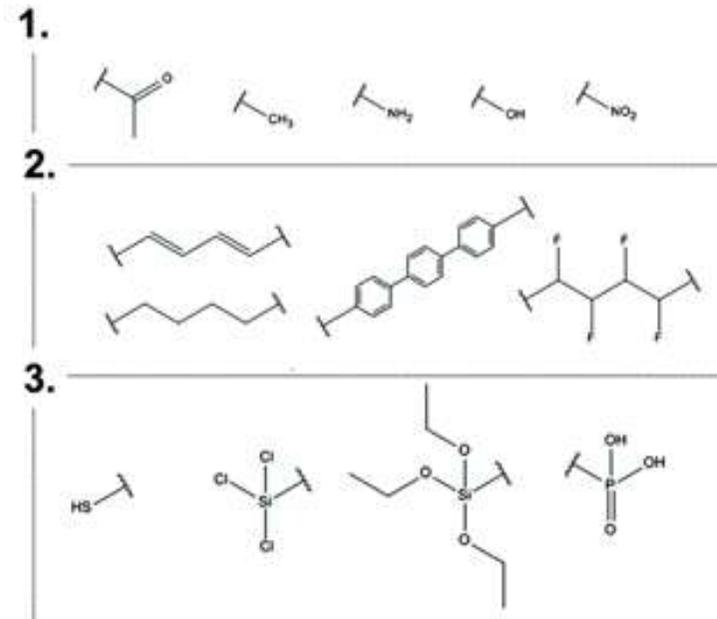
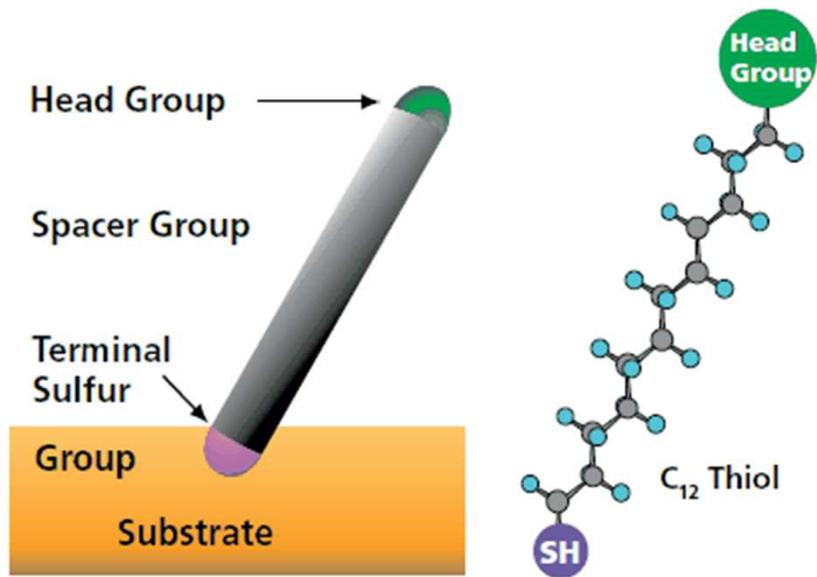
5 × 5 nm

