FUNDAMENTALS ON MICROSTRUCTURAL TECHNIQUES

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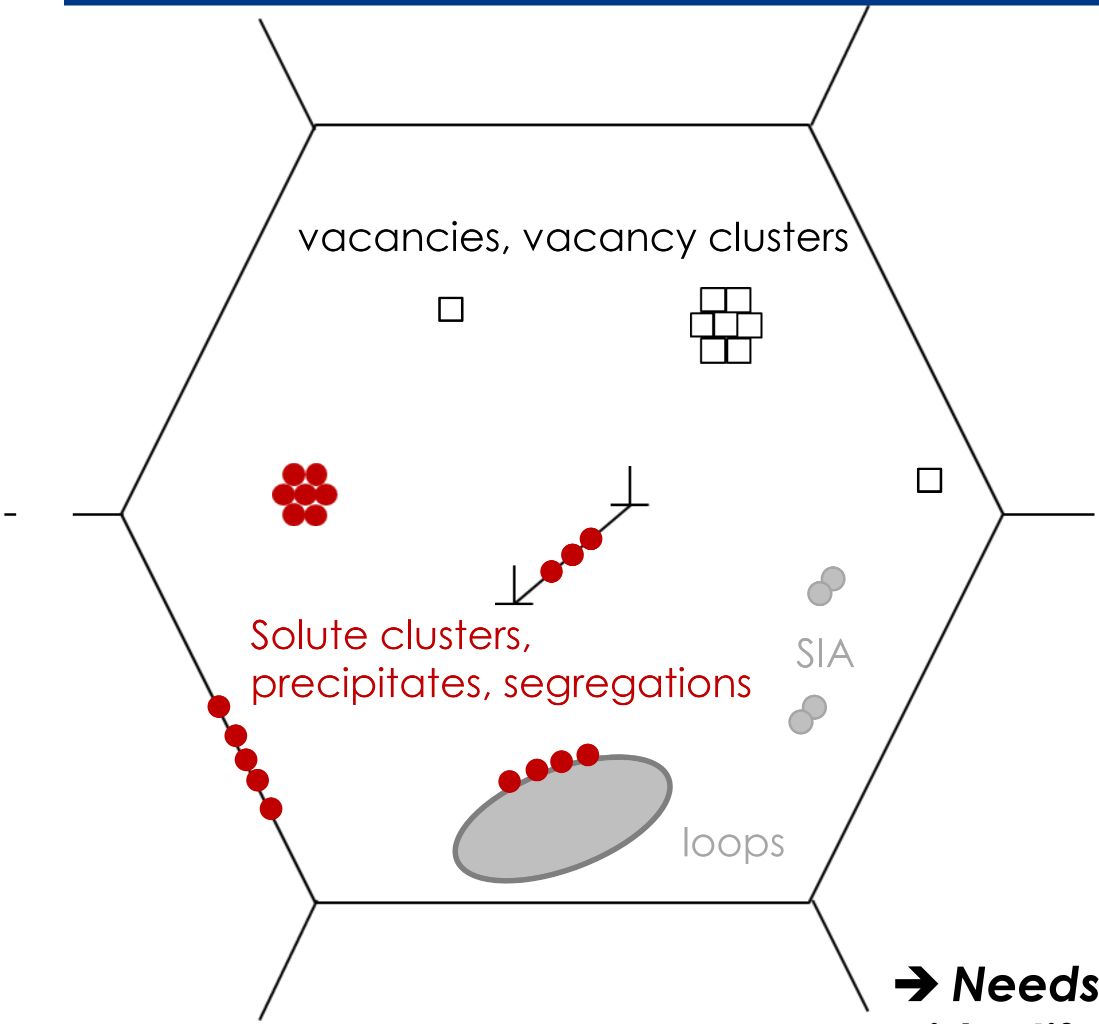
Introduction



- Irradiation produces different kinds of nano-features
- Need of quantitative data (size distribution, number density, chemical composition, distribution in material…) to predict structural evolution and correlate with properties
- Any technique is able characterize all kinds of features.

➔ ***Needs of complementary techniques to identify and quantify these nano-features (PAS, SANS, APT – FIM, TEM, SEM…)***

Which technique to observe what?

- Positon annihilation spectroscopy (PAS)
  - Principle: annihilation characteristics of positons into a sample (depend of electronic density and electron momentum distribution)
  - Raw data: Positon lifetime spectrum (PALS) and energy of the photons resulting from annihilation (CDB)
  - Microstructural information:
    - Size and density of vacancy-type defects (from mono vacancies to nano-voids)
    - Chemical environment of annihilation sites

- Small Angle neutron Scattering (SANS)
  - Principle: Scattering of mono-energetic neutron beam by a sample (submitted to magnetic field)
  - Raw data: Scattered intensity as a function of scattering angle (// and ⊥ to applied magnetic field)
  - Microstructural information: Size distribution, volume fraction, range of chemical composition of scattering features (solute clusters…)

Which technique to observe what?

- Atom Probe Tomography (APT) – Field Ion Microscopy (FIM)
  - Principle: field evaporation of a small sample
  - Raw data: position and chemical nature (APT) of atoms in the analysed volume (➔ 3D reconstruction)
  - Microstructural information:
    - shape, size distribution, number density, chemical composition of solute clusters, precipitates, segregation on crystalline defects (APT)
    - Size distribution, number density of small vacancy clusters (FIM)

- Transmission Electron Microscopy (TEM)
  - Principle: Interaction between incident electron beam and a thin sample
  - Raw data: Images in transmission of the sample (2D), spectra containing chemical information (EDS, EELS)
  - Microstructural information:
    - Size distribution, number density of dislocation loops, voids and precipitates
    - Grain size
    - chemical mapping (EDS, EELS), information about composition of different phases, intergranular segregation

Ex: Genesis platform

Zeiss – XB 540 SEM
(EBSD, EDS, FIB)

Jeol ARM 200F
(double corrected,
EELS, EDS, ADF,
HAADF…)

Specific environment
for radioactive
materials

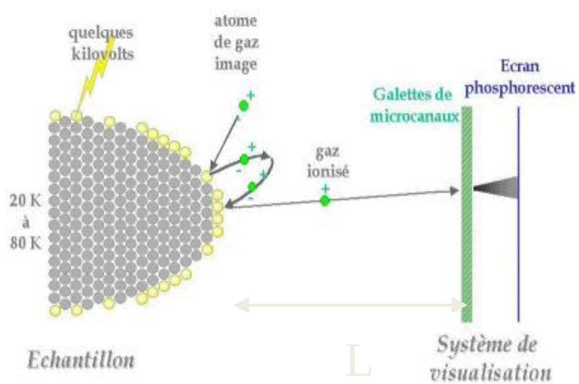
Cameca
LEAP 4000X HR

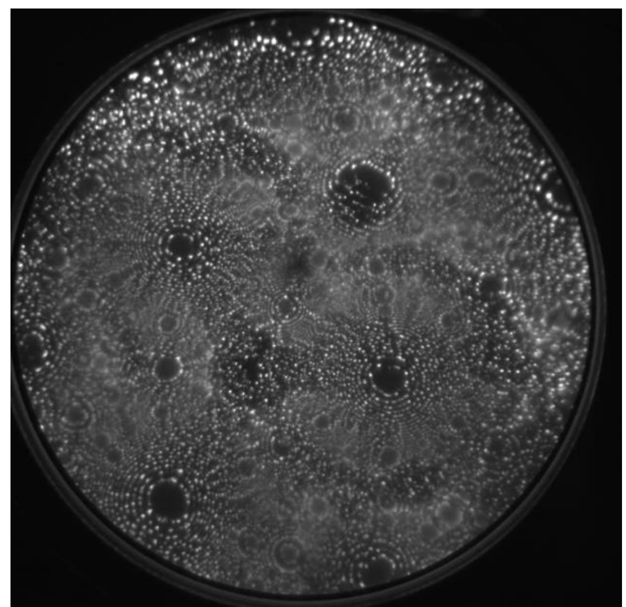
Field Ion Microscopy

- Sample:
  - in the shape of a thin needle (< 50nm),
  - cooled down cryogenic temperature (20-80K),
  - under low pressure (~10^{-5}mbar) of image gas (H, He, Ne),
  - submitted to high voltage (1-11kV).

$$\Rightarrow E = \frac{V}{\beta R} \sim 10 - 50 \text{ V/nm}$$

- Field ionization of the image gas $\Rightarrow$ *Image of the atoms at the surface*





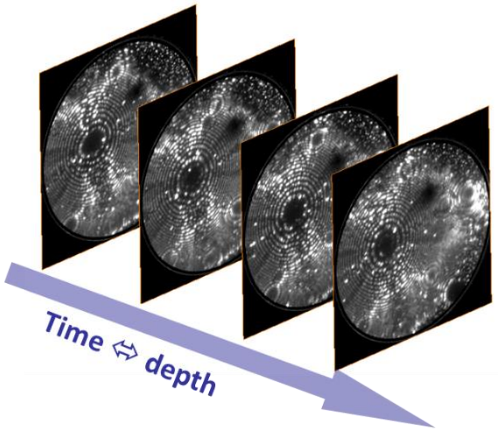
$$G = \frac{L}{(m+1)R}$$

$G \sim 10^6 - 10^7$

- Field evaporation of the surface atoms

3D – Field Ion Microscopy

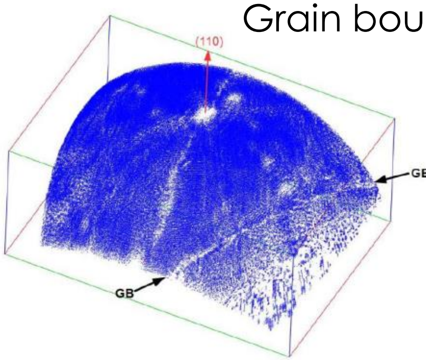
- Increment in depth from the number of evaporated plans

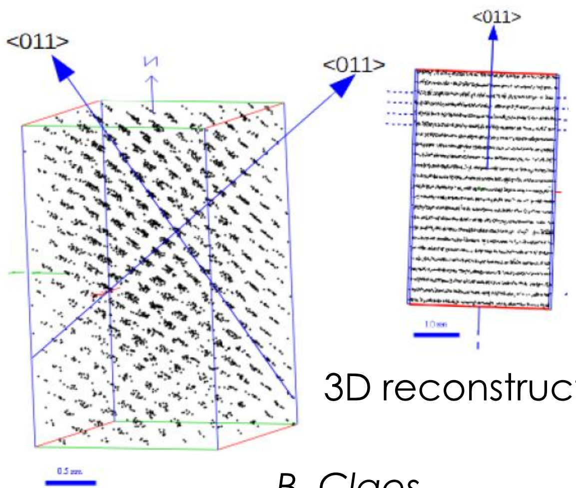


3D reconstruction of the volume:

- **high lateral and depth resolution**
- **~ 100% detection efficiency**
- **No/poor chemical information**

Grain boundary in W



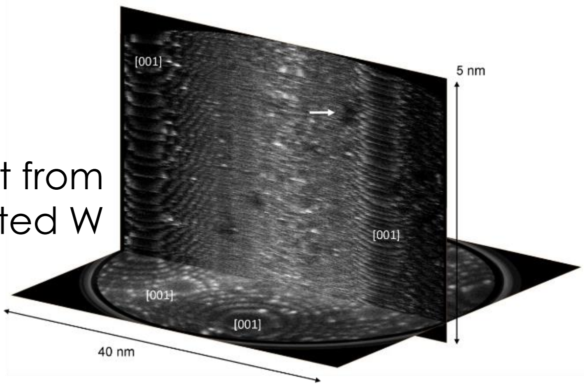


3D reconstruction of W

B. Claes

C. Hatzoglou

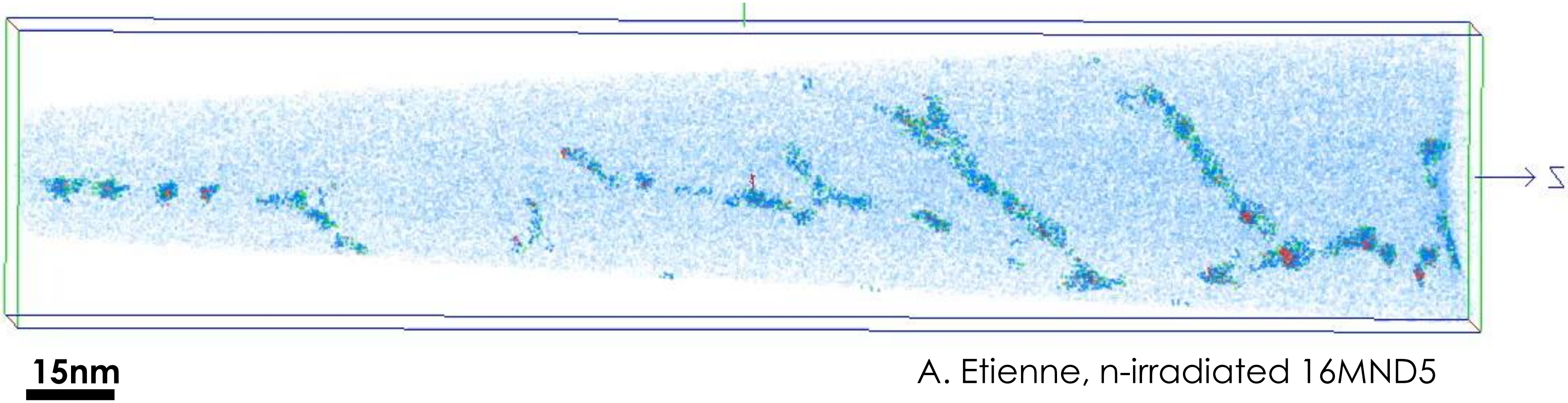
Dark contrast from nano-voids in irradiated W



Atom Probe Tomography

- Same principle than FIM but
  - No image gas (P~10^{-11}mbar)
    ➔ *Field evaporation of surface atoms*
  - Position sensitive detector
    ➔ *Localisation of atom position*
  - Time of flight mass spectrometry
    ➔ *Identification of the chemical nature*

➔ 3D reconstruction of the analysed volume, at atomic scale



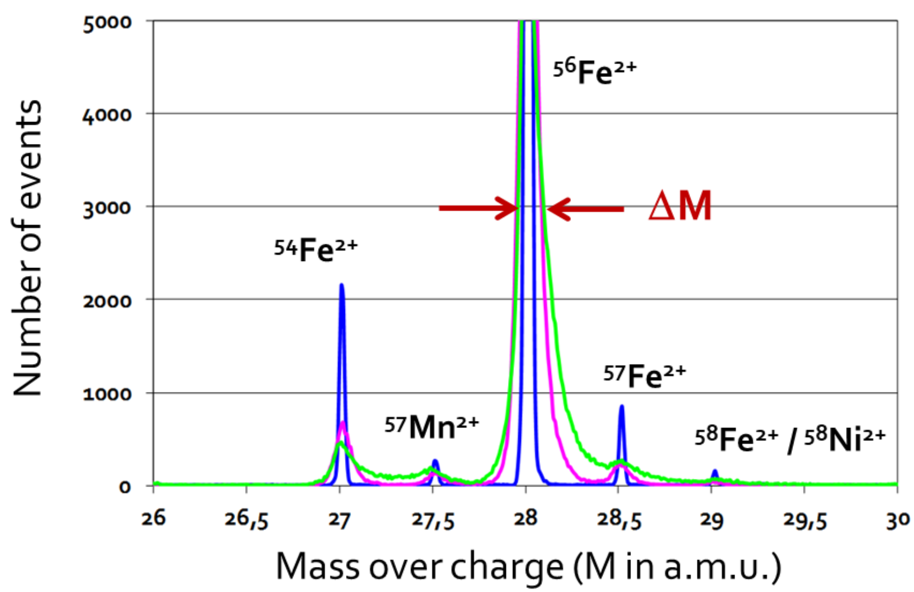
A. Etienne, n-irradiated 16MND5

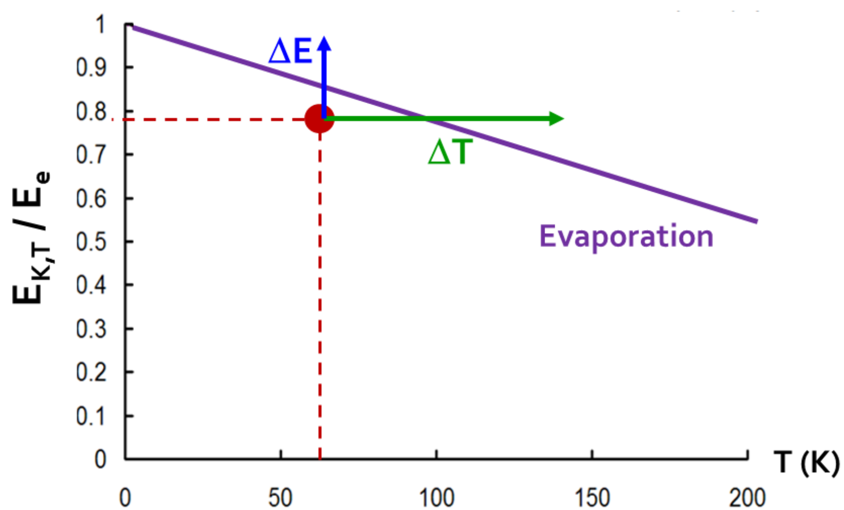
APT – tof mass spectrometry

- Assuming the whole potential energy if converted into kinetic energy :

$$\frac{m}{n} = 2eV\frac{t_f^2}{L^2} = kV\frac{t_f^2}{L^2}$$

- Evaporation pulse (laser or electric) is applied to the sample
  ➔ measurement of time-of-flight between pulse and arrival on detector

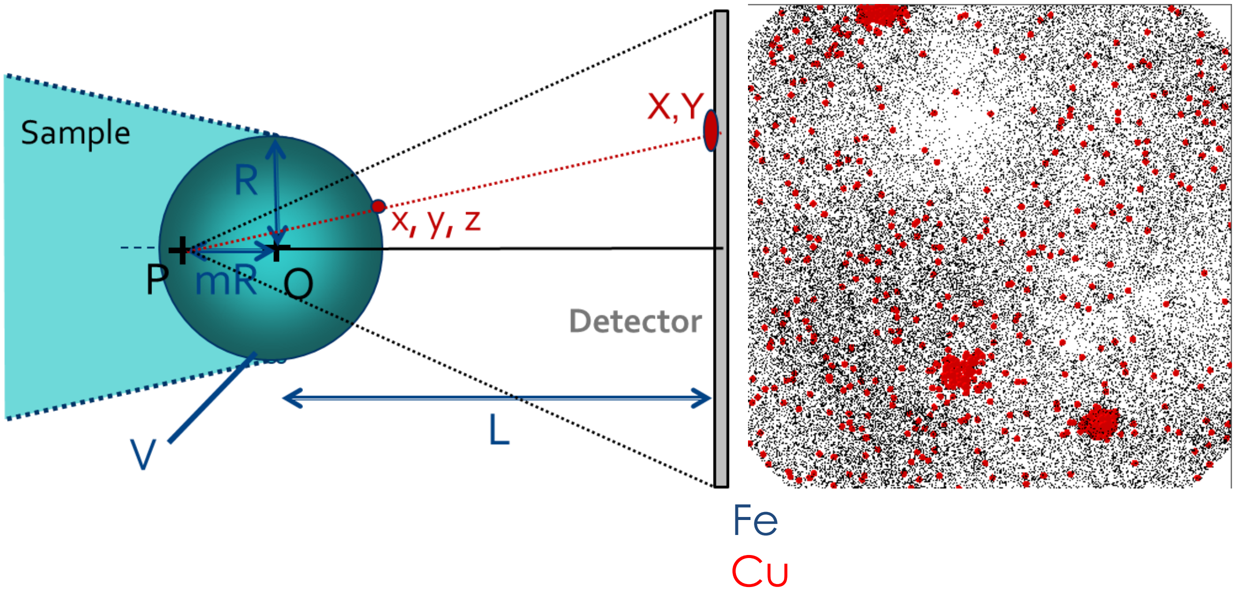




- Results are collected on a mass spectrum

APT – 3D reconstruction

Position sensitive detector + inverse projection ➔ Position of each atom at the surface



