Overview of Surface Measurements: What Do Surface Studies Tell Us about Q-Slope ?

High gradient Q-slope vs baking influence

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Preamble

- In the following TB stand for"texbook", namely:
  - Oxides & oxide films, J. Diggled, Editor. 1973, 2nd Ed 1981, New York. 5 volumes = « the Bible »
  - Encyclopedia of Electrochemistry of the Elements, A.J. Bard, Editor. 1974, M. Dekler: New York
  - University Lectures : solid state physics, metallurgy, band structure, electrochemistry…
- A tribute to J. Halbritter, but….

Source	J. Halbritter [1]	More recent *[Antoine, Ma, Kowalski…]*
Nb RRR	90	250-300
Oxide thickness @ eq.	~ 6 nm	< 5nm
Time to reach eq. (H_2O)	Some mn	4h => 1 week !

Nb reacts ≠ when purity ↑

Usual suspects…

Surface modification upon baking :

- Modification of adsorbed layers : H_2O, hydro-carbides,…
- Modification of the oxide layer
- Diffusion of light species (interstitials) : H, C, F… O

Experiments on baked cavities :

- No effect of exposure to air or water (HPR) [*Visentin*]
- No difference when baking in air [*Visentin*], (known to built up oxide layer [*TB, …Hellwig*],)

Diffusing species are the most probable suspects

Limits of RF measurement

- RF measurements @ 2K => ~ 50-100 nm,
- RF measurements @ 10K => ~1µm

But

- we are dealing with nm scale modifications !

=> We cannot measure very local modification of SC parameters with cavities.

Susceptibility @ B> Bc_2^{bulk} (=> $Bc^{surf} \equiv Bc_3$?)

[Steffen, *Casalbuoni*]

- Baking doesn't change bulk properties
- $Bc^{surf} > Bc_2^{bulk}$; higher for EP than BCP
- Further increased upon baking

Hydrogen case

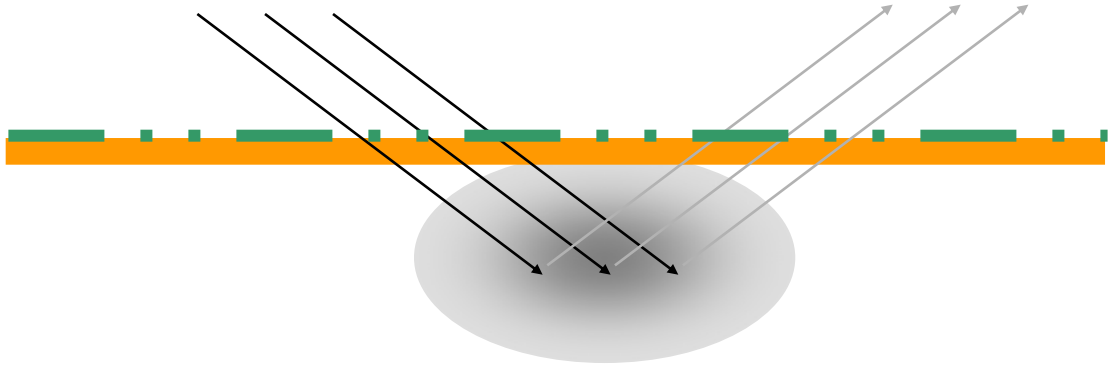
- Hydrogen is 10^{15} times more mobile than O or C [*Alefeld*].
- Hydrogen segregates near the surface [TB, *Antoine,...*]
- Upon baking : will diffuse uniformly inside the material (possibly very few outside with ↑ of T)
- Upon cooling, and staying @ RT : will diffuse to the surface and form segregates again, within hours (days ?).

=> Should rule out hydrogen as a suspect !

- contradiction with [*Giovati*]?

What surface technique ?

Need for sensitivity and depth resolution



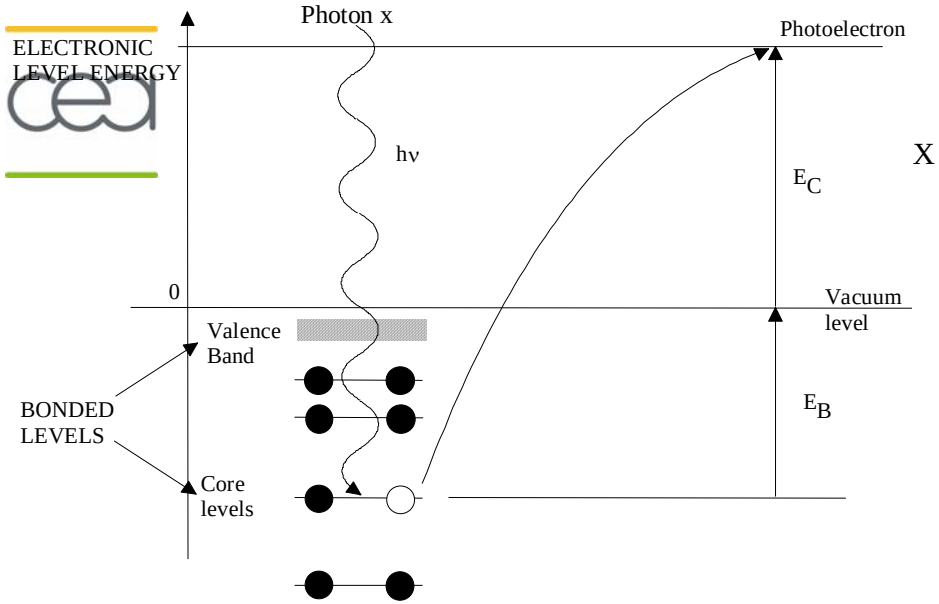
- too superficial => STM, LEED, REED…
  - need to cross ~ 5 nm Nb_2O_5 , only indirect info on the SC matrix;
- too “deep” => EDX, electron probe…
  - Explores ~1 µm depth
  - Only relative information
- roughness sensitive => X-Rays, reflectometry…
  - Work on monoXstal, special sample prepn

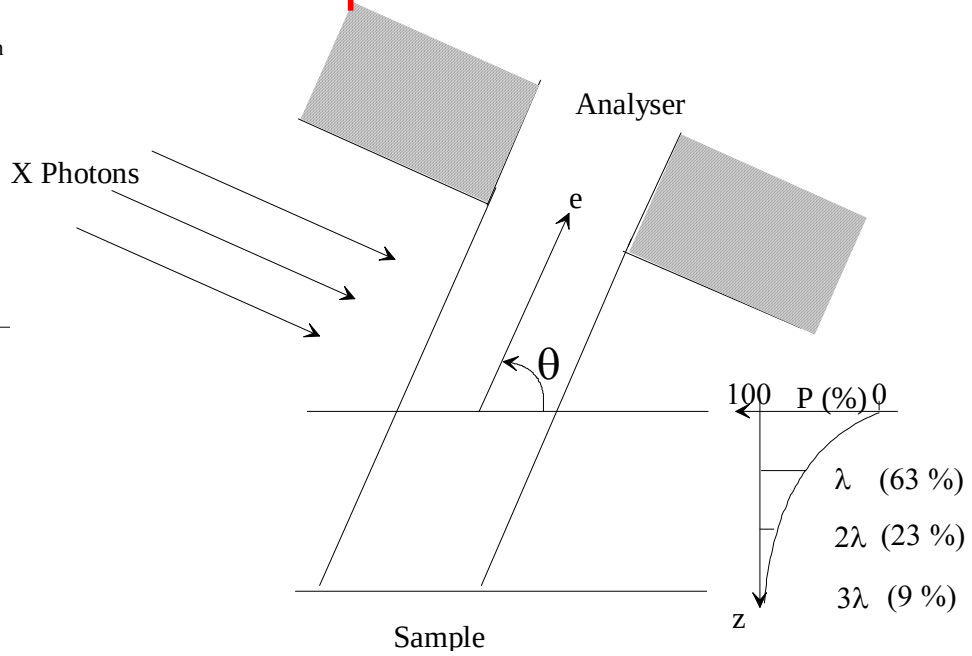
Profiling techniques

- Ion sputtering : troubles with preferential O sputtering…
  - Reduces depth sensitivity to ~ >10 nm
  - Only relative information, no way to tell oxide/Oi
- Thus : be careful with profiling (XPS, Auger…. and SIMS in standard conditions)
- Profiling with depth sensitivity :
  - TOF-SIMS (but can't tell oxides / O_i)
  - Angle-resolved techniques
- Angle resolved photoemission (XPS/ESCA)
  - Chemical sensitivity
  - Profiling
  - But ….

Photoemission (≡ ESCA ≡ XPS) / Auger

A unique way to get info from depth under oxide





$E_B = h\nu - E_C$

E_B(bonding energy) is characteristic from one element ; and is influenced by electronegativity of bonded neighbors ⇒ chemical environment information.

