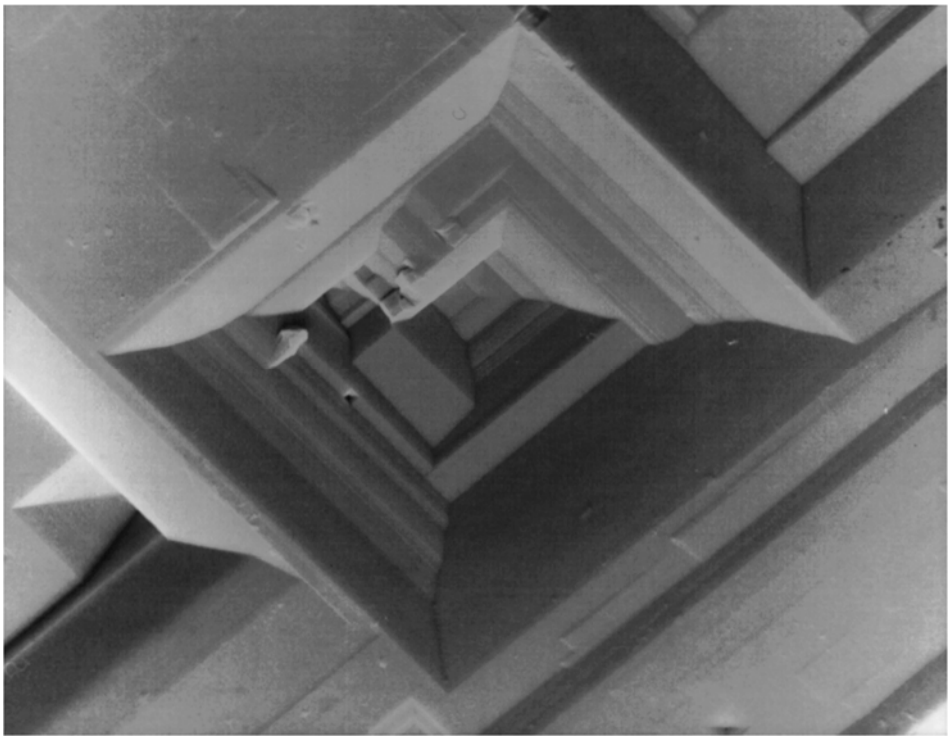
Electron Microscopy

SEM

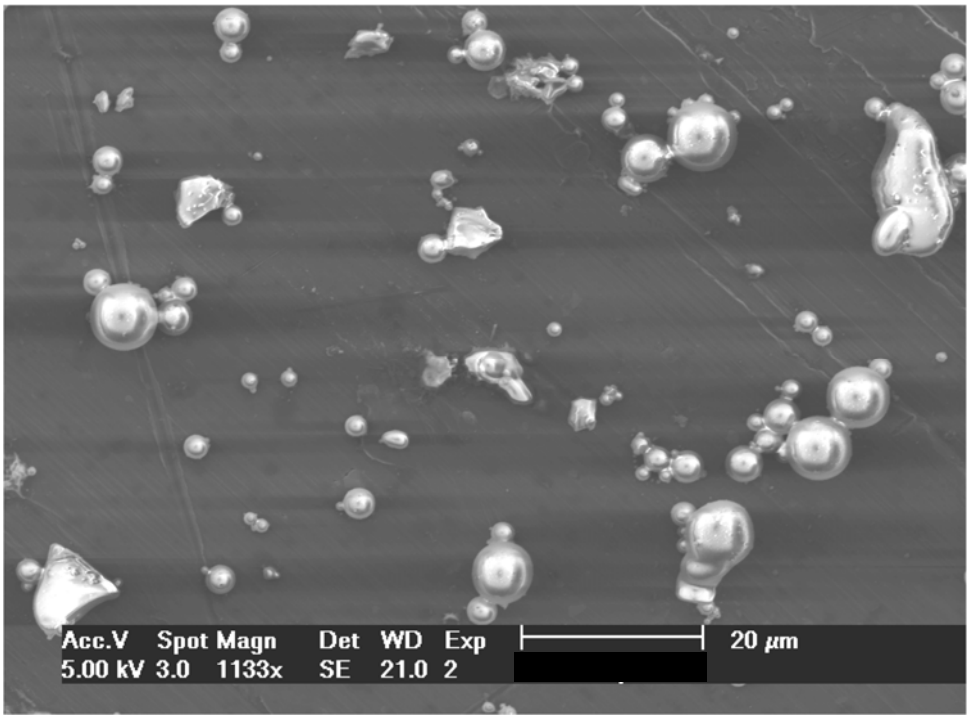
Image formation, detection,
resolution, signal to noise ratio,
interaction volume,
contrasts

