

## Surface sensibility, RHEED vs SXR

We aim comparing the depth sensibility of RHEED and SXR. To this purpose consider an electron (photons) beam with an incident angle  $\alpha = 1^\circ$  respect to the surface plane. The mean free path for 40 keV electrons is about  $\lambda_e = 10$  nm while the mean free path for 40 keV X-rays is about  $\lambda_x = 10$   $\mu\text{m}$ . Treating electrons and photons as classical particles, which is the penetration depth for electrons and photons?

Is SXR truly surface sensible?

## **Solution: surface sensibility, RHEED vs SXRD**

The penetration depth  $D$  is given by  $D = \lambda \sin(\alpha)$  with  $\alpha = 1^\circ$ . Taking  $\lambda_e = 10 \text{ nm}$  and  $\lambda_x = 10 \text{ }\mu\text{m}$  one obtains  $D = 0.18 \text{ nm}$  for electrons and  $D = 180 \text{ nm}$  for X-rays.

Obviously SXRD would not be a tool for surface analysis. However it is (see next exercise)

## Total reflection for grazing incident X-rays

We aim calculating the refraction index of a x-ray beam impinging at grazing incidence on a metallic surface. From the electrodynamics we get  $n^2 = \epsilon\mu$  where  $\epsilon$  and  $\mu$  are the medium dielectric constant and the magnetic permeability, respectively. We assume for simplicity a non magnetic material ( $\mu = 1$ ). The dielectric constant is defined by the relation  $\epsilon_0\epsilon E = \epsilon_0 E + P$  where  $P$  is the medium polarization given by  $P = N e s_0 \exp(i\omega t)$  with  $N$  the electron density  $e$  the electron charge and  $s_0$  the electron displacement generated by the x-rays beam. We assume that the x-ray photon can be described by a plane wave ( $E = E_0 \exp(i\omega t)$ ) and the electron-atom interaction by the harmonic oscillator equation ( $m \frac{d^2s}{dt^2} + fs = eE$ ) where  $f = m \omega_r^2$  and  $\omega_r$  is the electron resonance frequency.

- 1) Assuming  $s = s_0 \exp(i\omega t)$  find an expression for the amplitude of the electron motion
- 2) Find an expression for  $n$ .
- 3) Usually, diffraction experiments use hard X-rays having energy of the order of 10 keV. Demonstrate that the refraction index is approximately given by  $n = 1 - \delta$ .
- 4) The Snell law describing the wave refraction at the interface states  $\cos(\alpha_i)/\cos(\alpha_r) = n_r/n_i$  where  $n_i = 1$  (assuming the incident wave propagating in vacuum and the angles  $\alpha$  measured respect to the surface plane) and the refractive index of the medium is the one previously calculated. Demonstrate the existence of a critical incidence angle such that  $\alpha_r = 0$  (implying that the incident wave is totally reflected at the vacuum-medium interface -> surface sensibility)

## **Solution: total reflection for grazing incident X-rays**

1)  $s_0 = (e/m)E_0 / (\omega_r^2 - \omega^2)$

2)  $n^2 = 1 + N e^2 / [\epsilon_0 m (\omega_r^2 - \omega^2)]$

3) The electron bonding energy  $\hbar \omega_r$  is usually of the order of  $10\text{-}10^3$  eV. Thus,  $\omega_r^2 \ll \omega^2$  for hard X-rays having energy of the order of 10 keV. With this assumption the refraction index is given by  $n^2 = 1 - N e^2 / (\epsilon_0 m \omega^2)$  and thus  $n = 1 - \delta$  with  $\delta = N e^2 / (2 \epsilon_0 m \omega^2)$ . Note that  $\omega = 10^{19}$  and  $\omega_p = \text{sqrt}(N e^2 / (2 \epsilon_0 m)) = 10^{16}$ , implying  $\delta = 10^{-6}$

4) For  $\alpha_r = 0$  the Snell law gives  $\cos(\alpha_i) = n$ . Approximating  $\cos(x) = 1 - x^2 / 2$  one obtains  $\alpha_{ic} = \text{sqrt}(2 \delta) = 1.4 \cdot 10^{-3} = 0.1$  deg