- λ~ 0.5-2nm (Auger)
- λ~ 5nm (XPS)

But :

- Not very sensitive (0.5 At%)
- Deconvolution = very « tricky »

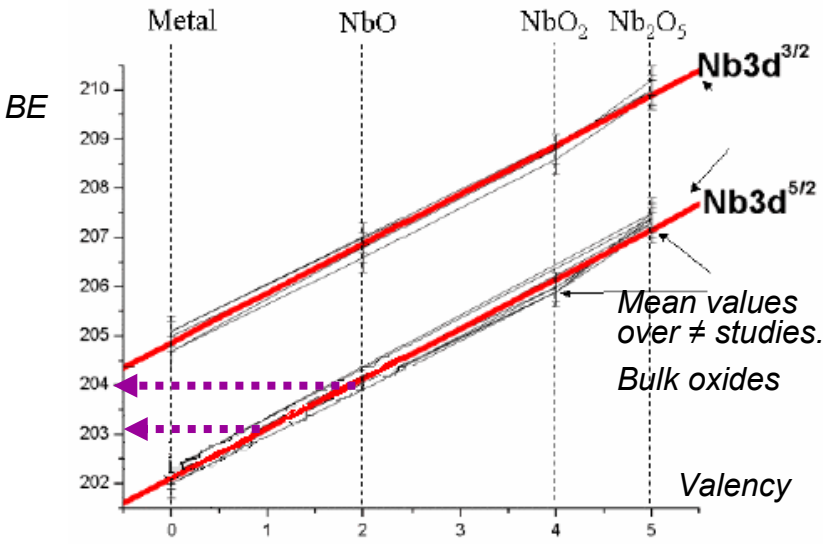
For $[x_i] < 10\%$, ∃ deconvolution signal ≠ ∃ physical cpd !!!

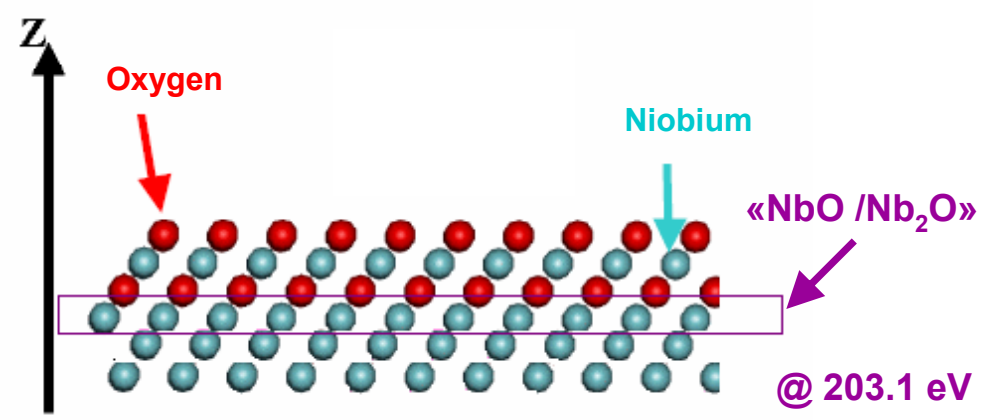
« Much ado about ~~nothing~~ … suboxides »

Suboxide (known phases = NbO, NbO_2) ≠ interstitials oxygens (Oi)

(standard XPS):

- If observed by profiling (ion sputtering) => you've just created them !
- If observed by deconvolution : be careful !!! if [x] ≤10%=> not significant with XPS alone !
- Should have precise B. E. (fig 1). Displacements caused by :
  - Interface or mixed state [*Arfaoui, Hellwig*] (fig 2)
  - Adsorbed species or dangling bond => surface polarization (valid only if thickness << 5 nm) [*TB*]
  - Interstitial oxygen inside the oxide/metal (seen by RBS [*Hellwig*], inferred in case of baking)





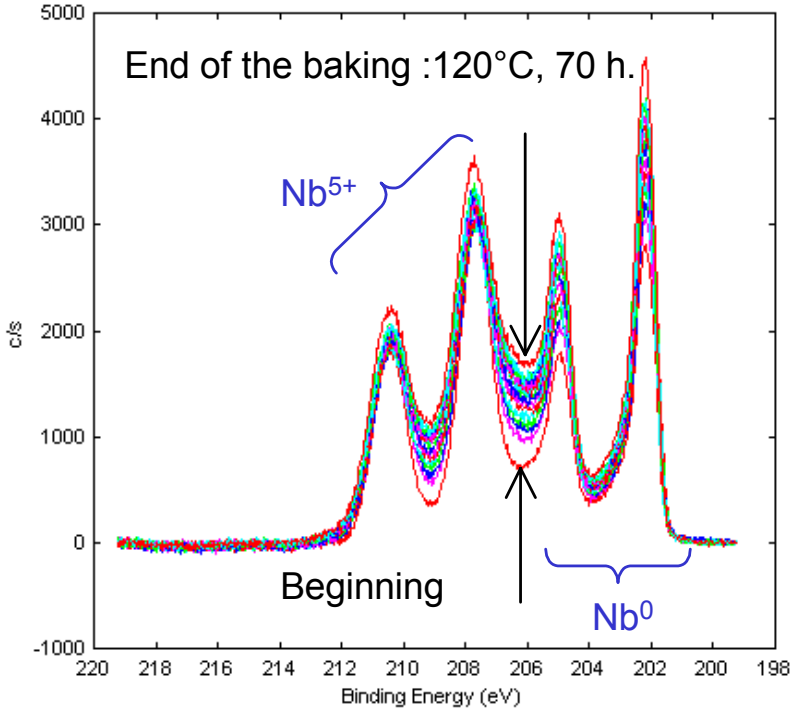
bulk/surf NbO is @ 204.1 eV !

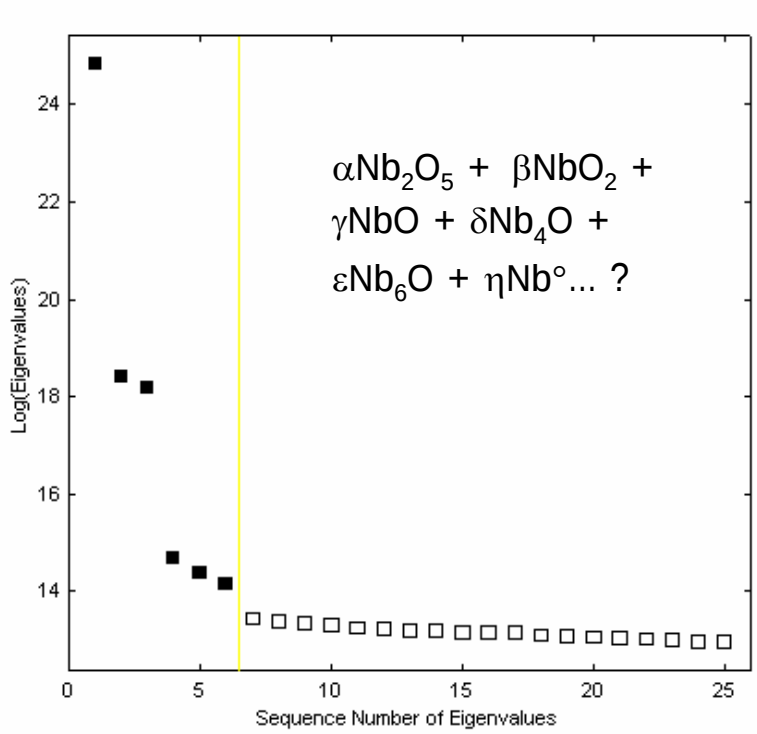
NbO/Nb_2O = INTERFACE =>~1-2 monolayer. Not a PHASE !

Photoemission : proof of ∃ Oi/Suboxides

[*Chincarini*]

Principal Components Analysis: ...





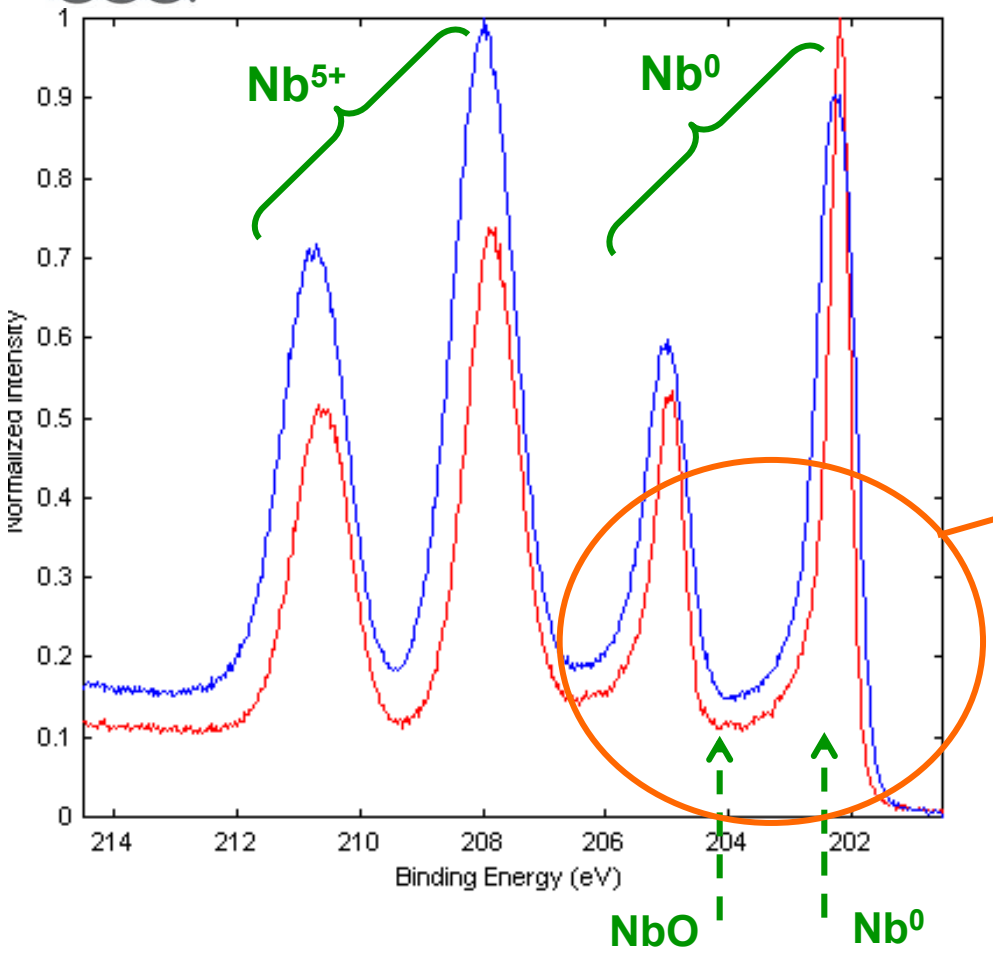
At least 6 statistically significant components...