SEM is easy! Just focus and shoot "Photo"!!!



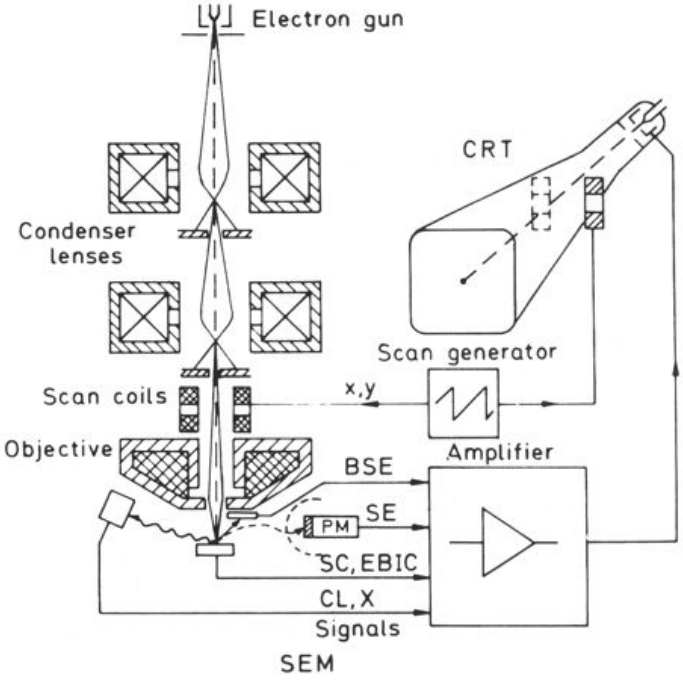
Any idea what it might be???

SEM is easy! Just focus and shoot "Photo"!!!

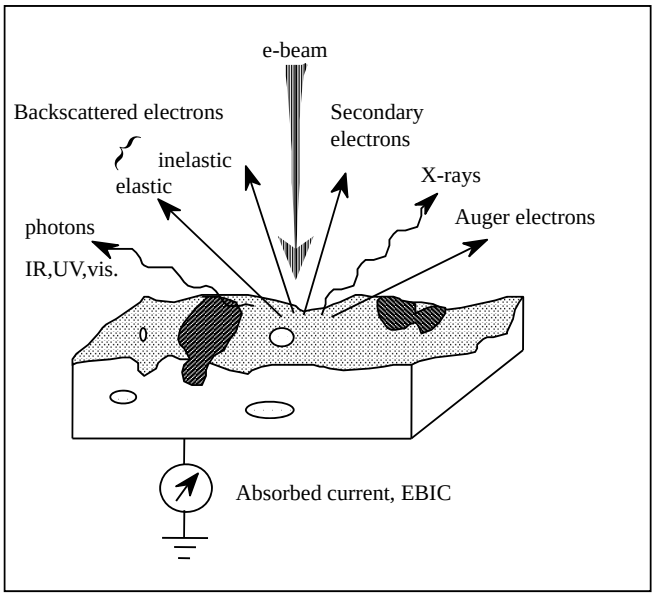


At least this one??