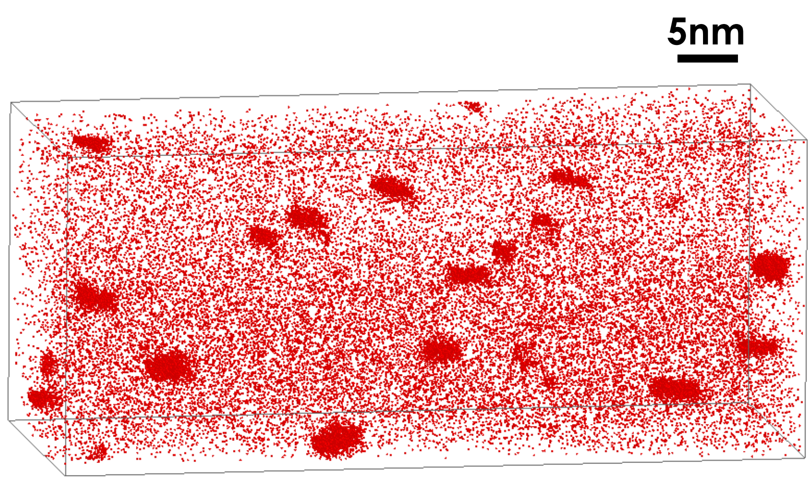
Magnification

$$G = \frac{L}{(m+1)R}$$

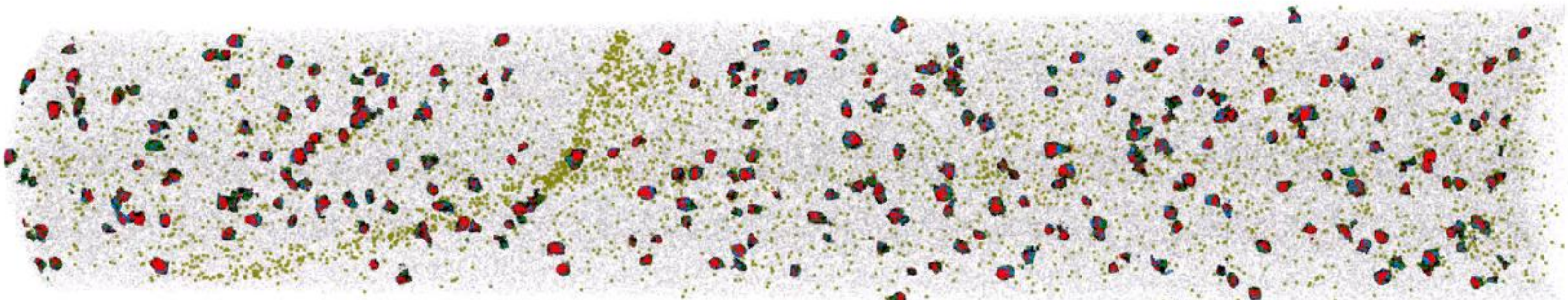
$G \sim 10^6 - 10^7$

For each detected atom, the reconstructed volume is incremented by V_{at}/Q

Knowing the analysed surface, it allows to reconstructed the 3rd dimension

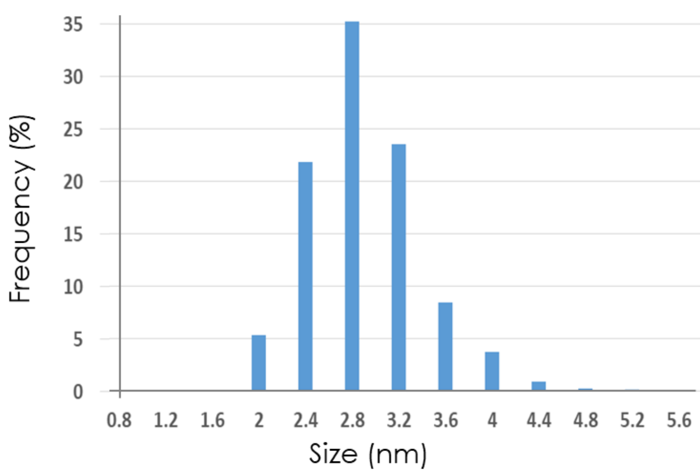


APT – n-irradiated RPV steel

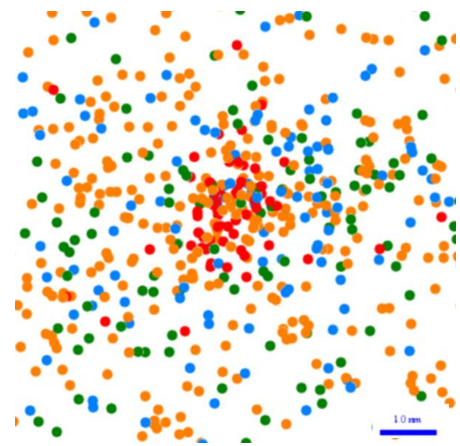


A. Etienne, SOTERIA, WP2 (RPV steel irradiated a high flux)

- **Solute clusters:**
  - composition: 2.6%Mn – 3.8%Si – 6.3%Ni – 5.3%Cu (Fe)
  - number density: 3.7×10^{23} m^{-3}
  - size distribution

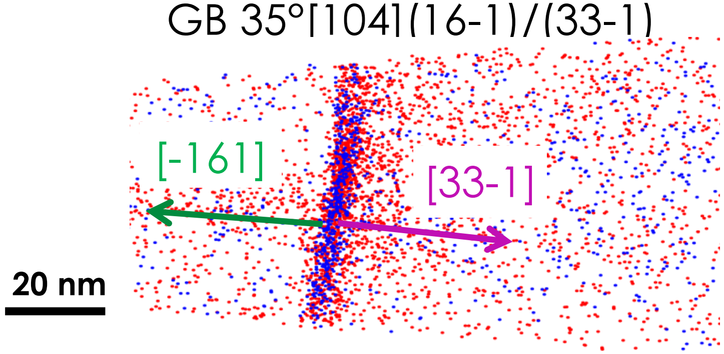


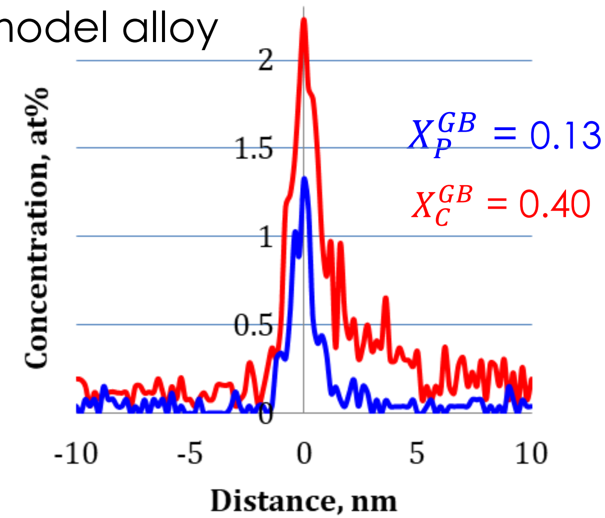
- **Segregation along dislocations:**
  - composition: 0.95%Mn – 1.1%Si – 2.4%Ni – 0.31%Cu – 3.9P – (Fe)
  - density: 1.1×10^{14} m^{-2}



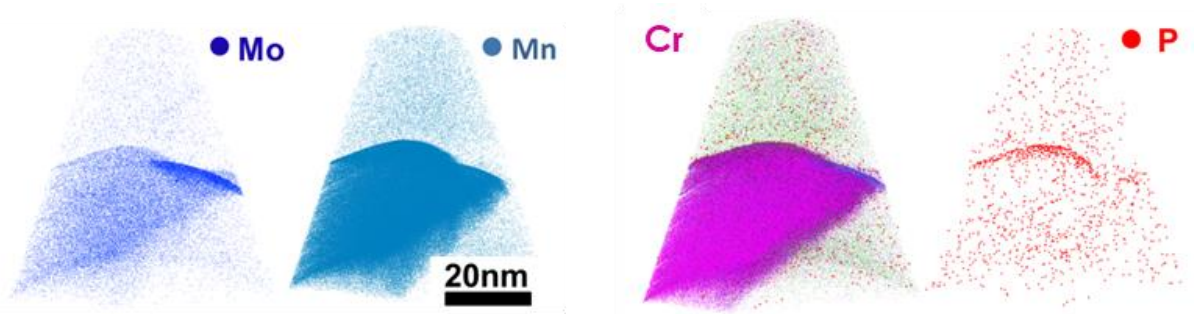
APT – GB and interfacial segregation

A. Akhatova: intergranular segregation in Fe-P-C model alloy





L. Zhang: P segregation at carbide-matrix interface in RPV weld



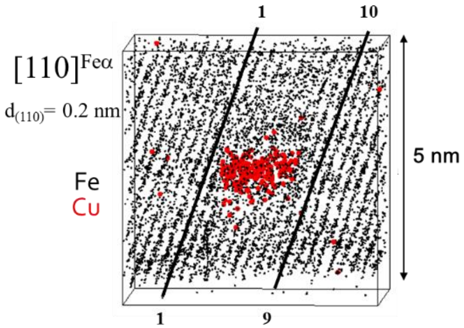
APT – Performances and limitations

Visible features

- Solute clusters and precipitates (0.5 – 50 nm): composition, number density, size distribution, shape, 3D repartition, volume fraction
- Segregation on crystal defects (dislocations, loops, GB…): density, composition, Gibbs excess…
- Matrix: chemical composition

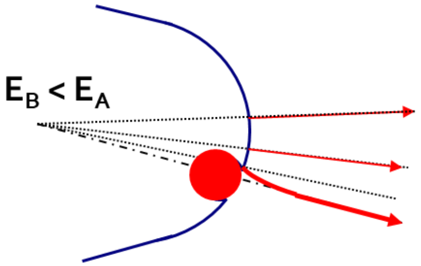
Performance

- detection efficiency: **35 to 80%**
- detection limit: **down 10 at. ppm in best cases**
- spatial resolution: **~ 0.2 nm in depth – 0.5-1nm laterally**
- Analysed volume: **~50x50x200 nm^3**

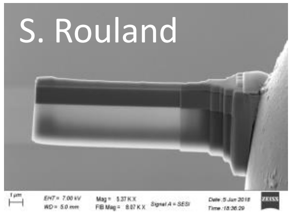


Limitations

- trajectory aberrations resulting from difference in evaporation field can induce bias atom positioning (shape of particles, chemical composition)



Transmission electron microscopy



3mm disk

❑ Sample:

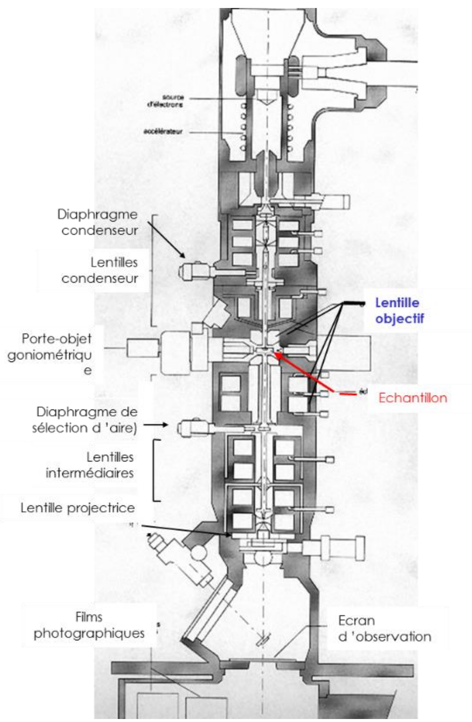
- in the shape of a thin foil (<100nm in thickness),
- under secondary vacuum (~10^{-5}-10^{-7}mbar),
- illuminated by electron beam (several10th to 100th of keV).