50 × 50 nm

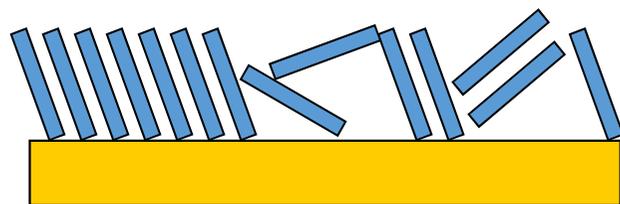




# Self Assembled Monolayers (SAMs)

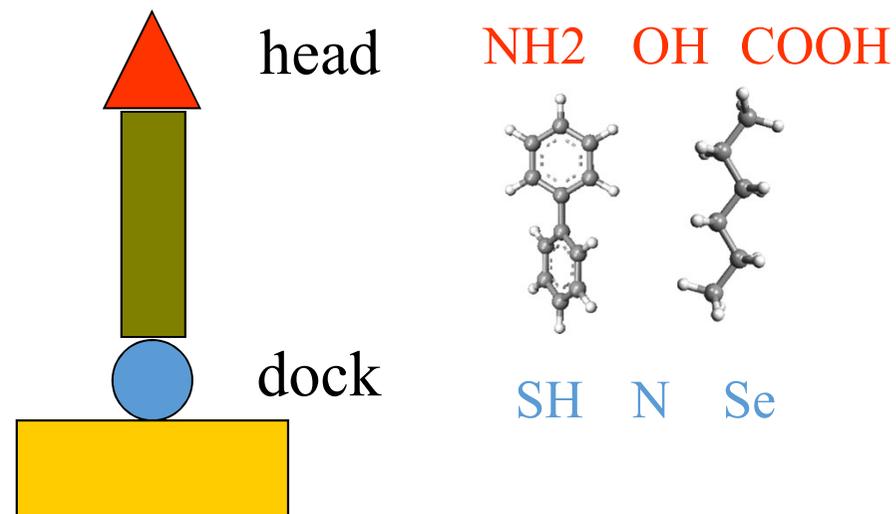
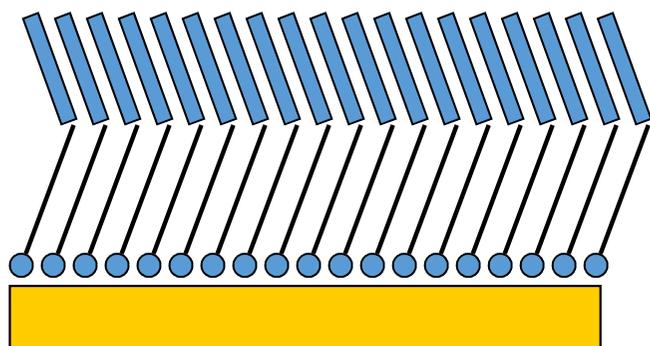


# Metal-organic interfaces



I difetti morfologici di un film organico  
Limitano le proprietà di trasporto e la  
riproducibilità delle caratteristiche del sistema

## Interposizione di un SAM

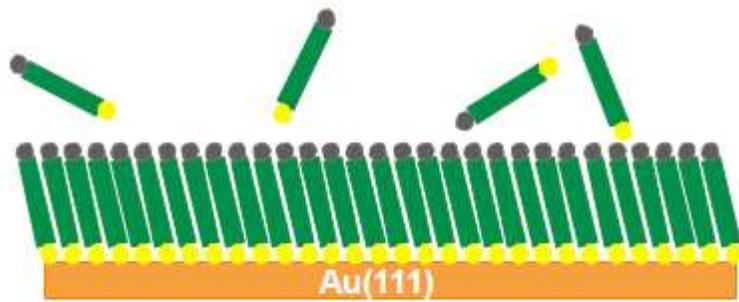
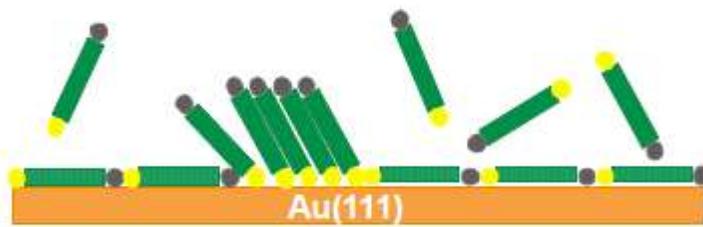
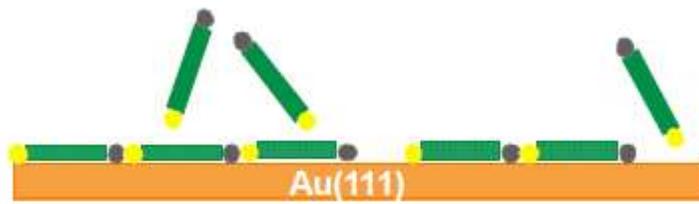