Image formation



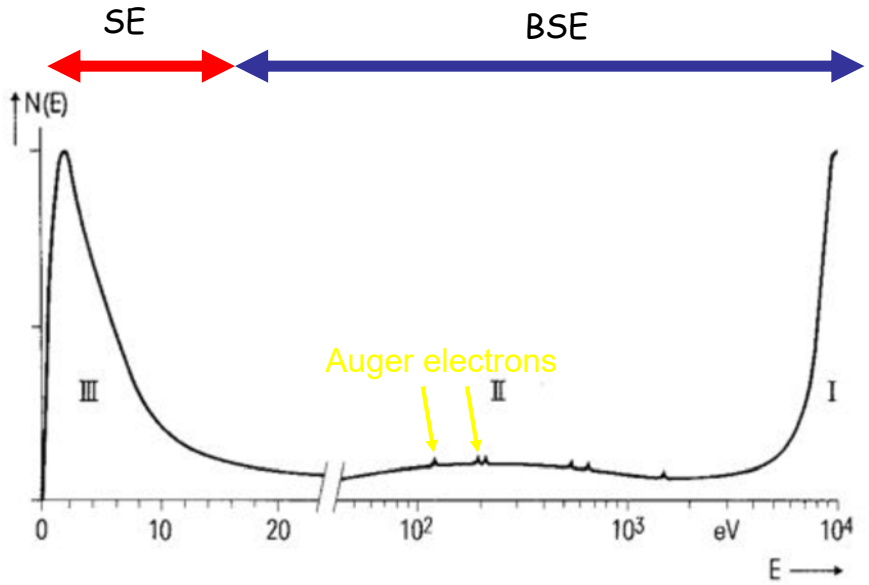
SEM, signals



- Secondary electrons (~0-30eV), **SE**
- Backscattered electrons (~eVo), **BSE**
- Auger electrons
- Photons: visible, UV, IR, **X-rays**
- Phonons, Heating
- Absorbtion of incident electrons (EBIC-Current)

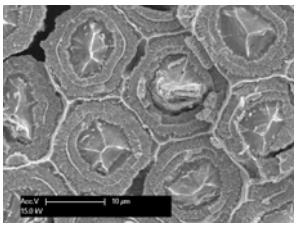
SEM imaging with electrons

- Energy spectrum of electrons leaving the sample

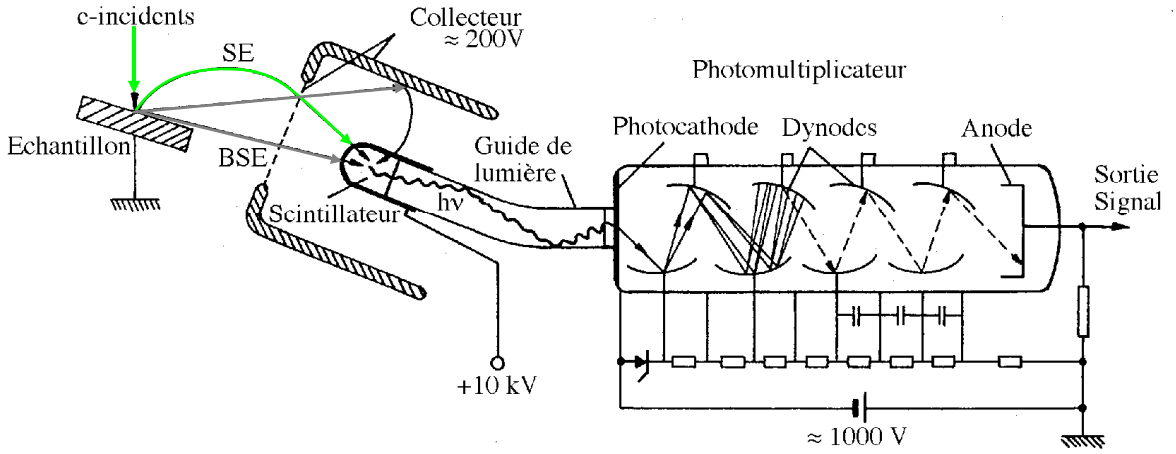


SE: secondary electrons 0-50eV
BSE: backscattered electrons E>50eV

Electron detectors

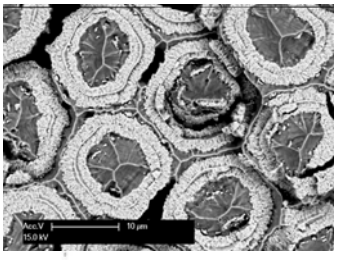


- Photomultiplier
- Everhart-Thornley detector

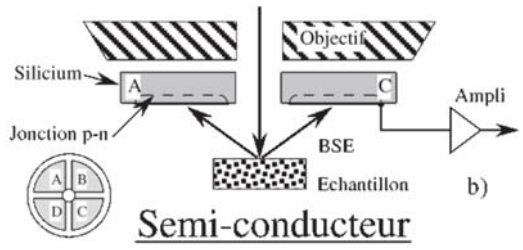


Collects and detects lower energy (<100eV) electrons: SEM backscattered electrons