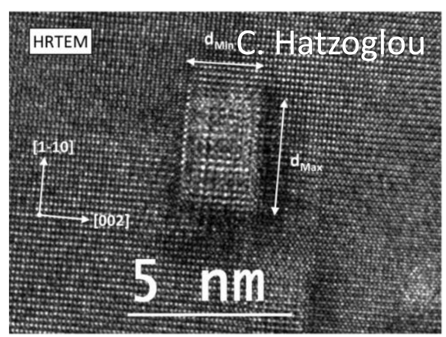
❑ Interaction electron-matter

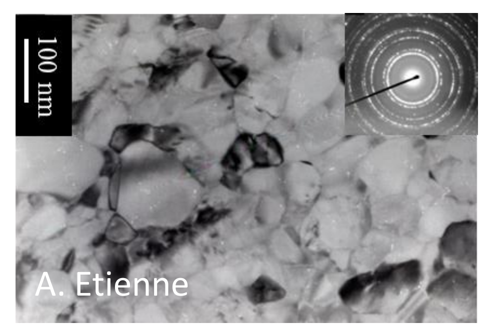
- diffraction, mass-thickness, phase contrasts
- energy loss, X-ray emission

❑ Image in transmission that can reach atomic resolution

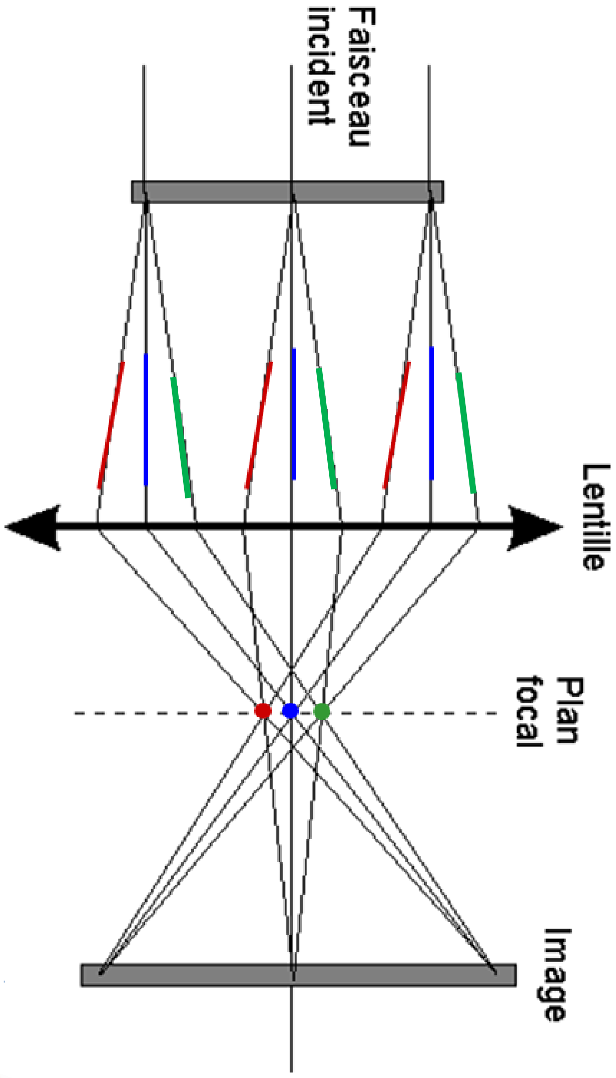
- information about phases, grain size, crystal defects…
- Chemical analysis possible with specific detectors





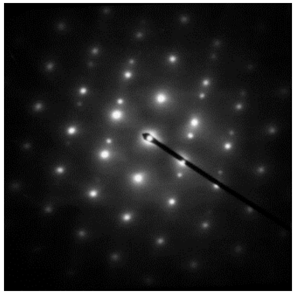


Diffraction contrast



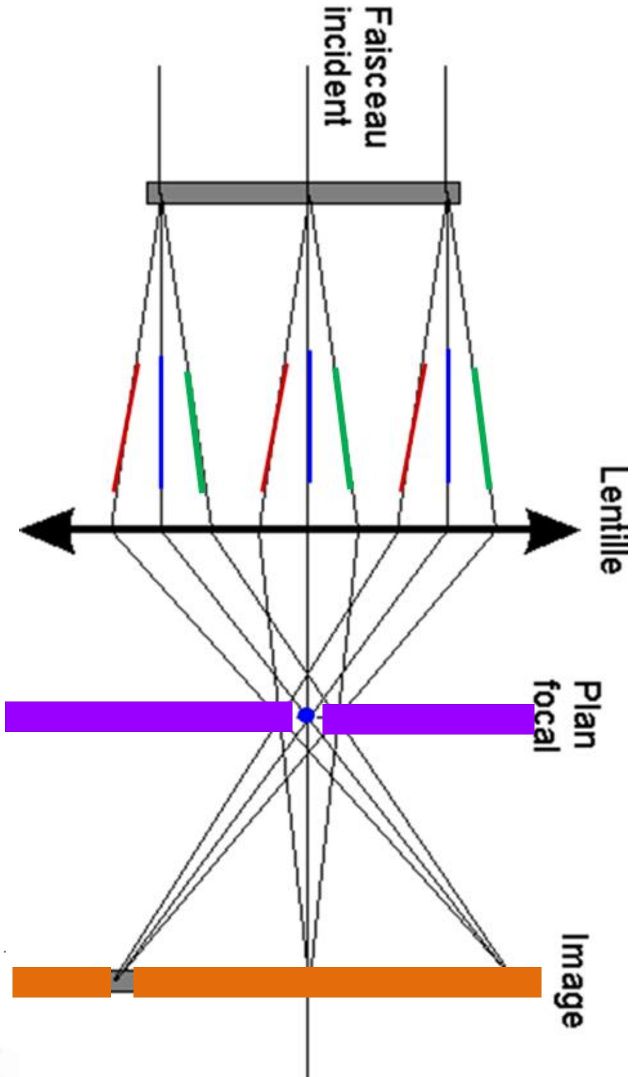
- A parallel beam of electrons can be diffracted by a family of reticular planes (hkl) in Bragg conditions
  - Electron non- diffracted converge to the center or the focal plane
  - Diffracted electrons by the same plane family converge to the same point of the focal plane.

    ➔ **Diffraction pattern in the focal plane**



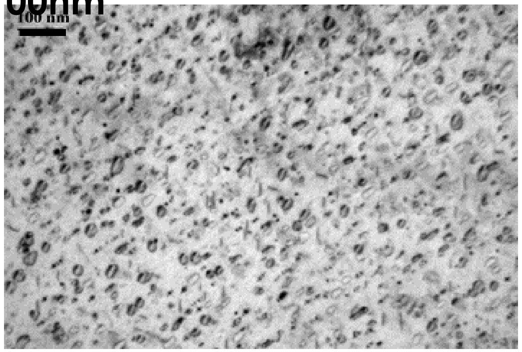
- Each electron coming from a same point of the sample converge on same point of image plane forming the **image into image plane of the objective**

Diffraction contrast

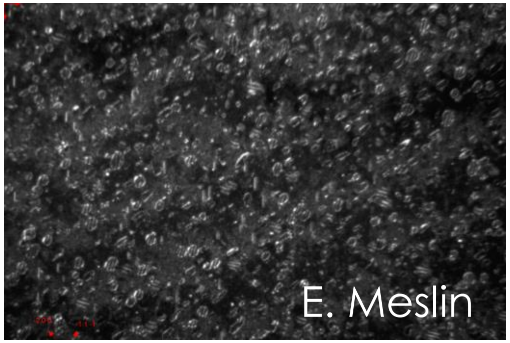


- The contrast is obtained by mean of **contrast aperture** located in the focal plane of the objective. This aperture allows to select electrons from direct beam or from one of the diffracted beam.
  - ➔ **Deficit or excess of electrons at the location of diffracting zones that appear more or less bright.**

BF



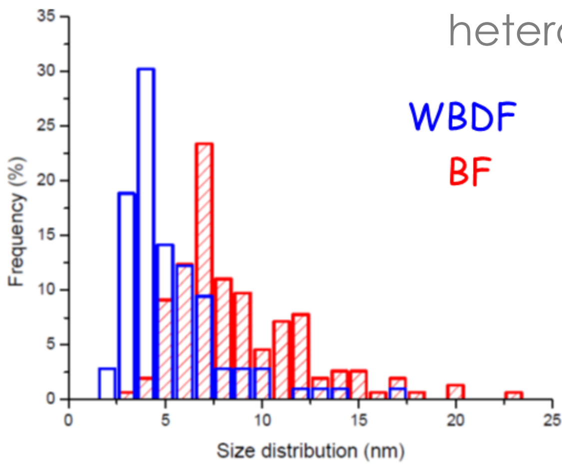
DF



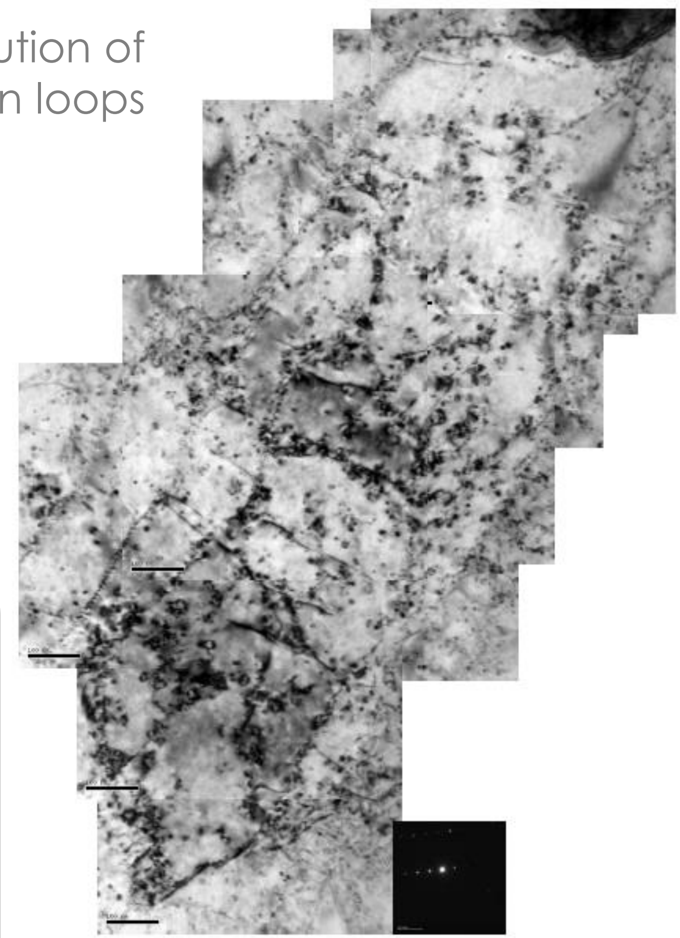
- The **area selection aperture** is located in the **image plane** of objective lens. It allows to select electrons coming from a give, area.
  - ➔**selection of the imaged area**