Photoemission : high resolution

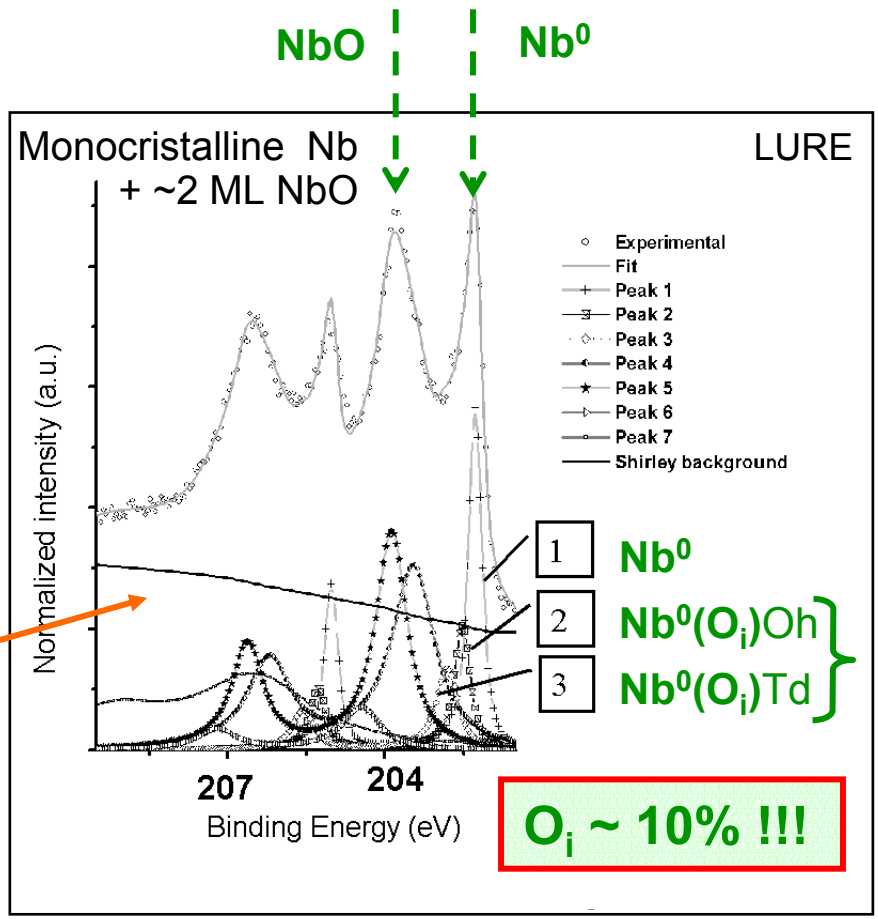
Classical XPS: resoln~1eV

EP annealed

EP not annealed



XPS with Synchrotron source

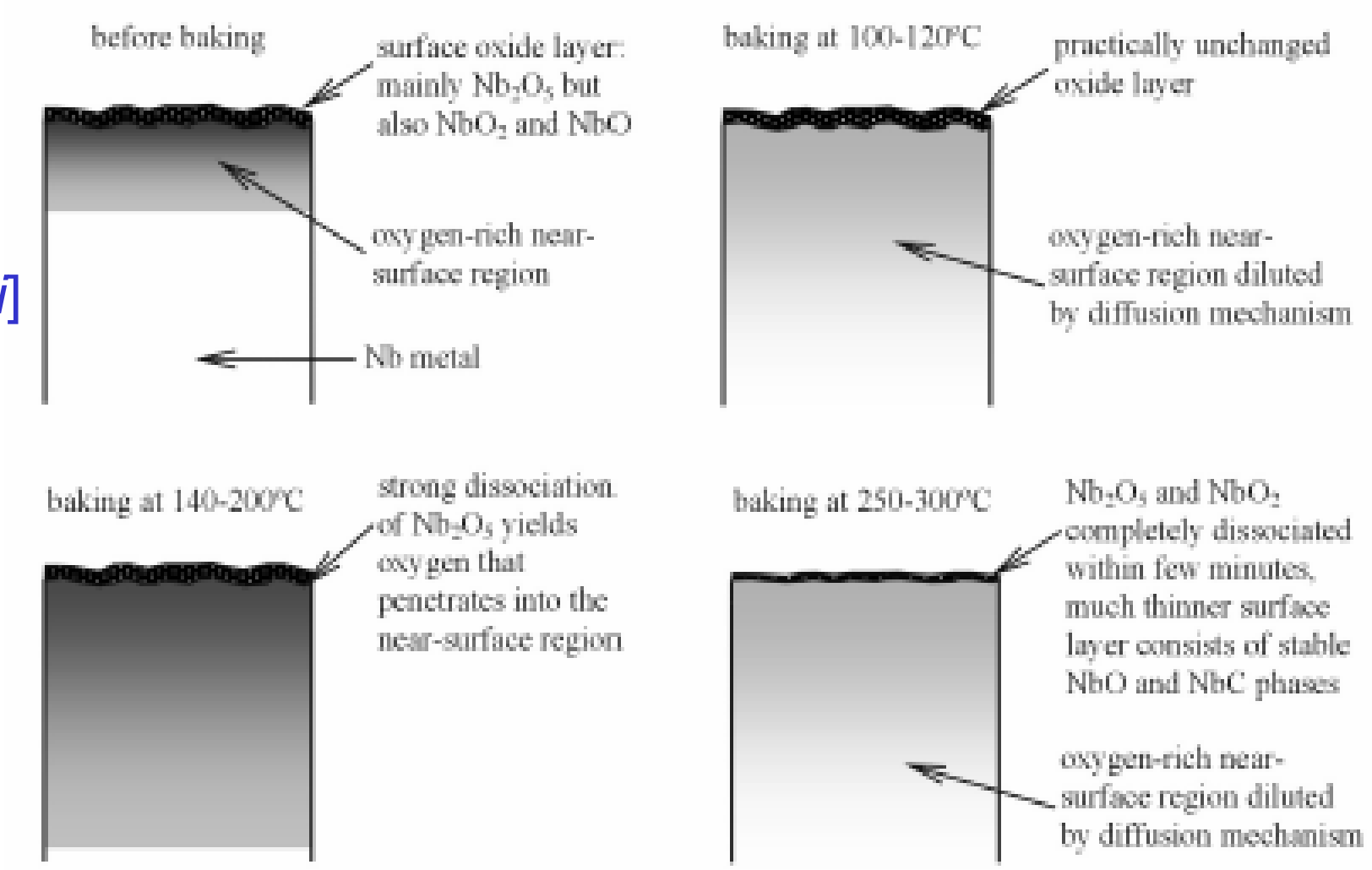


O_i ~ 10% !!!

$[O_i]_{3nm}$ >~ 200 x $[O_i]_{bulk}$!!!

The “right” scenario: as inferred from XPS

[*Kowalski*]
[*Antoine, Chincarini, Ma, ….*]



The Oi (Ci) scenario:

- Baking under vacuum : destruction of Nb_2O_5=> defects, dangling bonds, O_i => more localized states within the gap !!! *[Band theory !]*
- Baking in air : oxide is reconstructed (increased).

=> contradiction with the ITE model !?