Electron detectors



- semiconductor



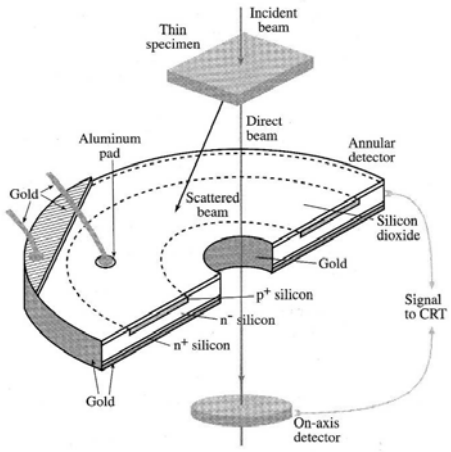


Figure 7.1. Semiconductor detector of the surface-barrier type, shown in a configuration where it would be used to detect high-energy forward-scattered electrons. The direct beam is detected by a small circular detector on the optic axis surrounded by a concentric wide-angle annular detector, which detects any scattered electrons.

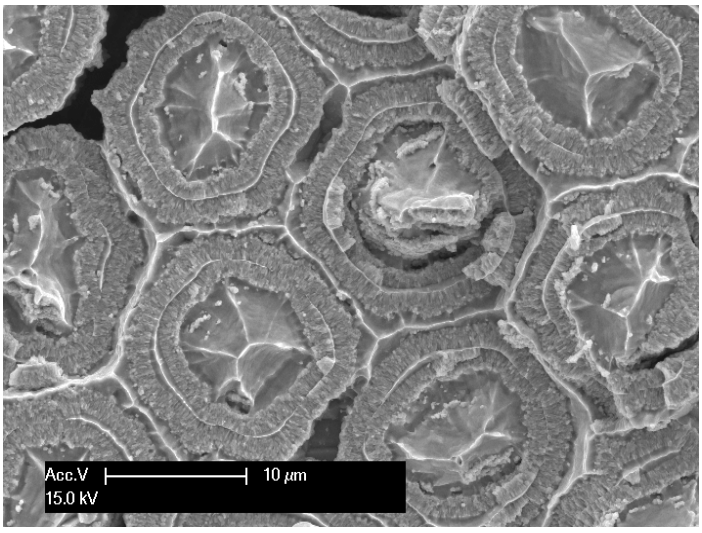
BSE semiconductor detector: a silicon diode with a p-n junction close to its surface collects the BSE (3.8eV/ehole pair)

- large collection angle
- slow (poor at TV frequency)
- some diodes are split in 2 or 4 quadrants to bring spatial BSE distribution info

Detects higher energy (>5kV) electrons: SEM backscattered electrons

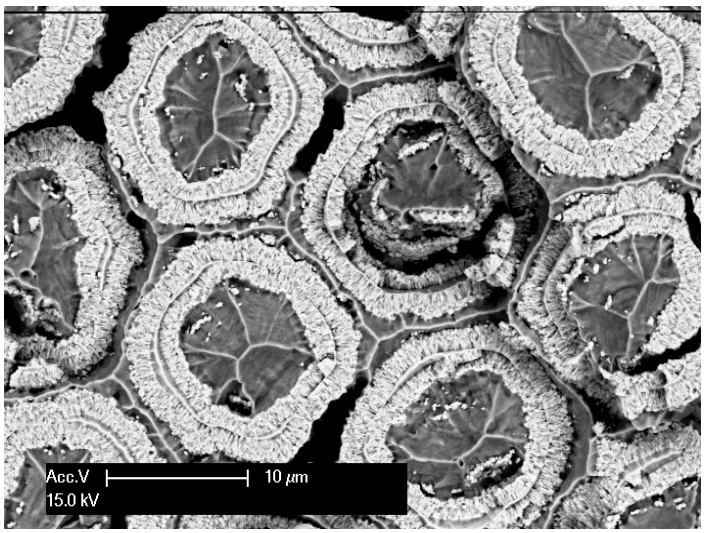
SEM, secondary electrons

- Electrons with low energy (0-50eV) leaving the sample surface
- Intensity depends on inclination of the surface
- topography