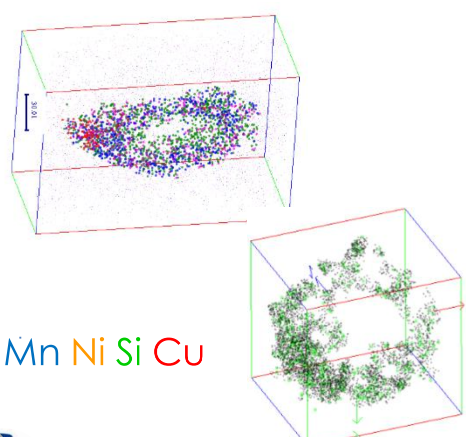
TEM - Example

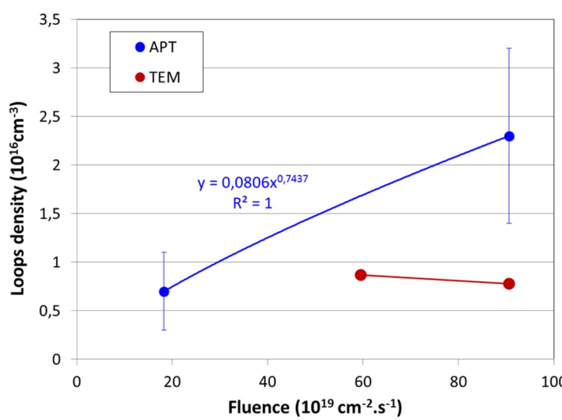
FP7 Longlife, D3.3 – RPV steel, n-irradiated at high dose (M. Mayoral)



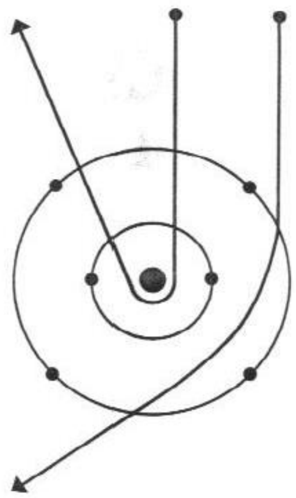
heterogeneous distribution of
dislocation loops







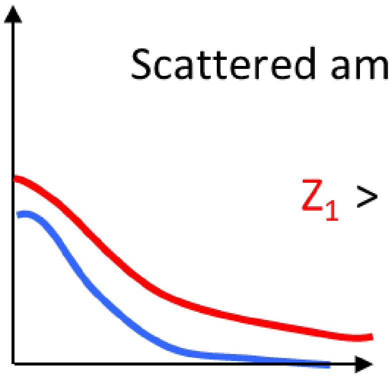
Mass - thickness contrast



- Elastic scattering of results from interaction of incident electrons with electronic cloud or atom nucleus.

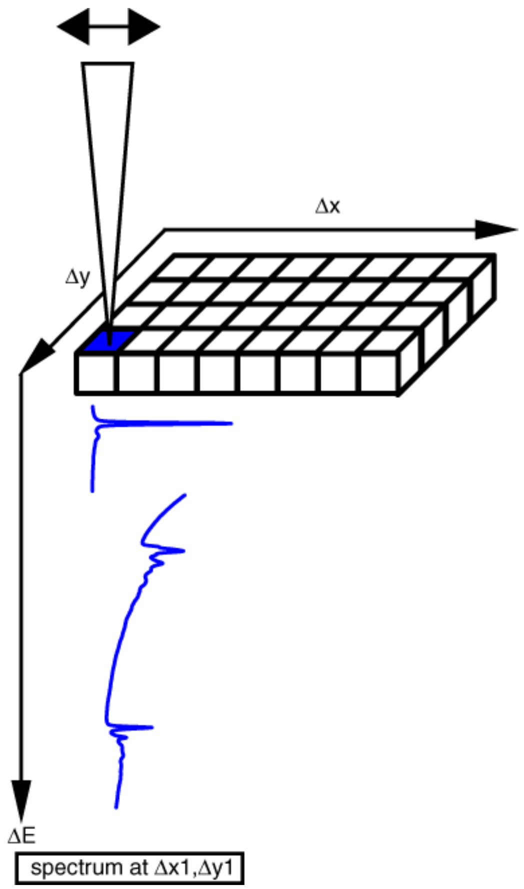
- It increases with:
  - Atomic number (Z)
  - Thickness of the sample

➔ **Through areas with high atomic number, electrons are more diffused (Z contrast)**



Scanning TEM

- The incident beam is focused on a point of the sample (probe)
- The probe (<1nm) is scanned on the sample
- For each location, different signals can be collected to form the image



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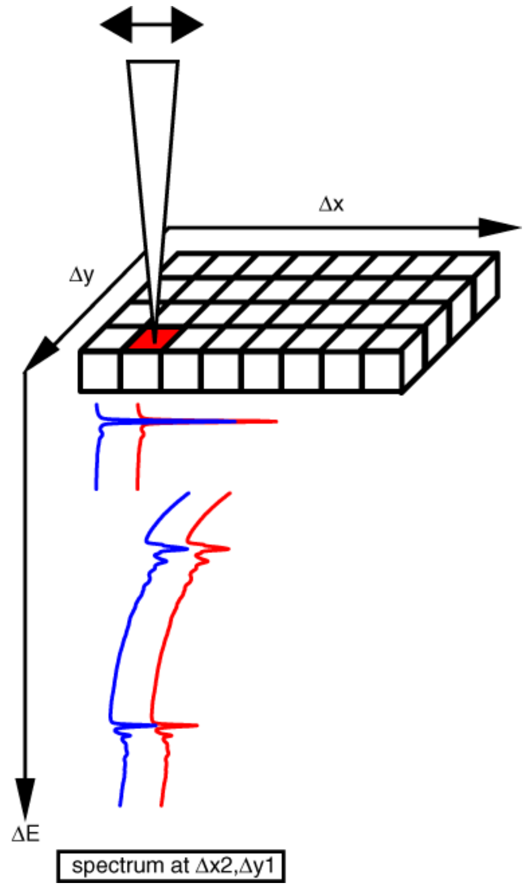

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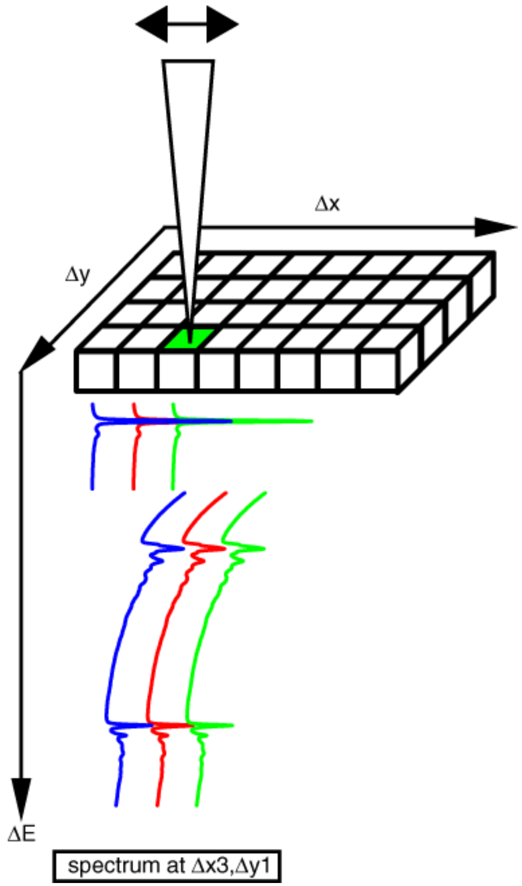
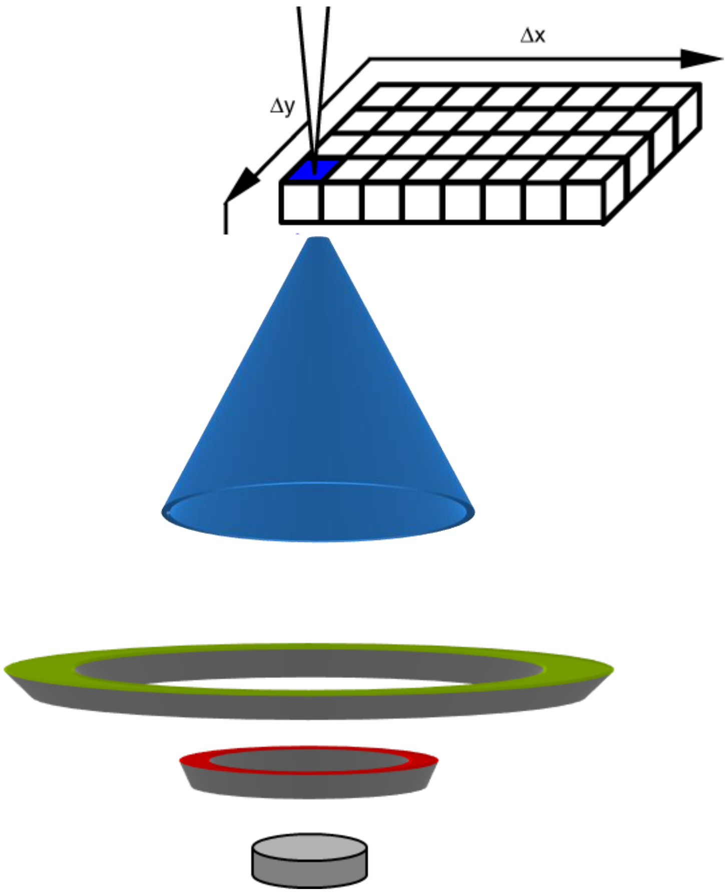