- ∃ C_i at metal-ox interface, poorly etched (neutral specie)
- Nb carbide forms @ 180-200° C [*Kowalski, Ma, Antoine, Chincarini, ….*]
- Observed appreciable degradation starting @ 180-200° C (Tc, R_S (10K), (depth ~1µm) *[Visentin]* , but…
- Degradation of R_{BCS} *[Visentin, Kneisel]*, & calculated Tc & λ *[Giovati],* as soon as 90°C (but no observed slope modif^n @ so low Tp°) (depth ~5 nm)
- Some recovering starting @ ~ 250°C (Nb_2O_5 = totally dissolved but carbides still there)

Oxide thickness: EP vs BCP

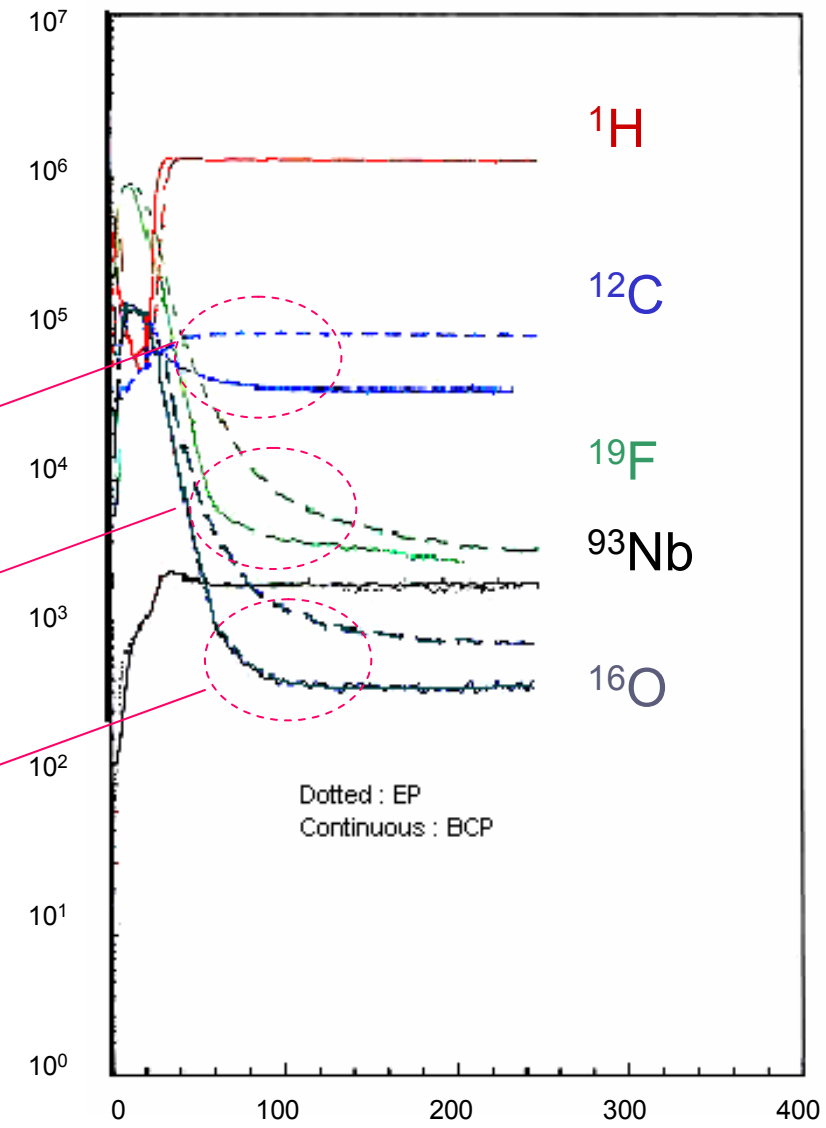
- After BCP : thickness ~ 5nm, serrated.
- After EP : a lot of discrepancies in the literature !

But

- Thickness of EP oxide: depends from time in the EP bath w/wt bias : 10 Volt => ~ 20 nm of oxide => dissolved / HF
- There are some indications that EP contains more Oxygen /BCP (also Carbon)
  - By profiling SIMS, RBS,GDL [*Antoine*], XPS, AES [*Asano*] , but oxide or O_i? hydrocarbide or C_i ?
  - Indirect: magnetization experiments [*Casalbuoni, Steffen*]

Oxide thickness: EP vs BCP

SIMS

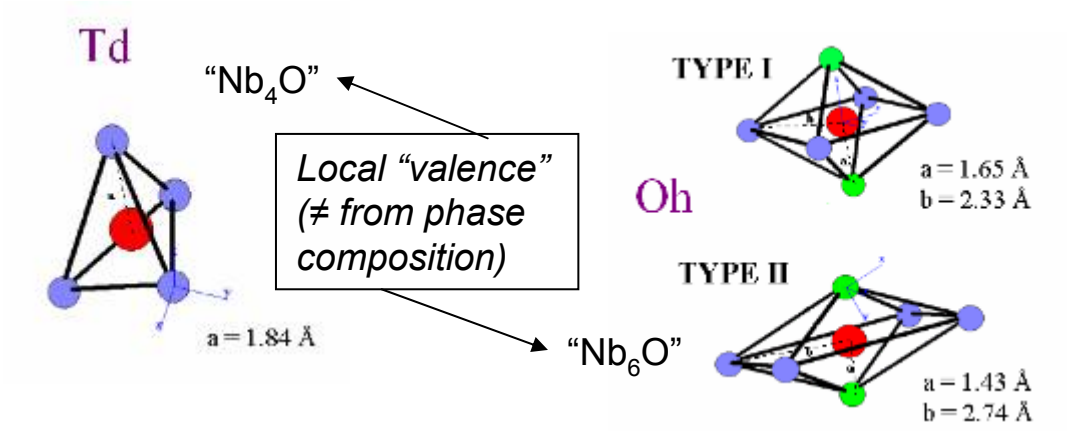


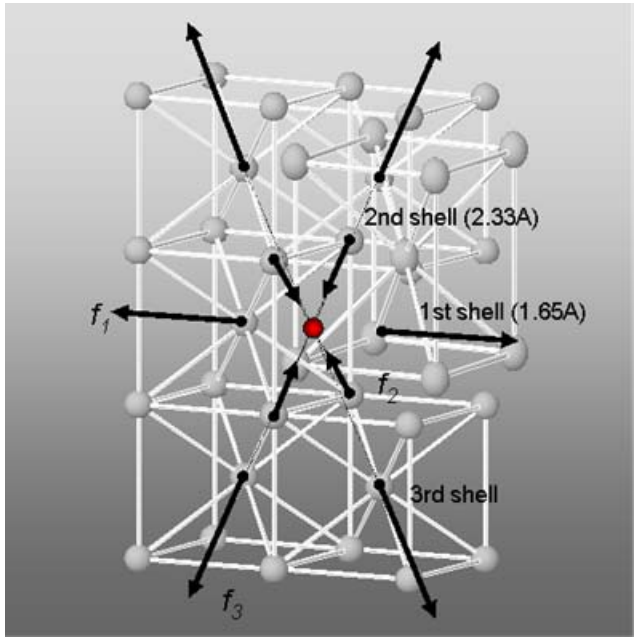
EP more contaminated than BCP ?

Interstitials oxygens (O_i)

(sometimes referred as “suboxide” clusters)

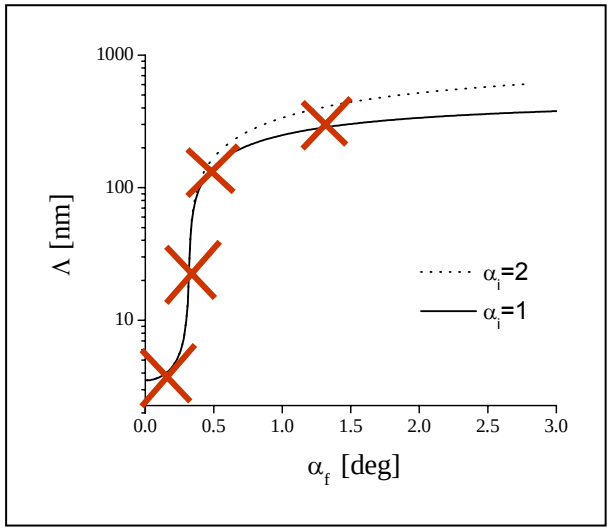
- **Segregation near metal-oxyde interface**
- [O_i] ranging from ~10 At% [*Arfaoui*] to ~70 At% [*Hellwig*] (5/7=0.714…)
- Origin:
  - Upon oxydation :competition between oxidation/Oi injection *[TB, Halbritter, Arfaoui, Hellwig...]*
  - Thermal diffusion (upon cooling) *[TB, ...]*

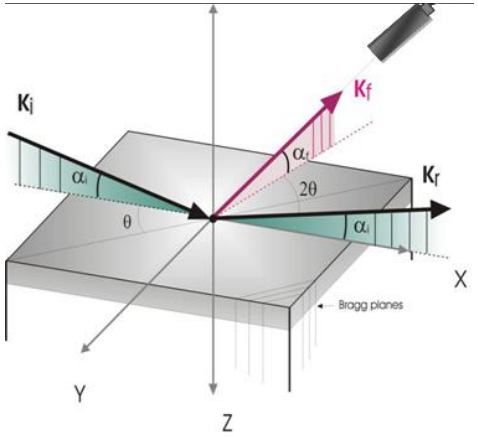


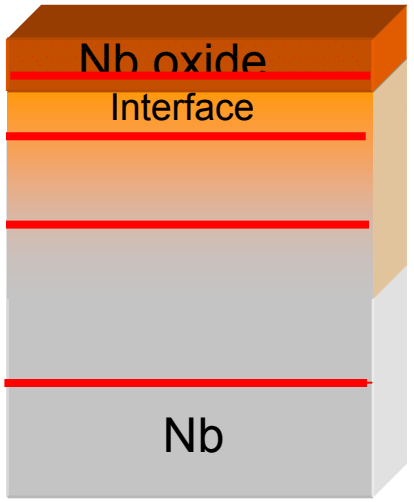


“Local distorsion” in the close neighborhood of randomly distributed defects (~1% O) : BCC → trigonal ω phase, seen on Nb monocrystal by diffuse scattering *[Dosch (bulk), Delheusy(surface, tbp)]*