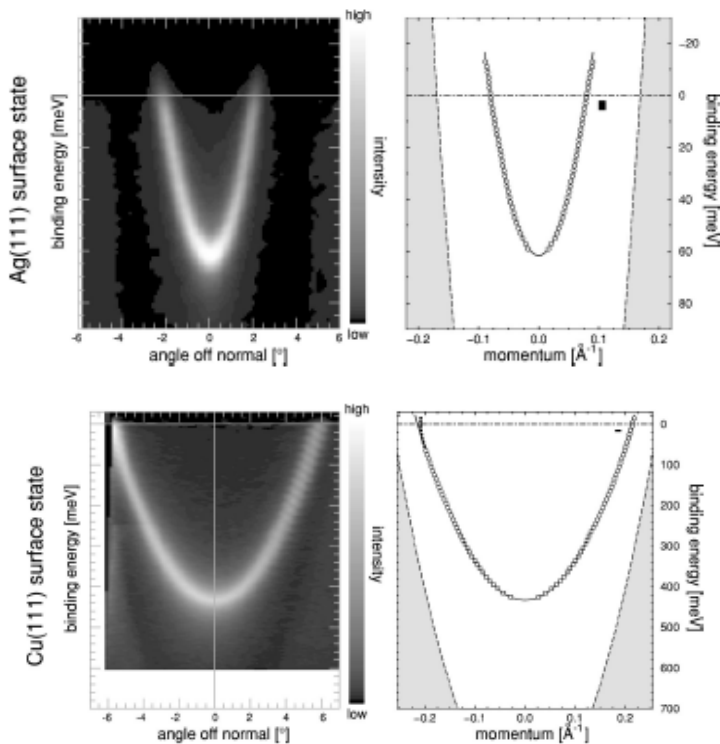
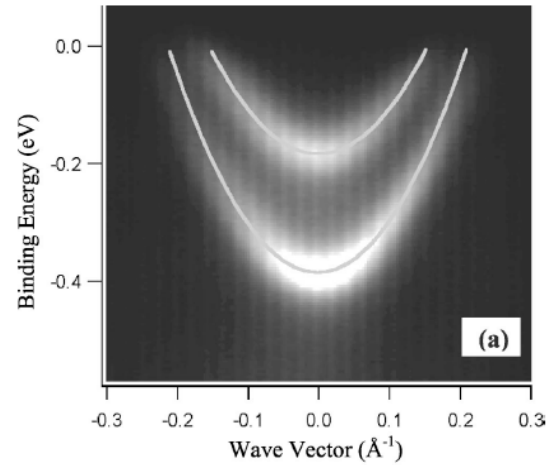
G. Renaud, Surf. Sci. Reports **32**, 5 (1998)

# Ag films on Cu(111): an ARUPS study

A. Bendounan *et al.*, Phys.Rev. B **67**, 165412 (2003)

The growth of Ag on Cu(111) has been studied by ARUPS. For a sub-monolayer coverage of 0.6 ML the photo-emission map observed at room temperature close to normal emission ( $\Gamma$  point) is shown on the right side.

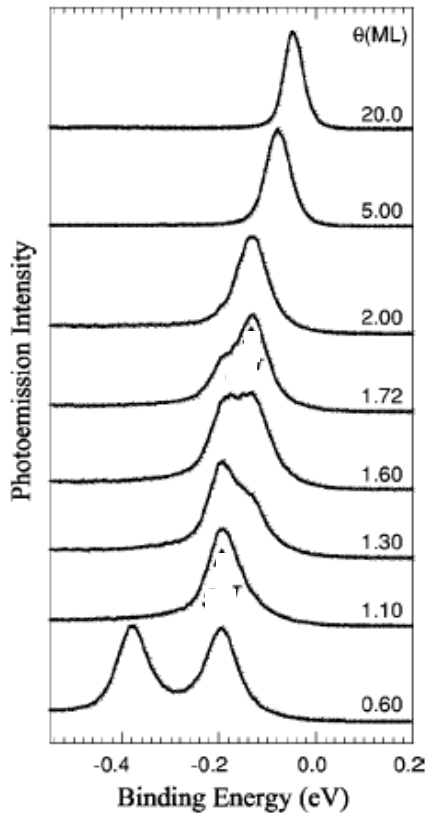
a) Comparing this result with the results of the same experiment on clean Ag(111) and Cu(111) surfaces (shown on the bottom page) which conclusion can you draw?.