Contrast in STEM

Contrast on image is obtained thanks to annular detectors



High Angle Annular Dark Field (HAADF) detector

➔ **Heavy elements appear bright (Z-contrast)**

Low Angle Annular Dark Field (ADF) detector

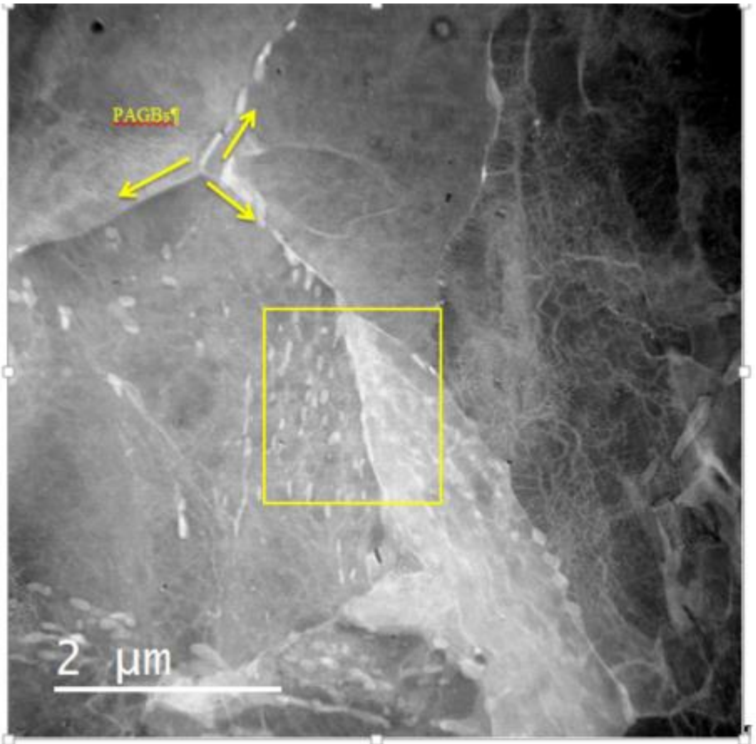
➔ **crystal defects bright (diffraction contrast)**

Bright Field (BF) detector

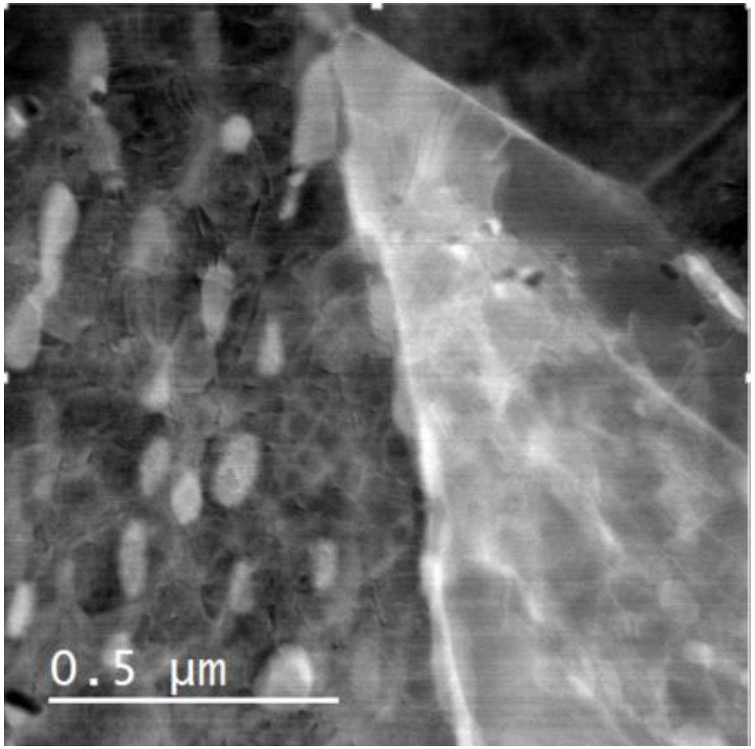
➔ **Crystal defects and areas rich in heavy elements appear dark**

Example

O. Startev et al, SOTERIA WP3

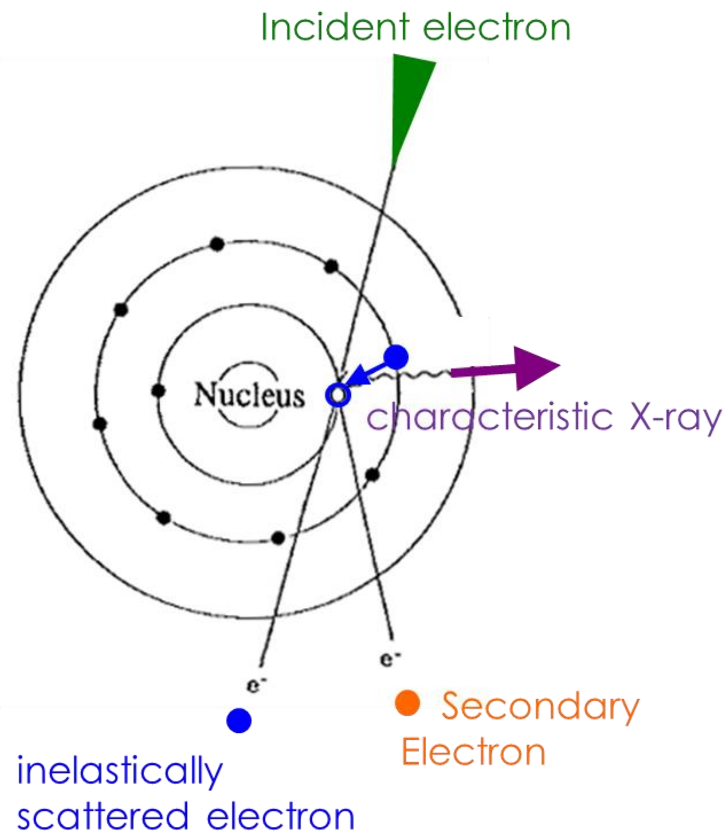


HAADF image of RPV steel



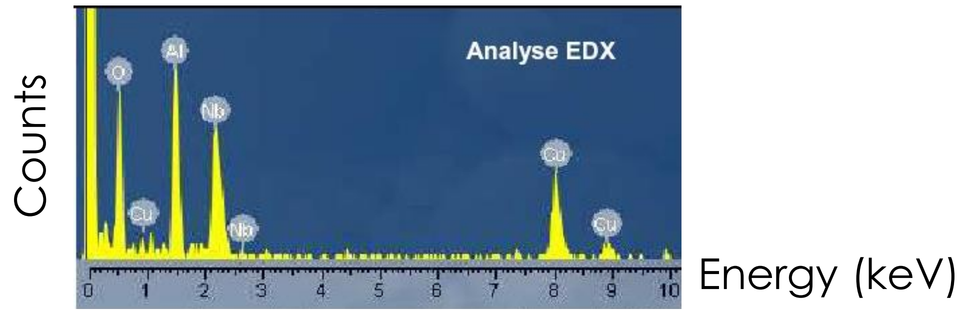
➔ **PAGB, lath boundaries and carbides**

Chemical analysis

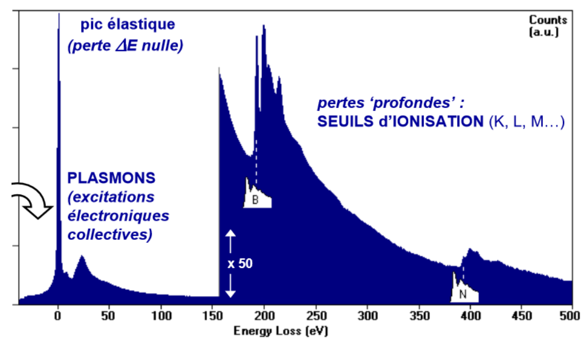


Inelastic interaction between incident electrons and electron clouds

Energy Dispersive Spectrometry (EDS)



Electron Energy Loss Spectrometry (EELS)



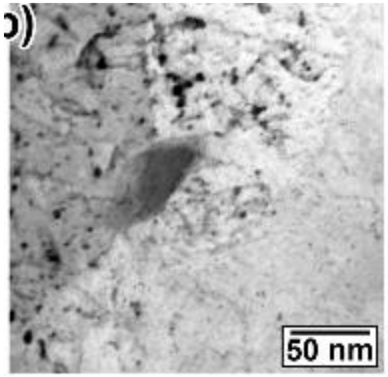
➔ **chemical mapping – Chemical composition (in transmission)**

Example

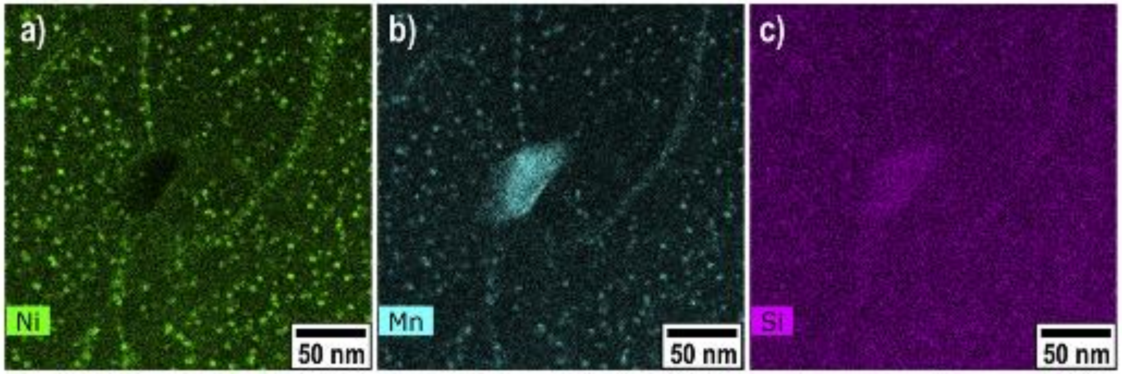
P. Edmondson et al, Acta Materialia (2017)