Depth-sensitive diffuse scattering in the near surface region: **first results**



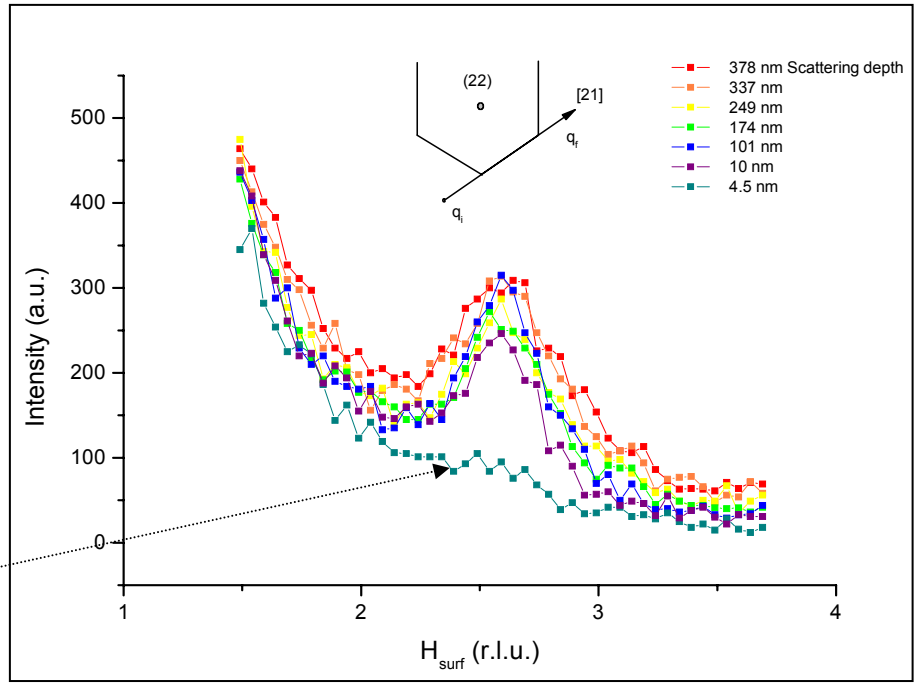




Scattering depth $\Lambda = f(\alpha_f, \alpha_i)$

Diffuse scattering intensity evolution for different scattering depths.

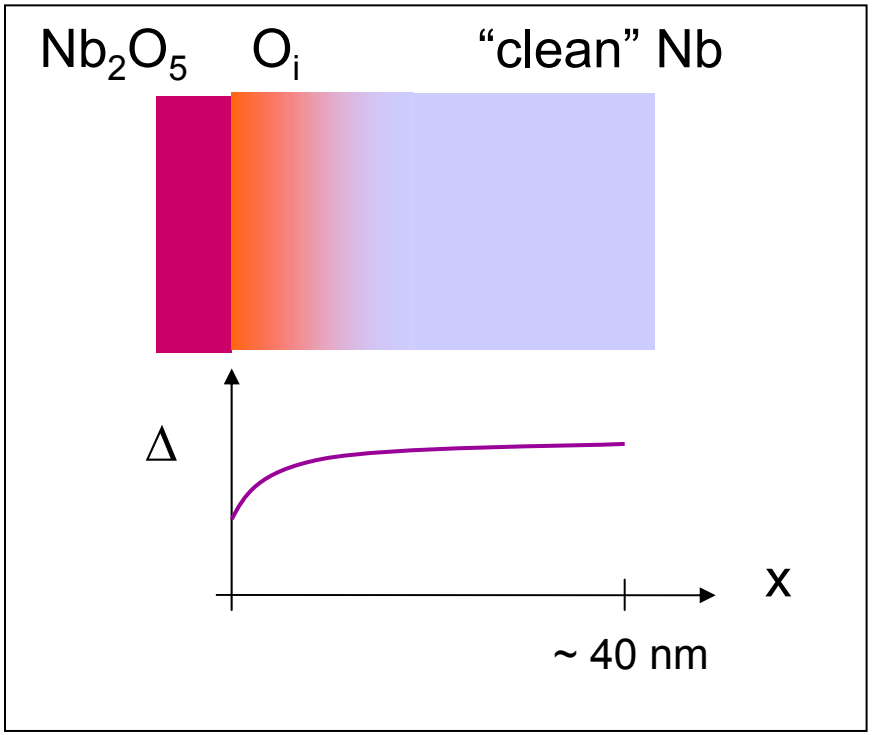
Inside the oxide : no signature of the distorsion



O_i : So what !?

- **How does O_i influence superconductivity ?**
- [O_i] might affect very locally the superconducting gap Δ (d_{char} ~ 1nm) [*Gurevich*]

$Rs \sim e^{-\Delta/T}$



O_i : So what !?

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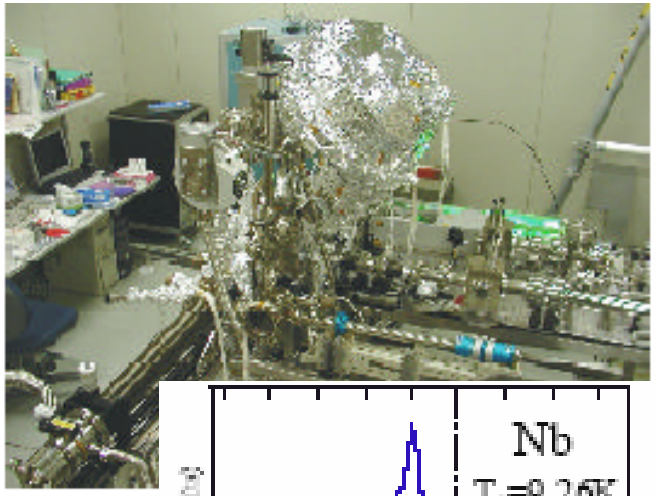
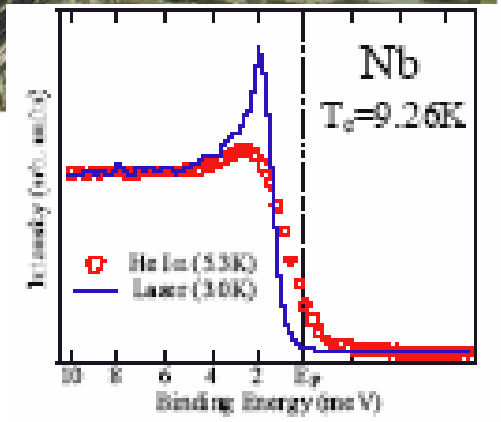
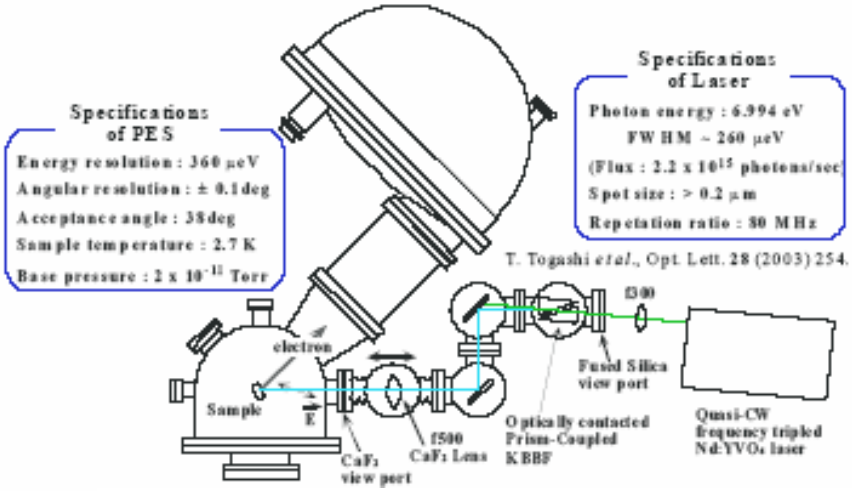
- [O_i] might affect very locally the superconducting gap Δ (d_{char} ~ 1nm) [*Gurevich*]
- Need for a nm sensitive probe !