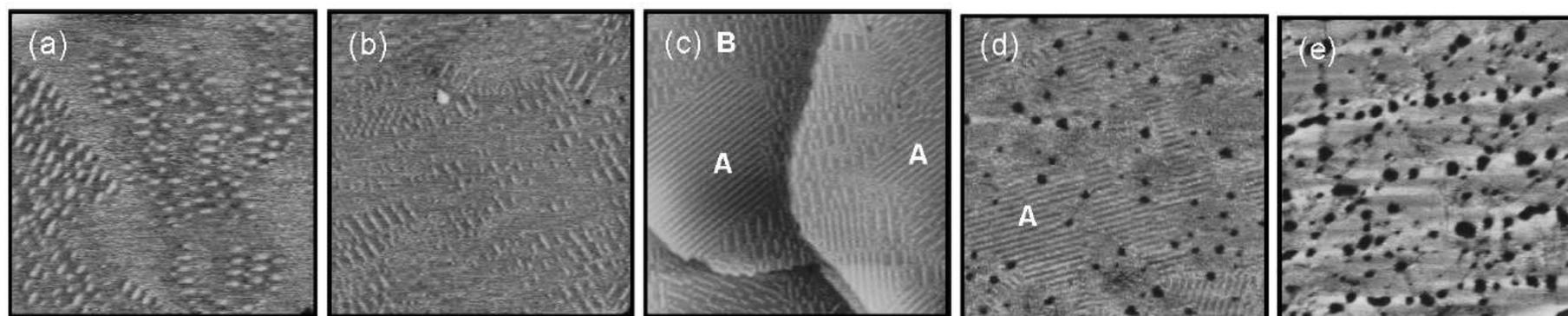
Interfaccia omogenea  
Miglioramento delle proprietà di trasporto