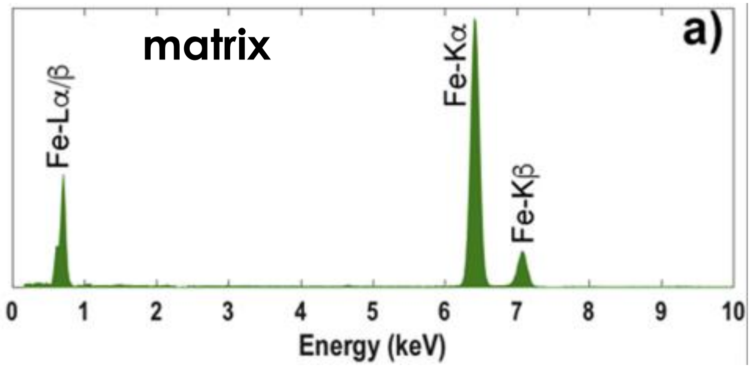
STEM EDS on n – irradiated high Ni weld

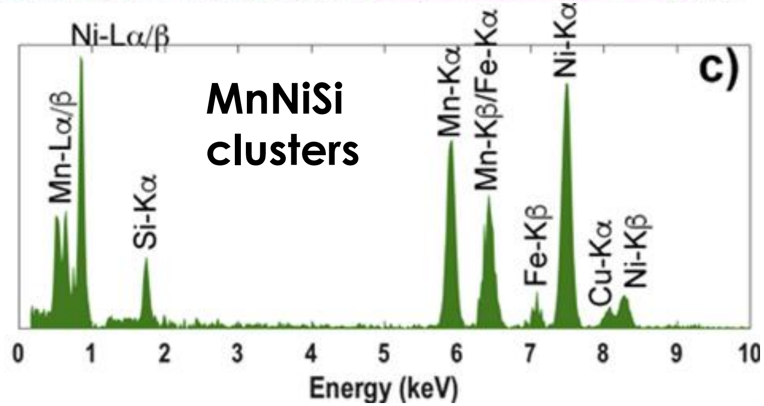
STEM BF



STEM EDS







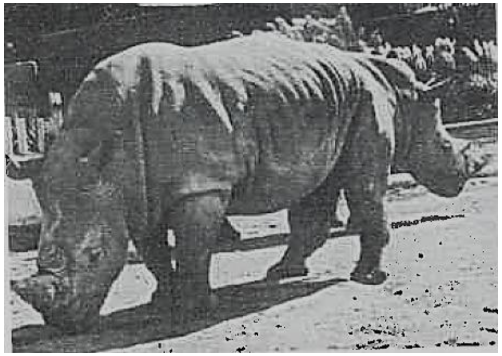
➔ correlation between crystalline et chemical information

(S)TEM – Performances and limitations

- Visible features
  - Crystalline defects (GB, dislocations, dislocation loops, voids…): Size distribution (> 1nm), number density
  - Precipitates: Size distribution (> 1nm), number density, chemical information (2D)
  - Segregation: chemical information

- Performance
  - detection limit: **~ 1% (EDS)**
  - spatial resolution: **~ 0.2 nm**
  - Analysed volume: **<100nm in depth x several μm^2**

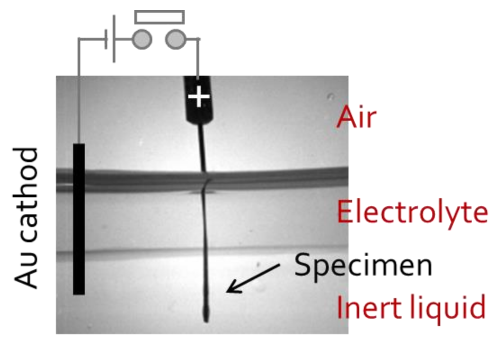
- Limitations
  - 2D image in transmission

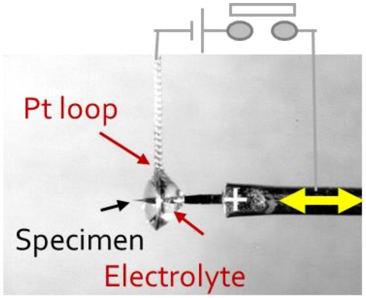


Sample preparation

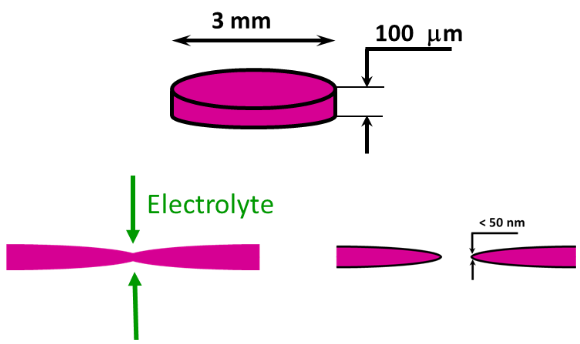
- Needs of very thin samples for FIM, APT and TEM (foil or needle)
- Electropolishing

APT needle: double layer, µloop





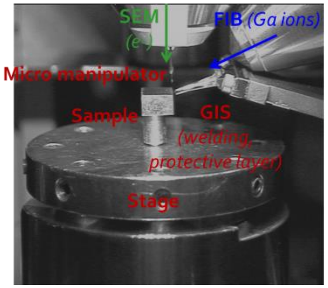
TEM foil: twin jet

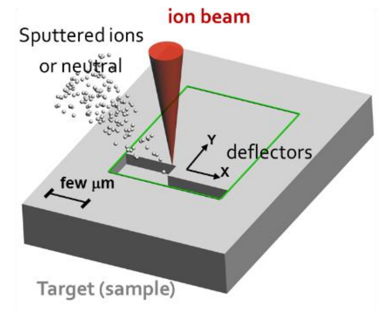


- "high" quantities of matter – can be a limitation for radioactive samples
- No control on the sample exact location
- limited to metals

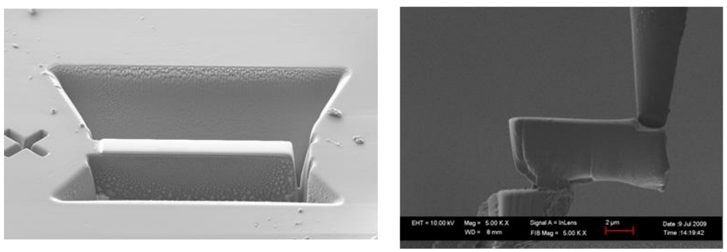
Sample preparation

- Focused Ion Beam milling:
  - Sputtering of sample atoms using ion beam (FIB)
  - Imaging using electron beam (SEM)

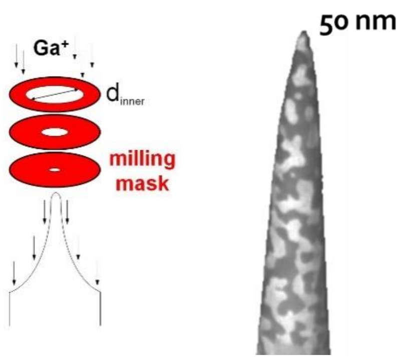




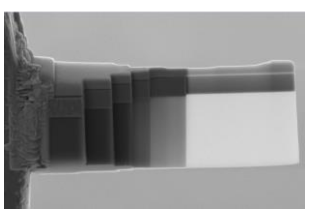
- Lift out



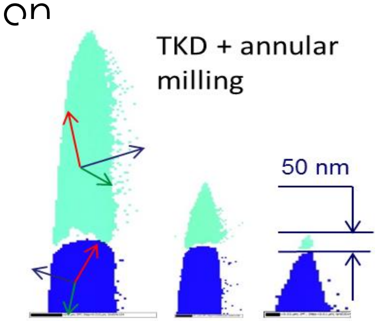
- Annular milling (neeles)



- TEM foil milling



- Reduce the amount of matter needed
- Applicable to all kinds of materials
- Control on the sample location



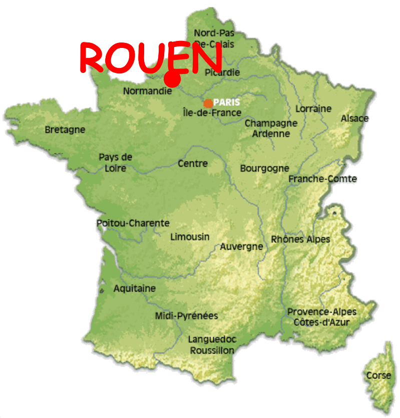
- Ga implantation !

Summary

Technique	Sample shape	Analysed volume	Crystal defects	Segregations	Precipitates Solute clusters
3D-FIM	thin needle	50x50x200nm^3	- dislocation, GB visible - voids (0.5-few nm): SD, ND	/	- visible in some cases
APT	thin needle	50x50x200nm^3	- visible if segregated	- shape, CC, ND	- SD (0.5-50nm), ND, CC, shape
(S)TEM	thin foil	20-100nm thick several µm^2	- GB - dislocation (D) - loops, voids, SFT (ND, SD) if > 1nm	- intergranular segregation: concentration profile	If size > 1nm - 2D chemical mapping - crystalline structure - information about CC
PAS	well polished plate	0-0.5mm depth several mm^2	- V-type (from mono-V to nm voids): Size and chemical env.	/	/
SANS	bulk	cm^3	/	/	- SD (1-100nm), f_v, CC range

CC = chemical composition / SD = Size distribution / ND = number density / CC = chemical composition
f_v = volume fraction