=> Ultrahigh resolution laser photoemission spectrometer



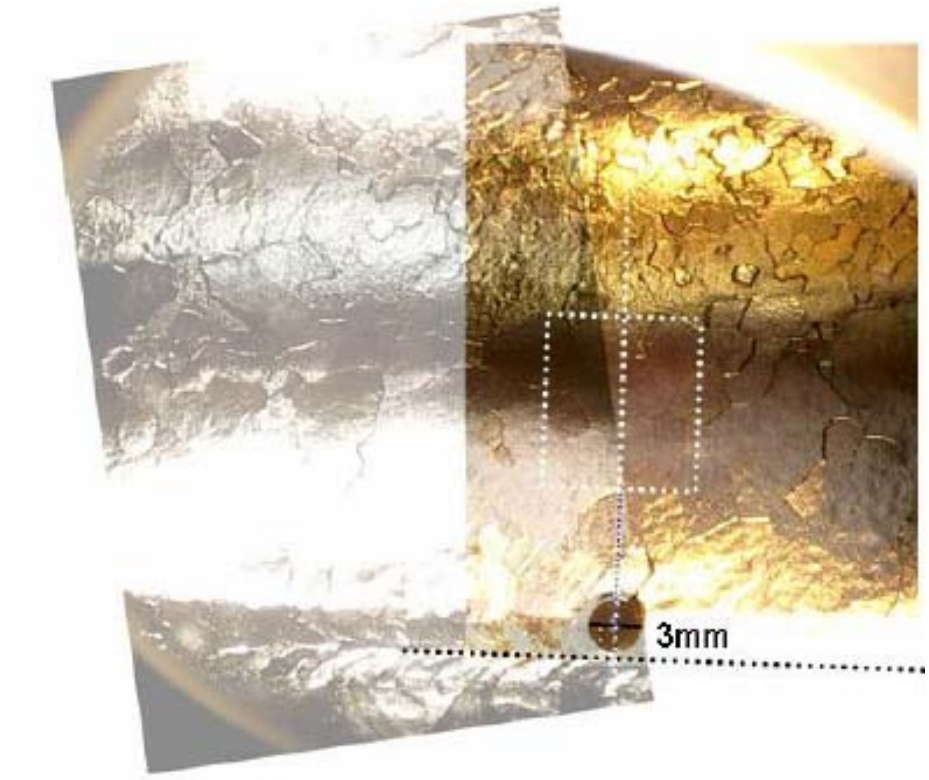


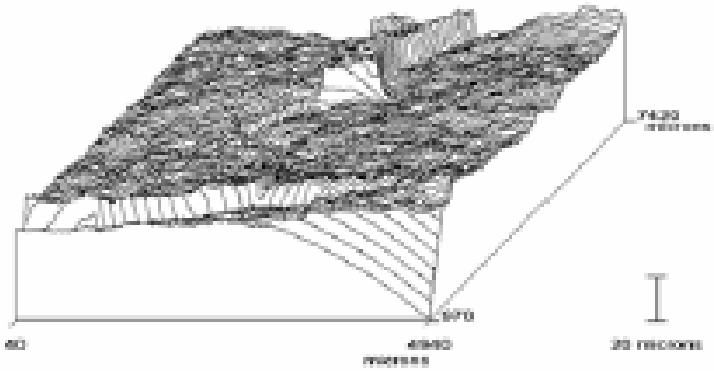
Comparison of the spectra of superconducting state of niobium between Laser PES and He discharge lamp PES



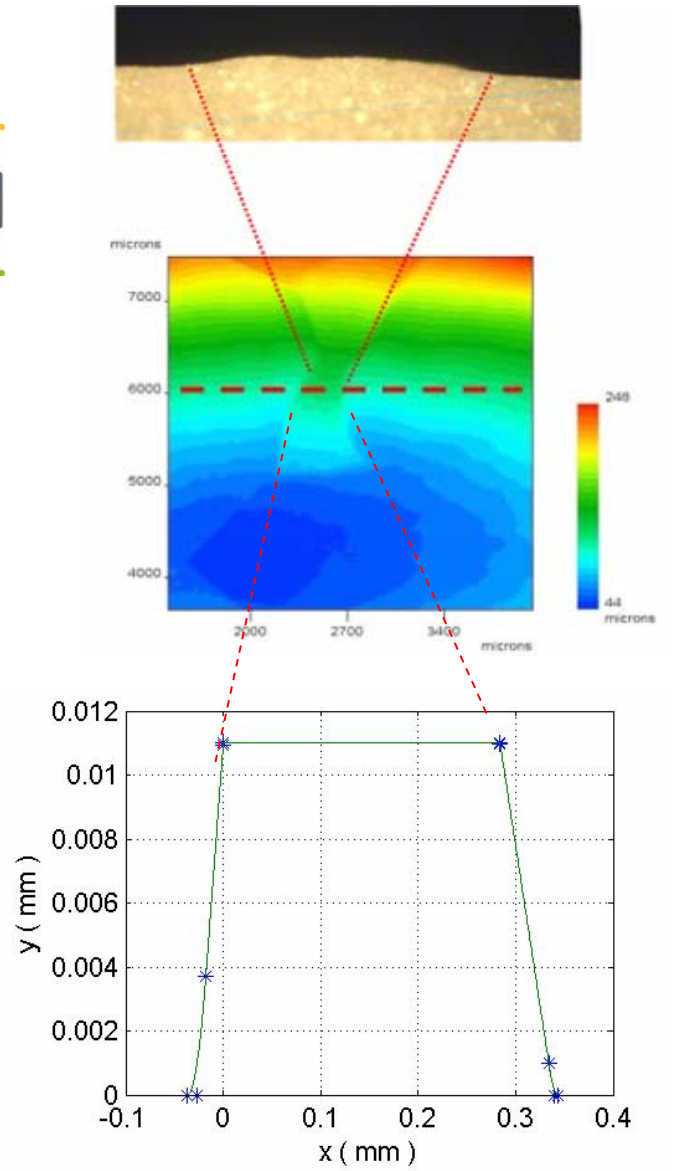
Angle resolved method + in situ baking => profiling is possible with nm resolution ! [*Kiss*]

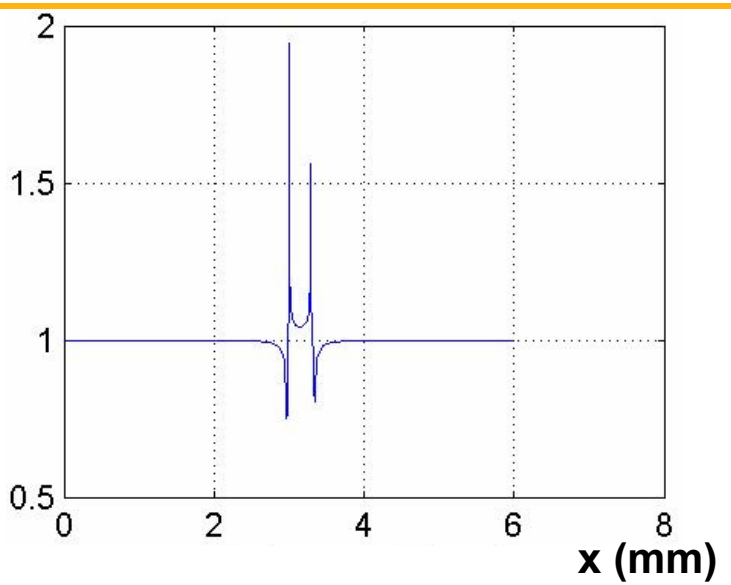
Morphology @ grain edges

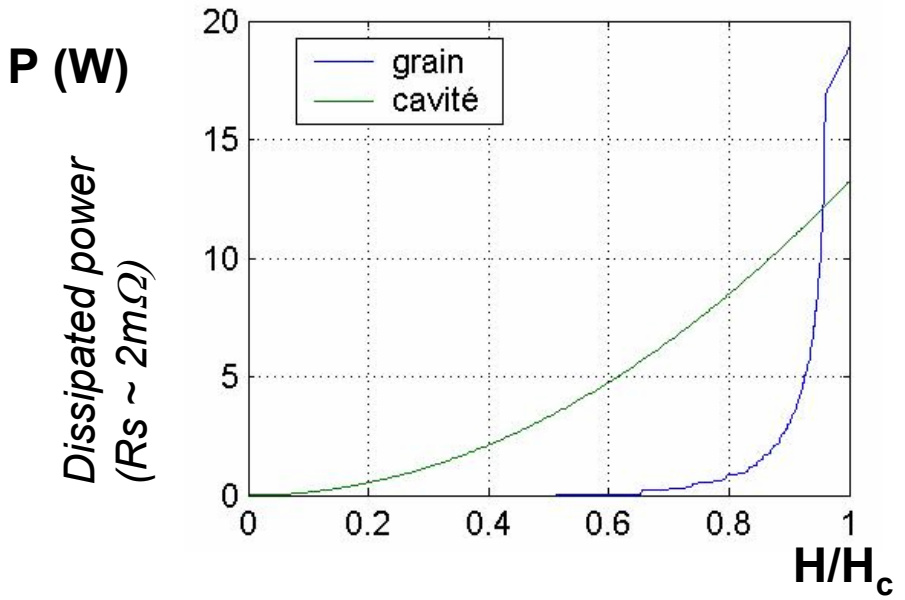




Replica @ the quench site…

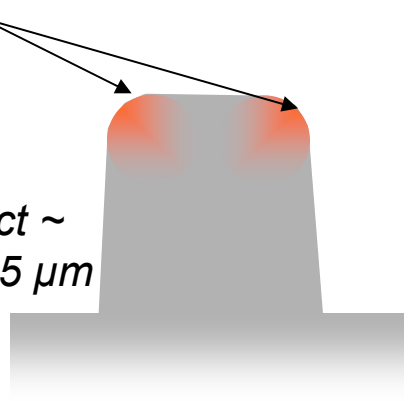






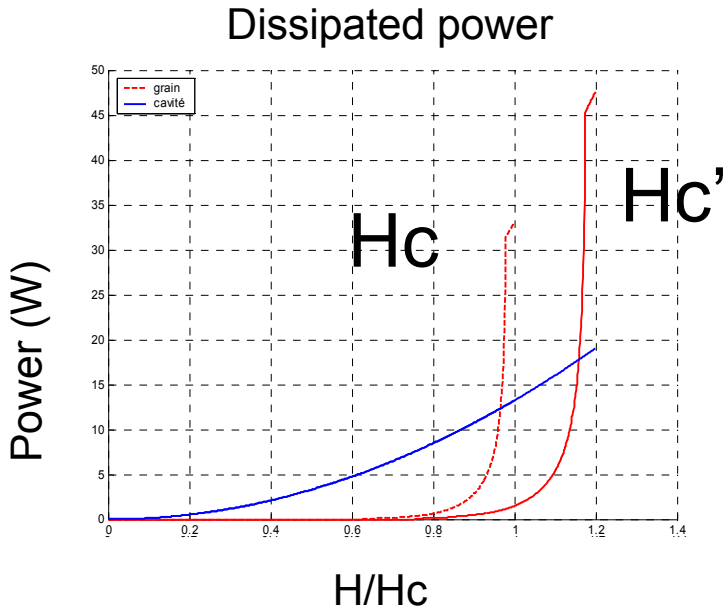
Replica @ the quench site…

- **Thermal behavior :**
  - *Edges thermally stabilized until T~ 5.35 K and W ~142mW*
  - *T<9.2 K but H> Hc*
  - *When W ~143 mW =>* ***Quench !***



morphology = trigger / thermal behavior = quench.