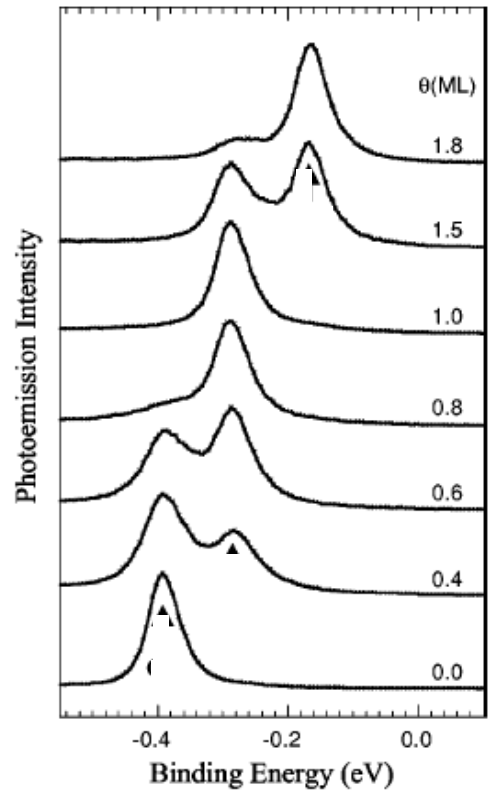
Dispersion of the Ag(111) and Cu(111) surface state. Left panel: gray-scale plot directly from the spectrometer; right panel: dispersion of maxima as a function of the momentum and least-squares fit result (solid line)

F. Reinert *et al.*, Phys. Rev. B **63**, 115415 (2001)

b) The normal emission spectra as a function of the film thickness were also acquired for two films grown at room temperature and at 150 K. What happens for the room temperature grown film as a function of the film thickness? Can you see any difference in the evolution of the two films?



Normal emission spectra for several films prepared at  $T=300$  K.

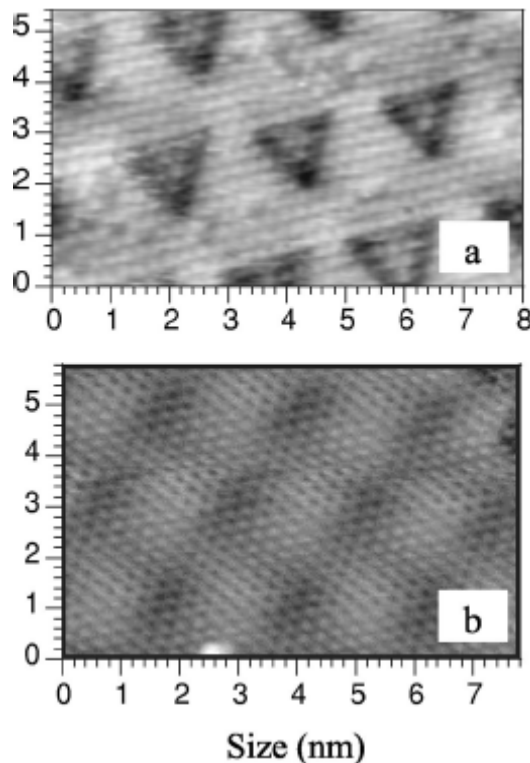


Normal emission spectra for several films prepared at  $T=150$  K.

## Solution: Ag films on Cu(111): an ARUPS study

- a) The spectrum clearly show two different surface states meaning that two kinds of spectra were obtained on Cu terraces and Ag islands. The two spectral features separated by about 200 meV suggest that two surface states coexist in this system, one confined in Cu terraces and the other one in Ag islands
- b) The spectra acquired on the film grown at room temperature show an evolution from the surface state at -190 meV observed for 1ML thick film to a second feature at -130 meV observed for the 2ML thick film which gently evolve toward the surface state characteristic of the Ag bulk surface. The spectra acquired on the film grown at  $T = 150\text{K}$  also show the formation of two different features for 1 ML and 2 ML thick film. These two features appear at different energies in comparison to the room temperature grown film suggesting a different morphological structure of the two films. This is in agreement with the STM images shown below

STM images of 1-ML-thick Ag film grown at room temperature (a) and at  $T = 150\text{ K}$  (b)



## Auger intensity

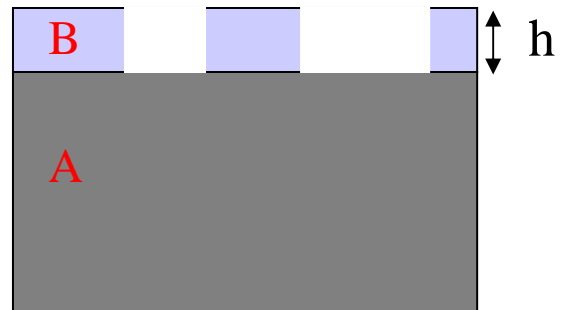
Consider an electron beam of intensity  $I(0)$  impinging with an angle  $\theta$  on the surface of a thick sample.