Controllo della funzione lavoro  
Allineamento dei livelli elettronici

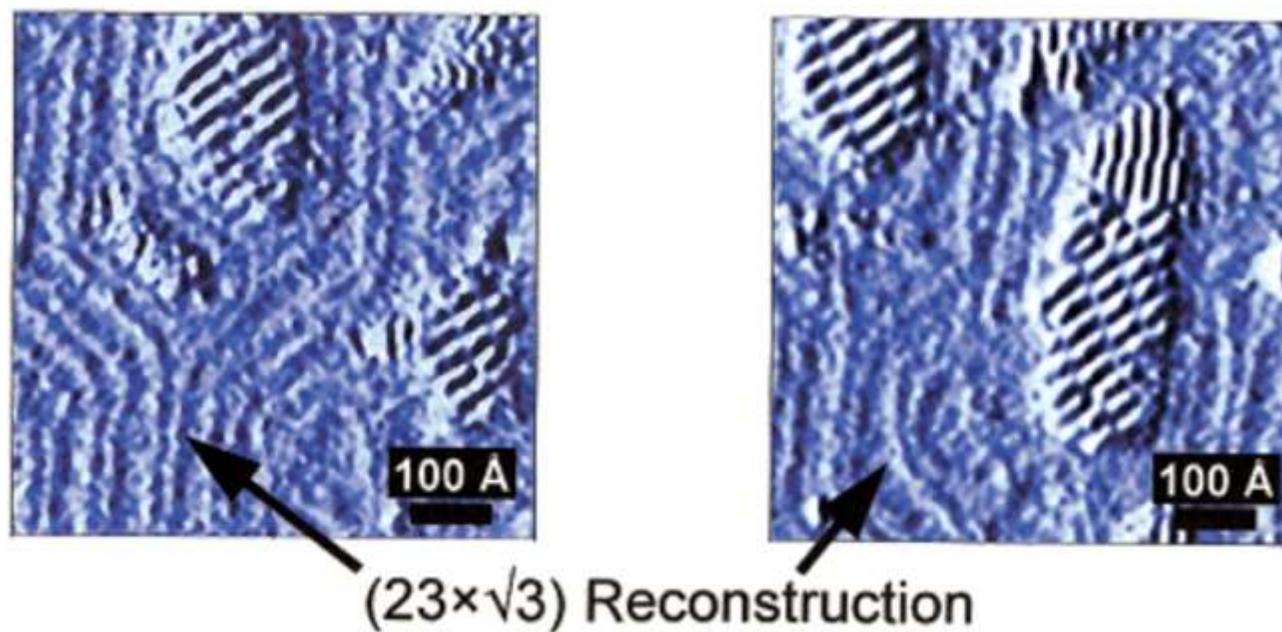
*I. Kymissis et al. IEEE 2001*

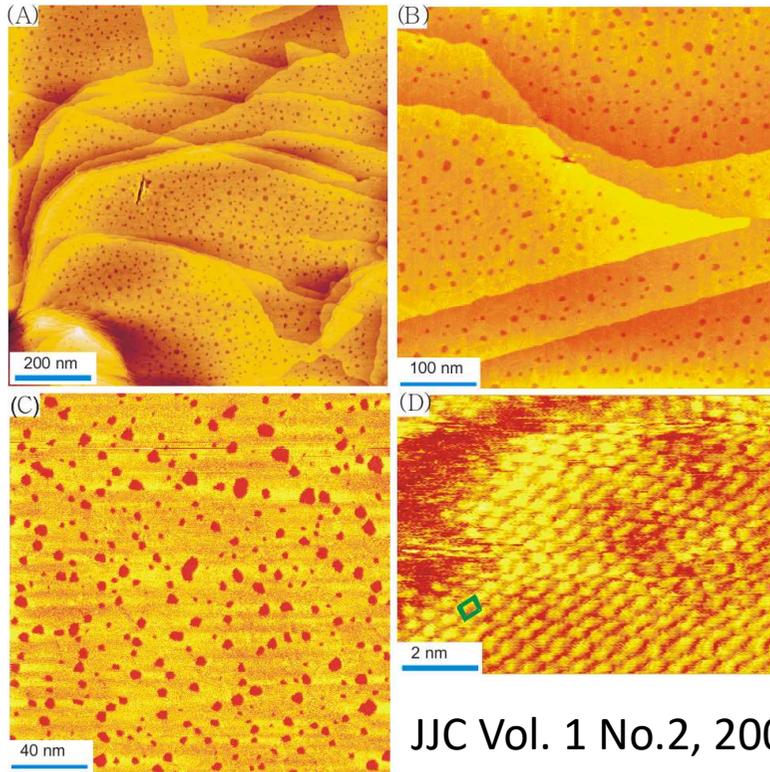
*Heimel et al. NanoLetters 2007*





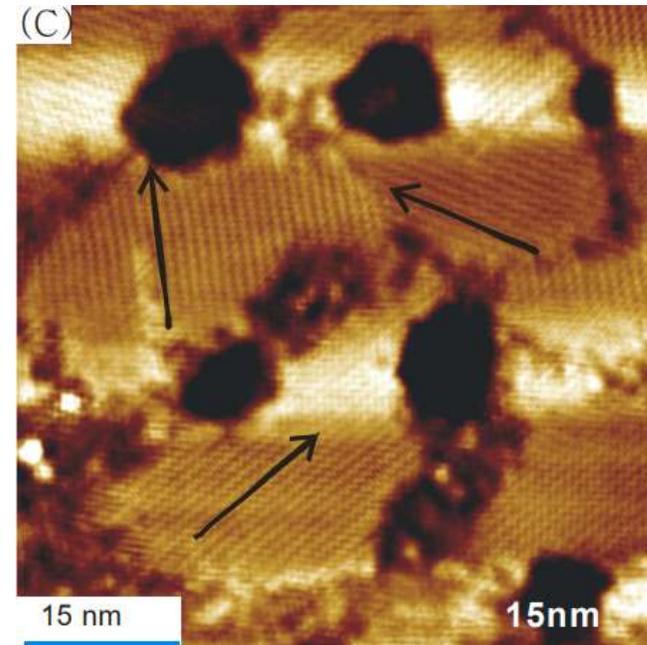
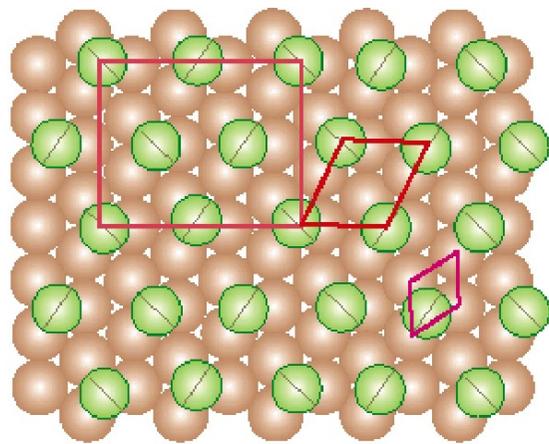
**Figure 1.** STM images showing the growth process of HDT SAMs on Au(111) after immersion of Au(111) surfaces in a 1  $\mu$ M solution as a function of immersion time: (a) 1 min, (b) 5 min, (c) 10 min, (d) 30 min, and (e) 24 h. The scan size of all STM images is 120 nm  $\times$  120 nm.

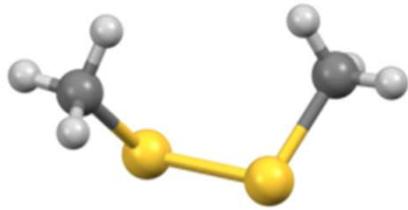




SAM di C10 ottenuto con immersione in soluzione di etanolo per 24 ore

JJC Vol. 1 No.2, 2006, pp. 143-154





- dimethyl disulfide
- dissociazione su Au(111)
- ricostruzione  $\sqrt{3} \times \sqrt{3}$  (monolayer)