- **Baking : ↑ Hc**
  - *Modelling of the defect contribution compared to the contribution of the whole cavity for Hc.*
  - *and Hc' >Hc.*



Local morphology: rather quench than Q-slope ?!

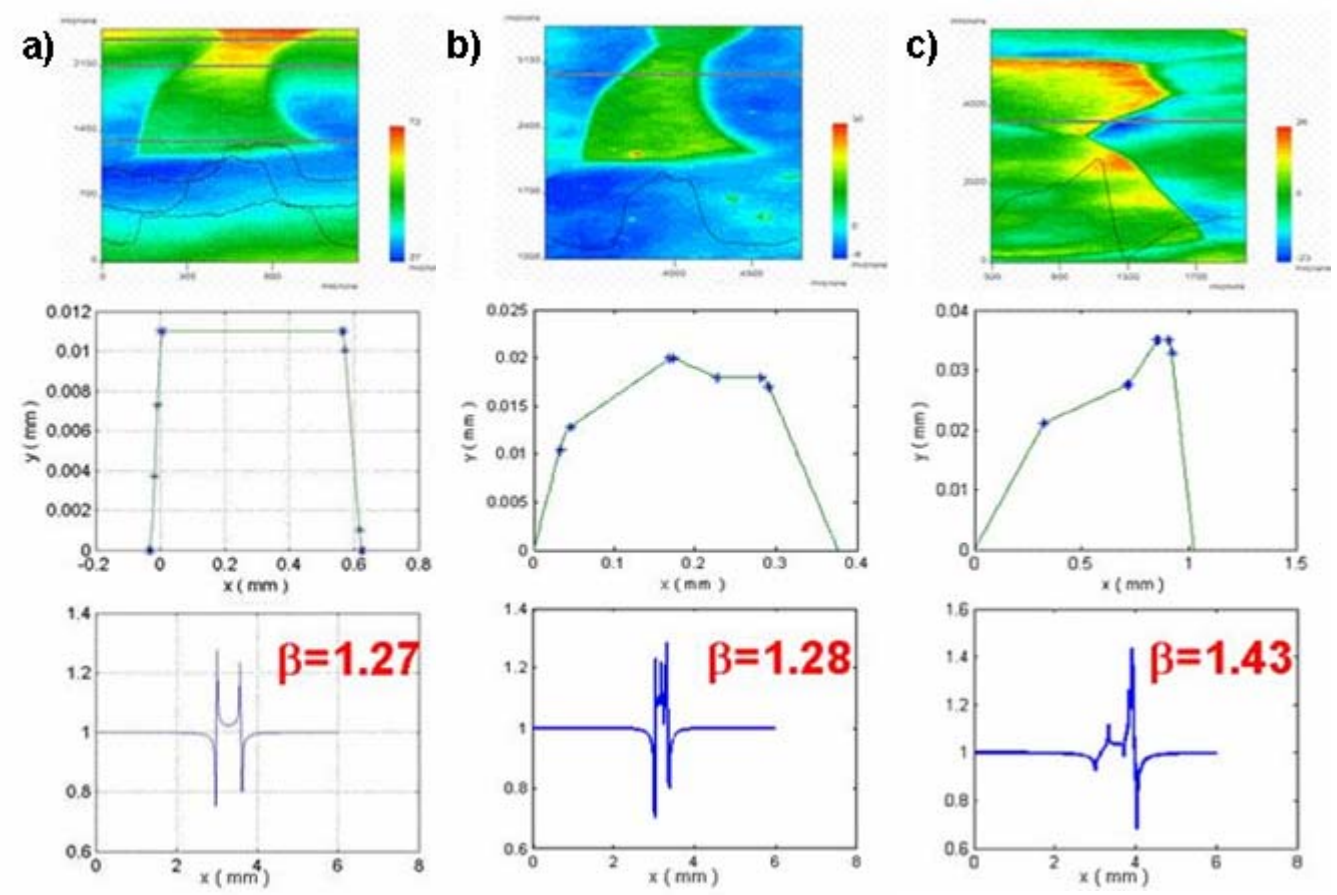
Replica @ the quench site

a) *first quench site,*
b) *same area after 20 µm (quench site @ a new location)*
c) *new quench location.*

Contour line of replicas

Modeling of the edge profile

β (field enhancement factor)



Local morphology is consistent for explaining the quench

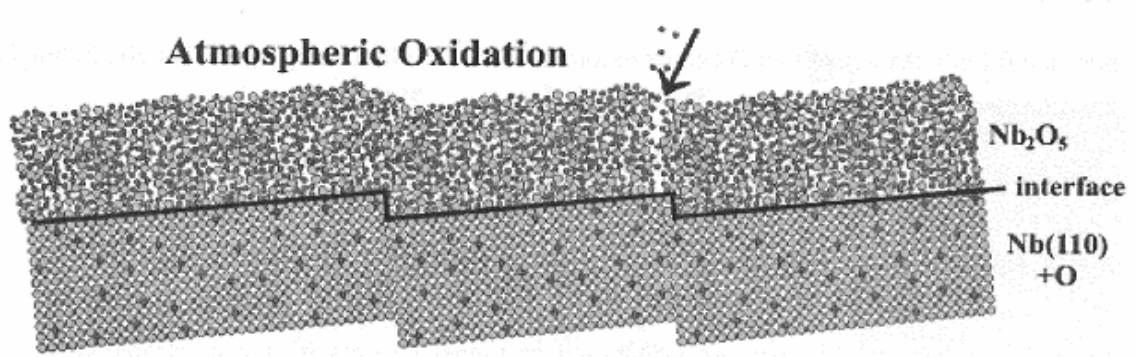
Conclusions about the Q-slope

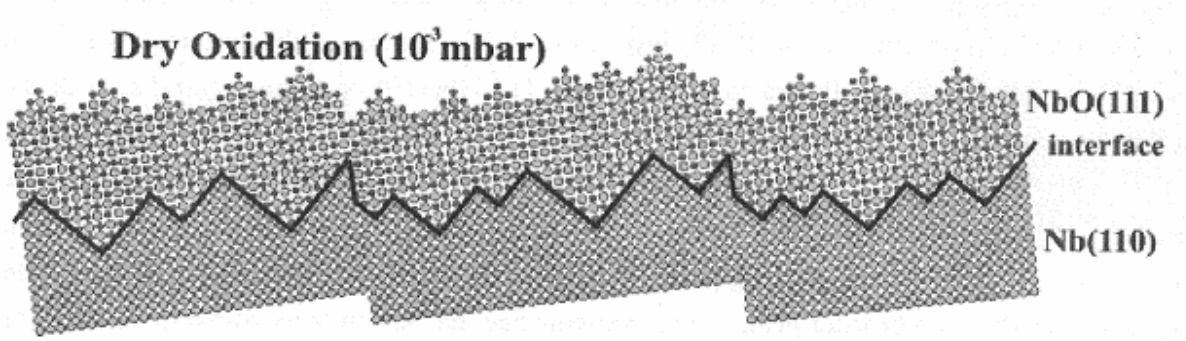
- Surface studies allow to rule out several hypothesis : adsorbed layer, modification of the oxide layer, hydrogen…and possibly ITE, morphology.
- Interstitial oxygen is the best suspect.
- Possible influence of Carbon (source = interstitial rather than hydrocarbon).
- There are (difficult) ways to check the variation of the oxygen distribution and/or to measure locally the superconducting gap.
- Morphology seems to better explain quench than slope

Further theoretical developments are needed

Oxygen ….