- Assuming an absorption factor  $r$  for each atomic plane which is the intensity  $J(z)$  of the electron beam at the depth  $z$ ?
- Which is the intensity of the resorting beam measured by a detector? (note that the adsorption factor for the Auger electrons is in general different from that of the impinging electrons. Why?)

c) You want to monitor by Auger spectroscopy the growth of a thin film (element B) on the sample surface (element A). Which is the evolution of the intensity of the Auger peaks for element B and A as a function of the film thickness  $h$  assuming a layer-by-layer growth and  $h < 4-5$  ML (very thin film)?



d) Which is the evolution of the intensity of the Auger peaks for element B and A as a function of the film thickness  $h$  if the film grows in a discontinuous way (keep the assumption of very thin film)?



$\theta$  fraction of the surface covered by the film



## Solution: AUGER intensity

- a) The intensity arriving on the first atomic plane is  $I$ , the one on the second atomic plane is  $J(2)=I(0)/r$ , on the third is  $J(3) = I(0)/r^2, \dots$ . In general  $J(z) = I(0) r^{-z/d}$  if  $d$  is the atomic layer thickness.
- b) Similarly to point a) the intensity of the Auger electrons emitted at a depth  $z$  and measured by the detector at the surface will be  $I(z) = I(0) r^{-z/d} s^{-z/d}$  where  $s$  is the attenuation factor for the out-coming electrons. The previous formula can also be written in the usual form  $I(z) = I(0) \exp(-z/d \ln(rs)) = I(0) \exp(-z/\lambda)$  with  $\lambda = d/\ln(rs)$  the electron mean free path. The total intensity measured by the detector is the summation over the contribution of all the atomic planes which means  $I = \int_0^z I(z) dz = I(0) \lambda (1-\exp(-z/\lambda))$ . Actually the measured intensity depends by an other multiplicative factor taking into account the effective ionization section which depends on the material i.e.  $I = I^\infty (1-\exp(-z/\lambda))$ .  
Note that we can define an impinging mean free path  $\lambda_i = d/\ln(r)$  and an Auger mean free path  $\lambda_{\text{Auger}} = d/\ln(s)$  in such a way that  $1/\lambda = 1/\lambda_i + 1/\lambda_{\text{Auger}}$ . Because the energy of the impinging electrons is of the order of 3 KeV while typically Auger electrons have energy of 100-500 eV,  $\lambda_i \gg \lambda_{\text{Auger}}$  meaning that the mean free path  $\lambda$  is the one of the Auger electrons
- c) The intensity due to the element B is  
 $I_B = \int_0^h I(z) dz = C_B \lambda_B(E_B) (1-\exp(-h/\lambda_B(E_B)))$  where the multiplicative factor due to the ionization section is explicitly included and  $\lambda_B$  depends on the attenuation factor for the element B and the energy  $E_B$  of the Auger electrons emitted by atoms of type B.  
Concerning the element A we have to take into account the assumption of very thin film. This implies that the impinging electrons travel practically undisturbed the element B and that the signal measured by the detector is than due to the Auger electrons generated in A attenuated due to the traveling in B.

The intensity due to the element A at the interface A-B is

$I_{A-B} = \int_0^{\infty} I(z) dz = C_A \lambda_A(E_A)$ . This intensity is attenuated during traveling in B. The intensity on the detector is  $I_A = I_{A-B} \exp(-h/\lambda_B(E_A))$  where  $\lambda_B$  depends on the attenuation factor for the element B and the energy  $E_A$  of the Auger electrons emitted by atoms of type A.

d) The intensity due to the element B is now proportional to the fraction of the surface covered by the film. Using the previous result

$$I_B = \theta C_B \lambda_B(E_B) (1 - \exp(-h/\lambda_B(E_B)))$$

Similarly  $I_A = C_A \lambda_A(E_A) [(1-\theta) + \theta \exp(-h/\lambda_B(E_A))]$  where the  $(1-\theta)$  term takes into account the uncovered A surface