Thank you for you attention

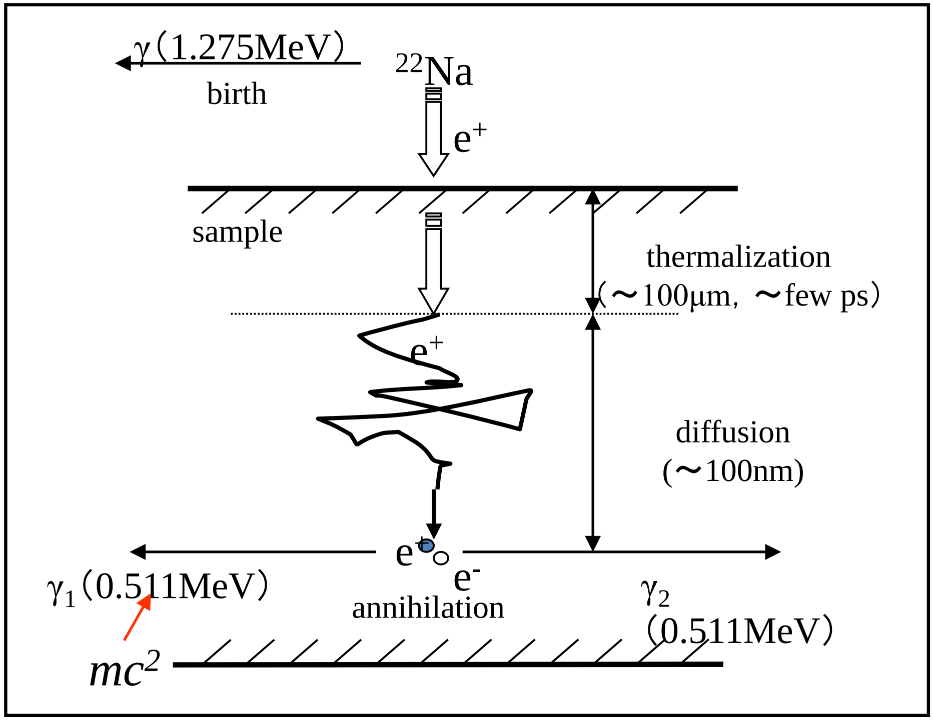


http://gpm.labos.univ-rouen.fr/
http://genesis.univ-rouen.fr/

bertrand.radiguet@univ-rouen.fr

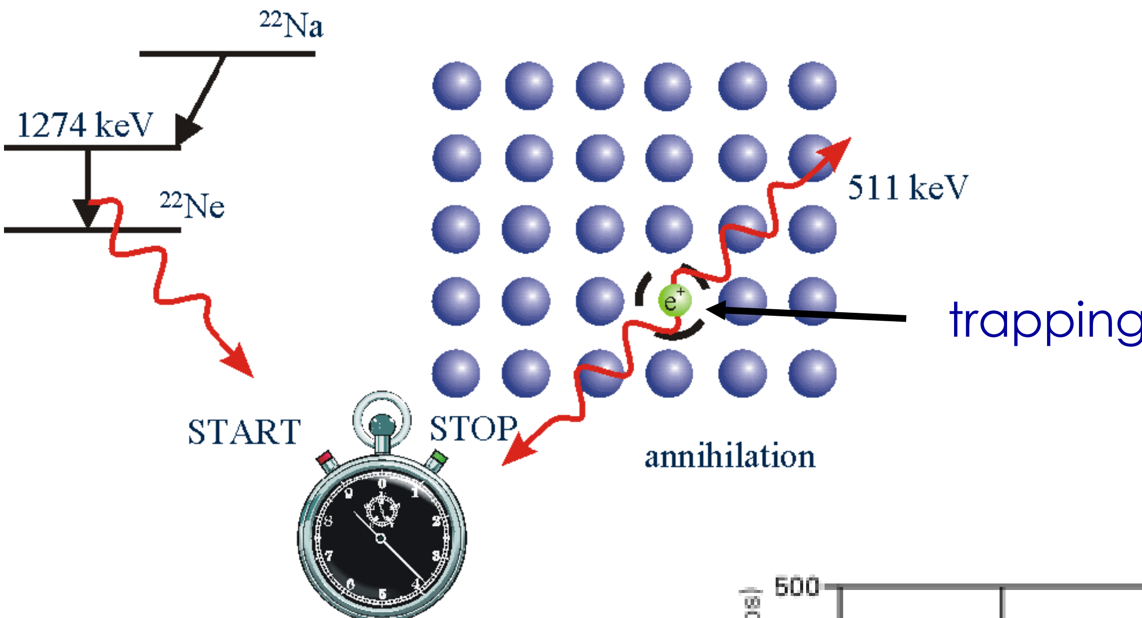
Additional slides

Positon Annihilation Spectroscopy

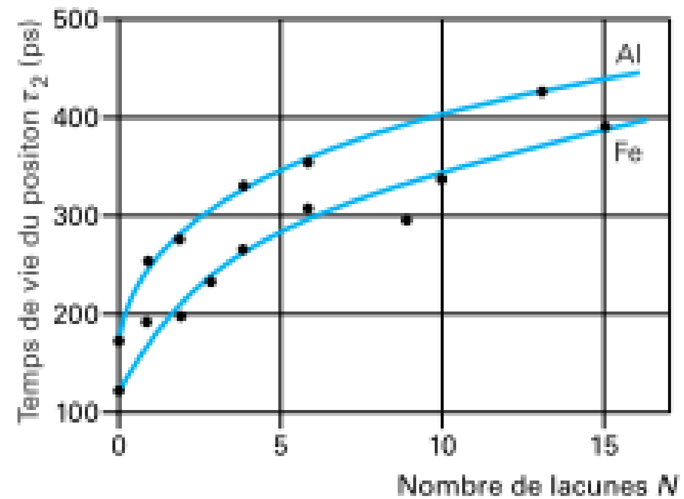


- Positons (emitted by the desintegration of a radioelement) go through the sample
- After thermalisation, positons diffuse into the material where they can:
  - be trapped by vacancy-type defects
  - Annihilate with electrons from the material
- Annihilation results in the emission 2 photon in opposite directions

PALS

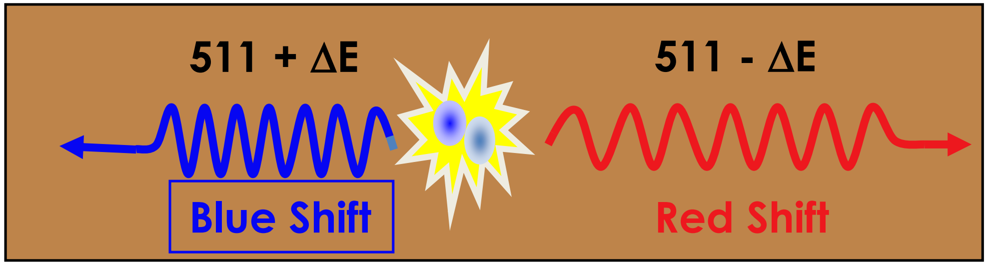


Life time ➔ size of vacancy clusters



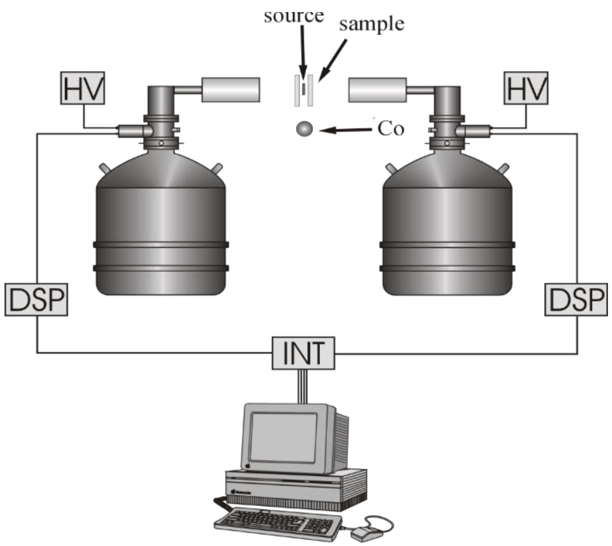
CBD

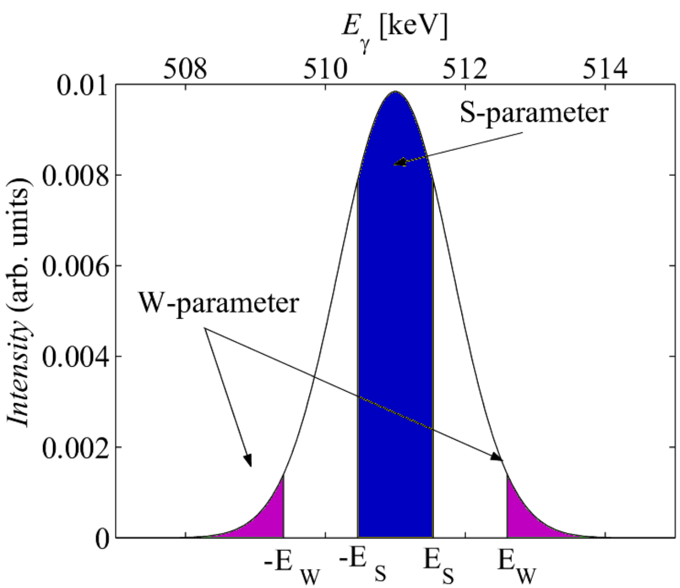
Doppler shift probes the local electron momentum



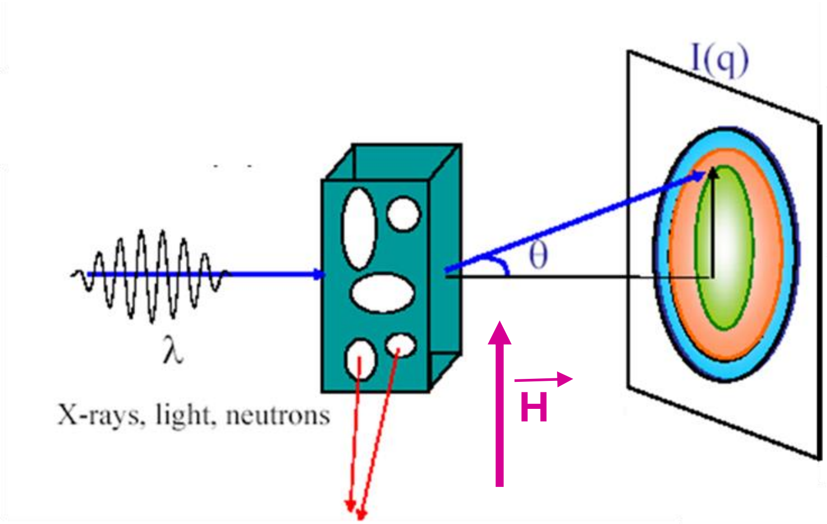
Doppler shift, ΔE is proportional to electron momentum, p_L

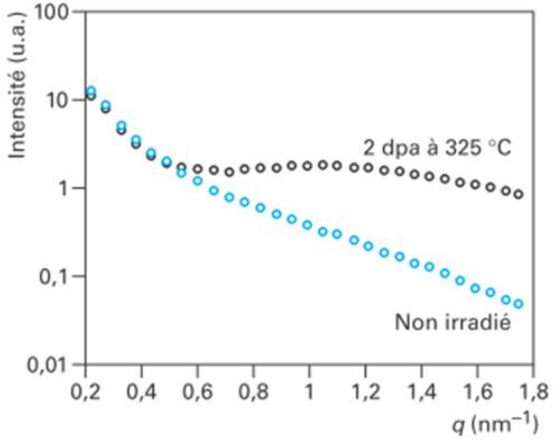
➔ **Depends of the chemical environment**





Small angle neutron scattering





Size, density, nature, shape

- Mono-energetic neutron beam goes through a bulk sample
- Scattered intensity as a function of scattering angle contain information about size distribution, shape and volume fraction of features

$$I(\vec{q}) \approx f_p(\Delta\rho^2_{nuc} + \Delta\rho^2_{mag}\ \sin^2\alpha)\left|F_p(R,\vec{q})\right|^2 S(\vec{q})$$

- A-ratio contains information about chemical composition of features