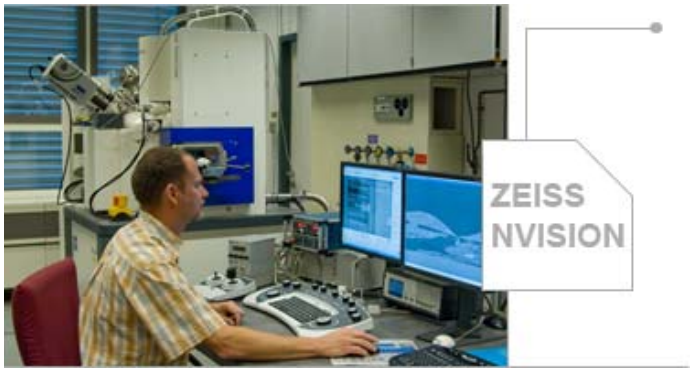
SEM, backscattered electrons

- Electrons with high energy (~Eo) backscattered from below the surface
- Intensity depends on density (atomic weight)
- ~composition



Nb_3Sn in Cu matrix

Some typical SEM



At CIME:
Zeiss NVision40
(FIB)

Zeiss Ultra
HR-SEM

Resolution

1.0 nm @ 15 kV, 1.7 nm @ 1 kV, 4.0 nm @ 0.1 kV

Magnification12 - 900,000x in SE mode
Acceleration Voltage0.02 - 30 kV

Probe Current4 pA - 10 nA

Standard Detectors:
EsB Detector with filtering grid
High efficiency In-lens SE Detector
Everhart-Thornley Secondary Electron Detector

SEM: Limiting parameters on resolving power

1. ***High magnification***

   The probe size (generation of SE1)