Clean interface ?





from [Hellwig, 2000]

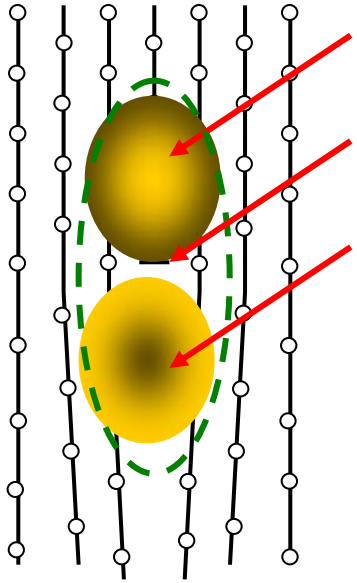
Segregation : mecanism

- defect in lattice $\Rightarrow$ lattice distorsion (elastic strain)
- light impurities interact with defect (interaction energy ΔW)

$\Delta W_{interface} > \Delta W_{dislocation} > \Delta W_{isolated\ atoms/vacancies}$

- + preferential diffusion in “disordered” regions (interaction with vacancies)

“ Cotrell cloud ”

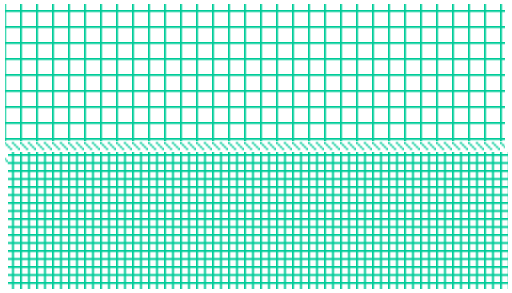


Compression area

dislocation

Expansion area

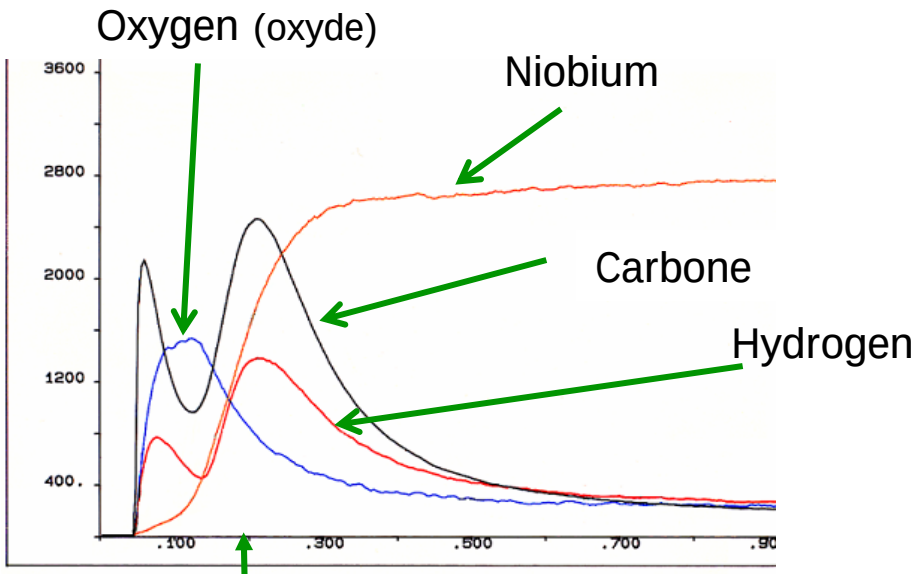
<u>Interface :</u> ~ an array of dislocation



Pure metals : not many “defects” in bulk
$\Rightarrow$ surface, interface segregation

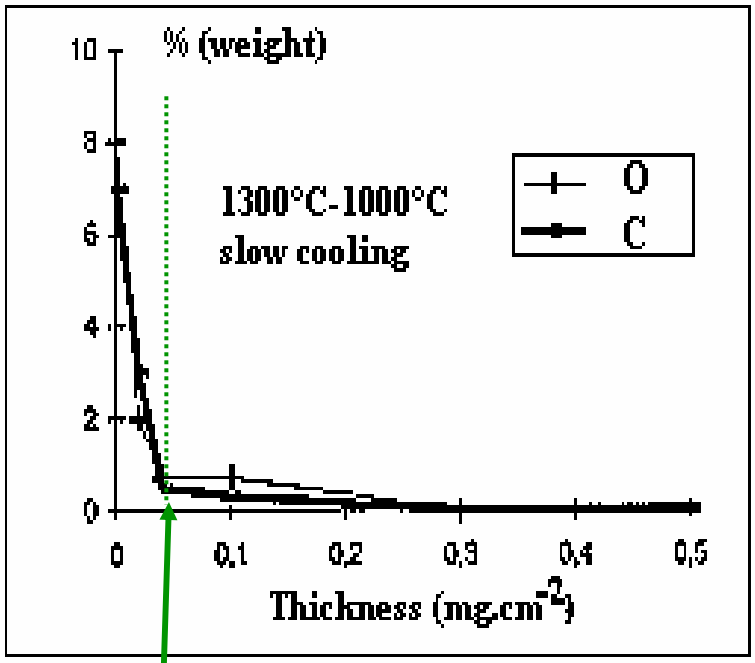
Surface segregation : experimental evidences

- Glow Discharge Luminescence (GDL)



~ oxide-metal interface

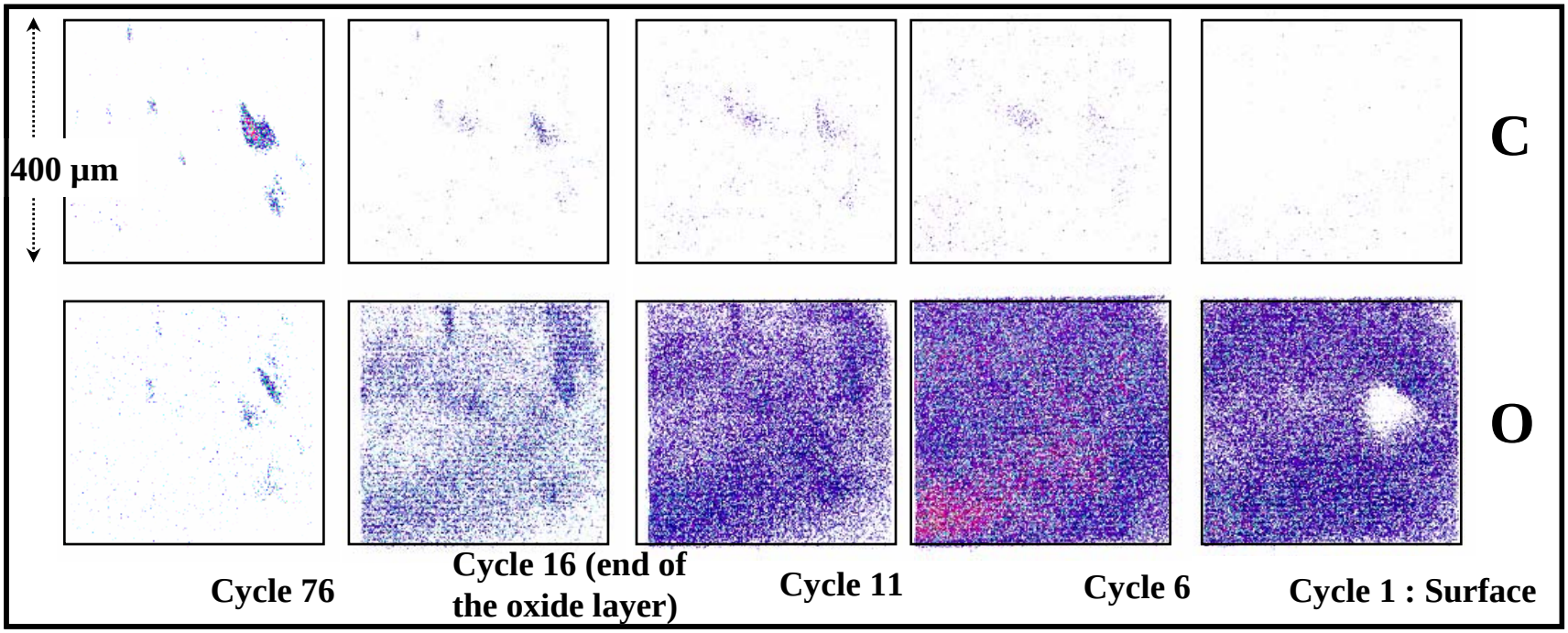
- Nuclear resonant reactions



~ oxide(Ti)-metal interface

Local segregation : experimental evidences

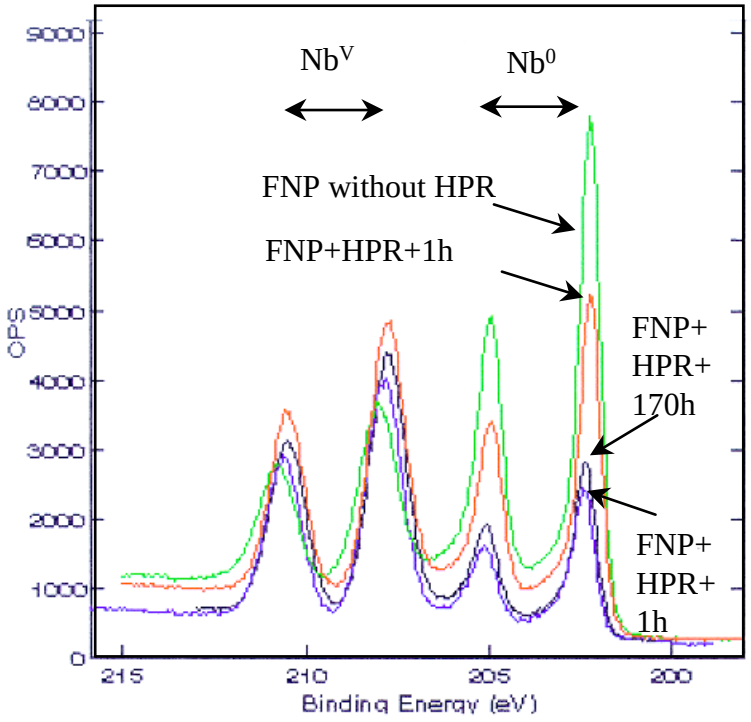
- *SIMS(TOF-SIMS), UHV*



Niobium surface studies…

Effect of HPR

- ESCA



- TOF-SIMS