## Alloying during epitaxial growth of Ni on Au(100)

The room temperature growth of Ni on Au(100) has been studied by Auger spectroscopy as a function of the film thickness  $n$ . The experimental data and the fits with different models are shown in Fig1.

a) Model 0. Assuming the Ni growing in a layer-by-layer fashion, give an expression for the normalized Au Auger intensity as a function  $n$ . The monitored Au Auger peak is at 69 eV. Assume an equal mean free path  $\lambda$  for electrons traveling Au and Ni. Is the model fitting the experimental data?

b) Model I. We assume that alloying takes place with mixing between gold and nickel atoms limited to the first surface plane. We also introduce a parameter  $K$  representing the fraction of the Au atoms of the topmost surface plane that are mixed with the Ni incoming atoms. The model is schematically represented in fig. 2. Give an expression as a function of  $K$  and  $A = \exp(-1/\lambda)$  for the normalized Auger intensity after depositing 1 ML of Ni?

c) Using the model I, which is the expression for the normalized Auger intensity after depositing 2 ML of Ni?

d) Can you find a recurrence relation between the intensity measured after  $n$  and  $n+1$  deposited layers?

e) Assuming  $\lambda = 2$  ML try to estimate the value of  $K$  using the experimental points

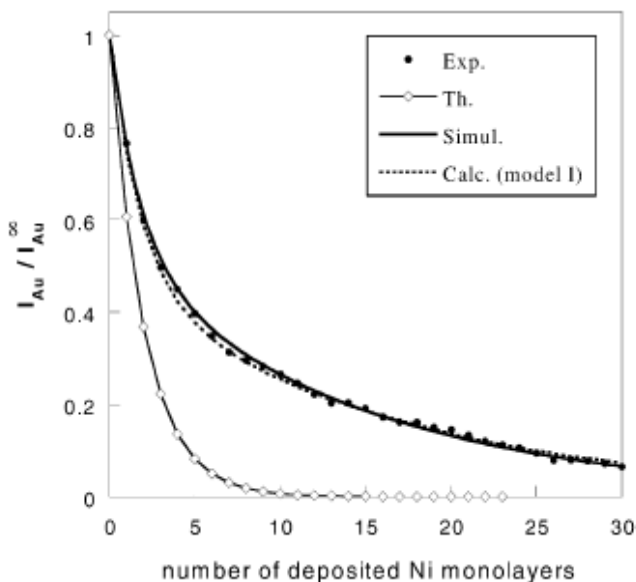


Fig.1 Normalized Au Auger intensity ( $I_{Au}/I_{Au}^{\infty}$ ) as a function of the number  $n$  of deposited Ni ML: experimental data (\*), theoretical intensity in the absence of segregation effects (model 0), simulated intensity obtained by adjusting the parameter  $K$  to the experimental data for each  $n$  (model I).

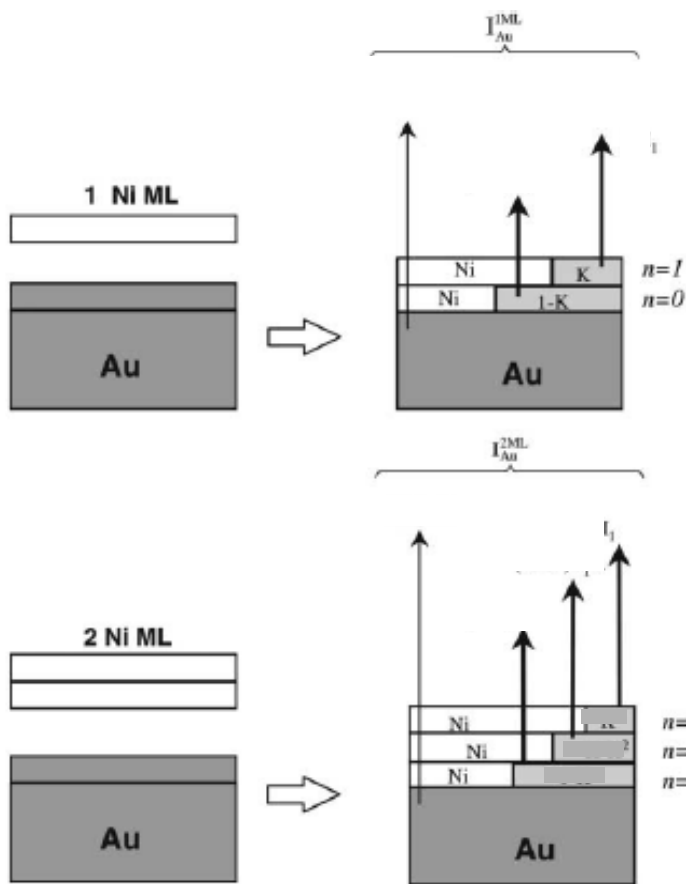
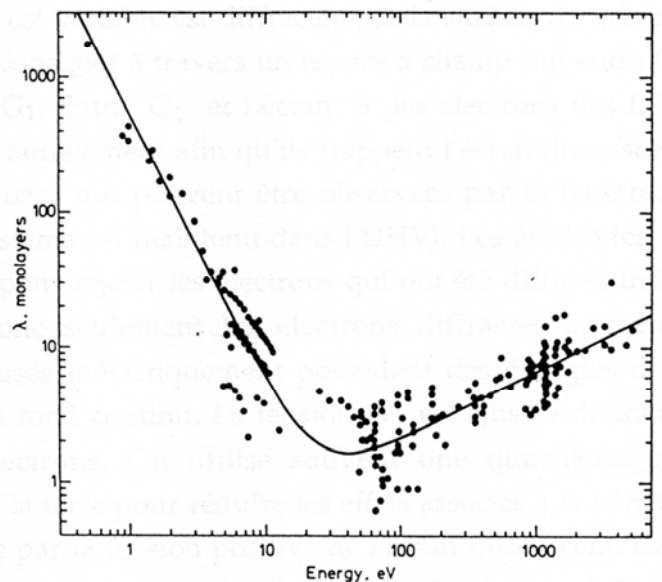


Fig. 2. Schematic representation of the alloying model used to calculate the Au Auger intensities for one ( $I_{Au}^{1ML}$ ) and two ( $I_{Au}^{2ML}$ ) Ni ML deposited on Au ( $n = 0$  refers to the topmost Au surface plane before the Ni deposition,  $K$  is the atomic exchange coefficient between the Au atoms of the topmost surface plane and the incoming Ni atoms,  $A$  the attenuation factor relative to one atomic layer).

$\lambda$  (electron mean free path) as a function of the electron energy



## Solution: Alloying during epitaxial growth of Ni on Au(100)

- a)  $I(n) = I_{\text{Au}}^{\infty} \exp(-n/\lambda)$  with  $\lambda = 2$  ML for an energy of 69 eV
- b) Indicating with  $A$  the quantity  $\exp(-1/\lambda)$  and looking to fig.2 we have a fraction  $K$  of the surface giving  $I^{\infty}$ , a fraction  $(1-2K)$  giving  $I^{\infty}A$  and a fraction  $K$  giving  $I^{\infty}A^2$ . The normalized intensity is then given by  $J(1) = K + (1-2K)A + K A^2 = A + (1-A)^2K$
- c) The mixing is confined to the topmost layer meaning that a fraction  $K$  of the previous  $K$  fraction of surface Au (i.e.  $K^2$ ) stays at the new surface ( $n=2$  in fig2) and a fraction  $(1-K)$  of the previous  $K$  fraction (i.e.  $K-K^2$ ) stays in the first sub-surface layer ( $n=1$  in fig2), while the previous  $(1-K)$  fraction stays unchanged ( $n=0$  in fig2). The normalized intensity is then given by  $J(2) = K^2 + (K-2K^2)A + (1-2K+K^2)A^2 + KA^3 = A [A + (1-A)^2K] + (1-A)^2K^2 = A J(1) + (1-A)^2K^2$
- d) Generalizing  $J(n+1) = A J(n) + (1-A)^2K^{n+1}$
- e) Assuming  $\lambda = 2$  ML we get  $A=0.605$ .  
Using the formula calculated in b) and c) one obtains  $K=1.06$  and  $K=0.93$ .  
The best fit using all the experimental data points gives  $A = 0.57$  or  $\lambda = 1.8$  ML and  $K = 0.94$   
Note the strange value for  $K$  in the case of just one monolayer ( $K$  has to be inferior to 1). A better agreement is obtained refining the alloying model and assuming that the alloying concerns the two topmost surface planes.