   The instrument

   $r \approx d_{probe}$

2. **The volume of interaction (generation of SE2+SE3 from BSE)**

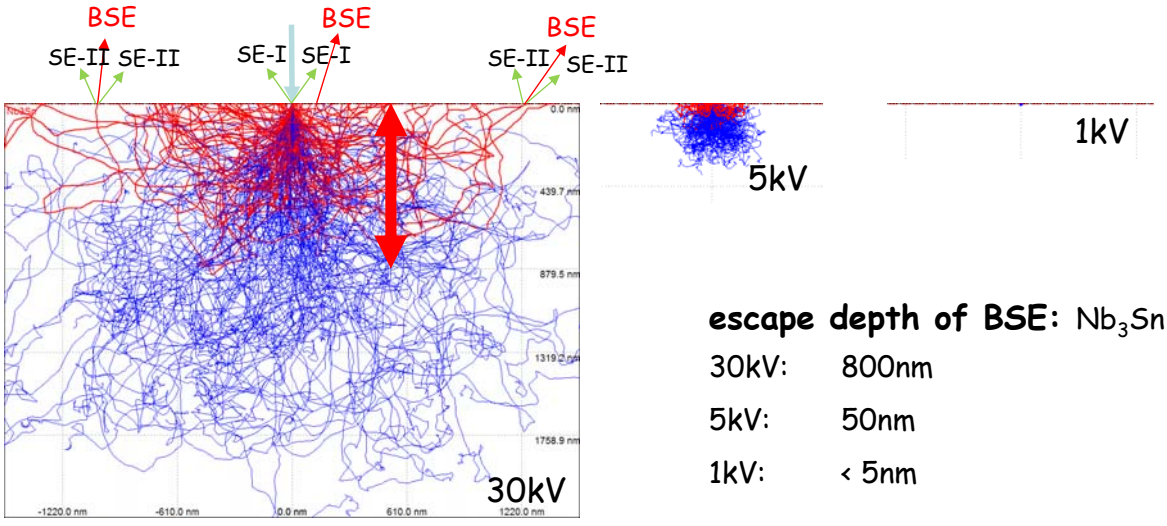
   The sample

The interaction volume: Monte-Carlo simulations

- **Electron Flight Simulator** ($$$ **Small World /** D. Joy)
  - old… DOS !!!!
  - **http://www.small-world.net**
- **Single Scattering Monte Carlo Simulation** (Freeware)
  - **"Monte Carlo Simulation" Mc_w95.zip**
  - by Kimio KANDA
  - **http://www.nsknet.or.jp/~kana/soft/sfmenu.html**
- **CASINO** (Freeware)
  - **" monte CArlo SImulation of electroN trajectory in sOlids "**
  - by P. Hovongton and D. Drouin
  - **http://www.gel.usherbrooke.ca/casino/What.html**

SEM interaction volume

Electron trajectories in matter



escape depth of BSE: Nb_3Sn

30kV: 800nm

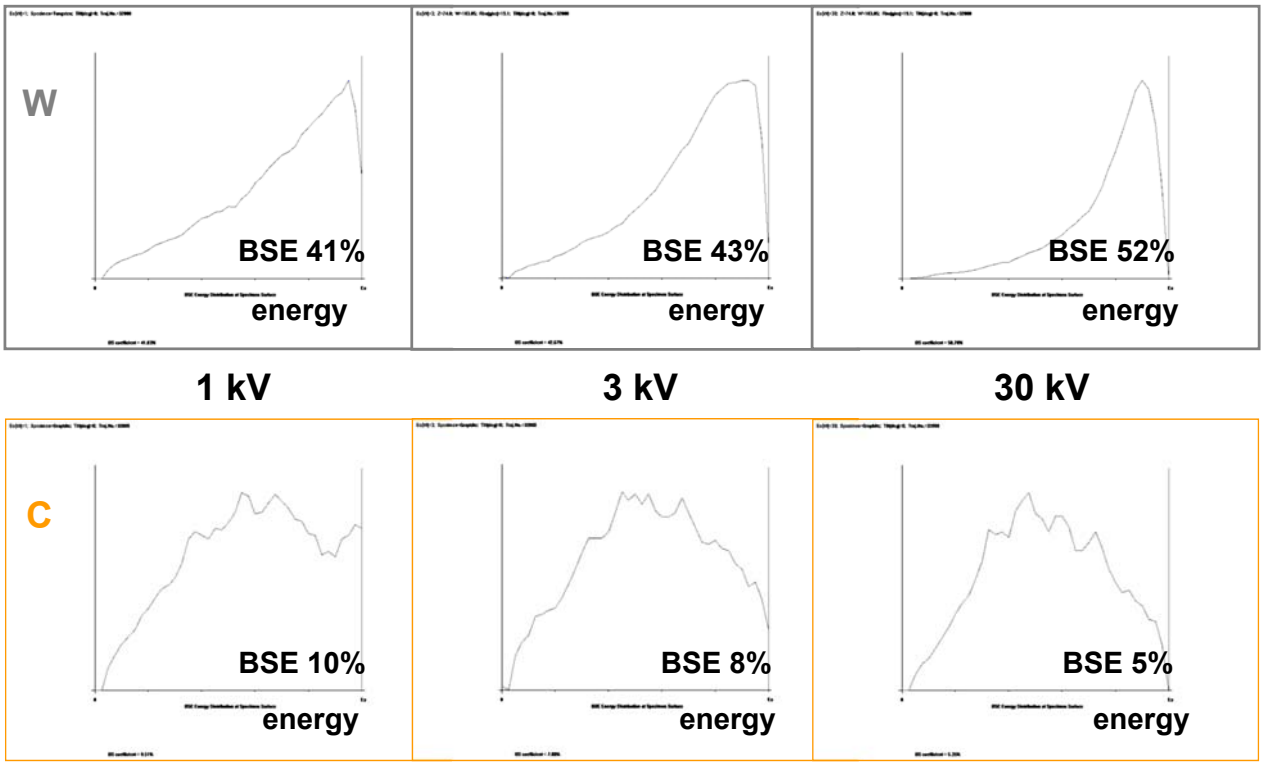
5kV: 50nm

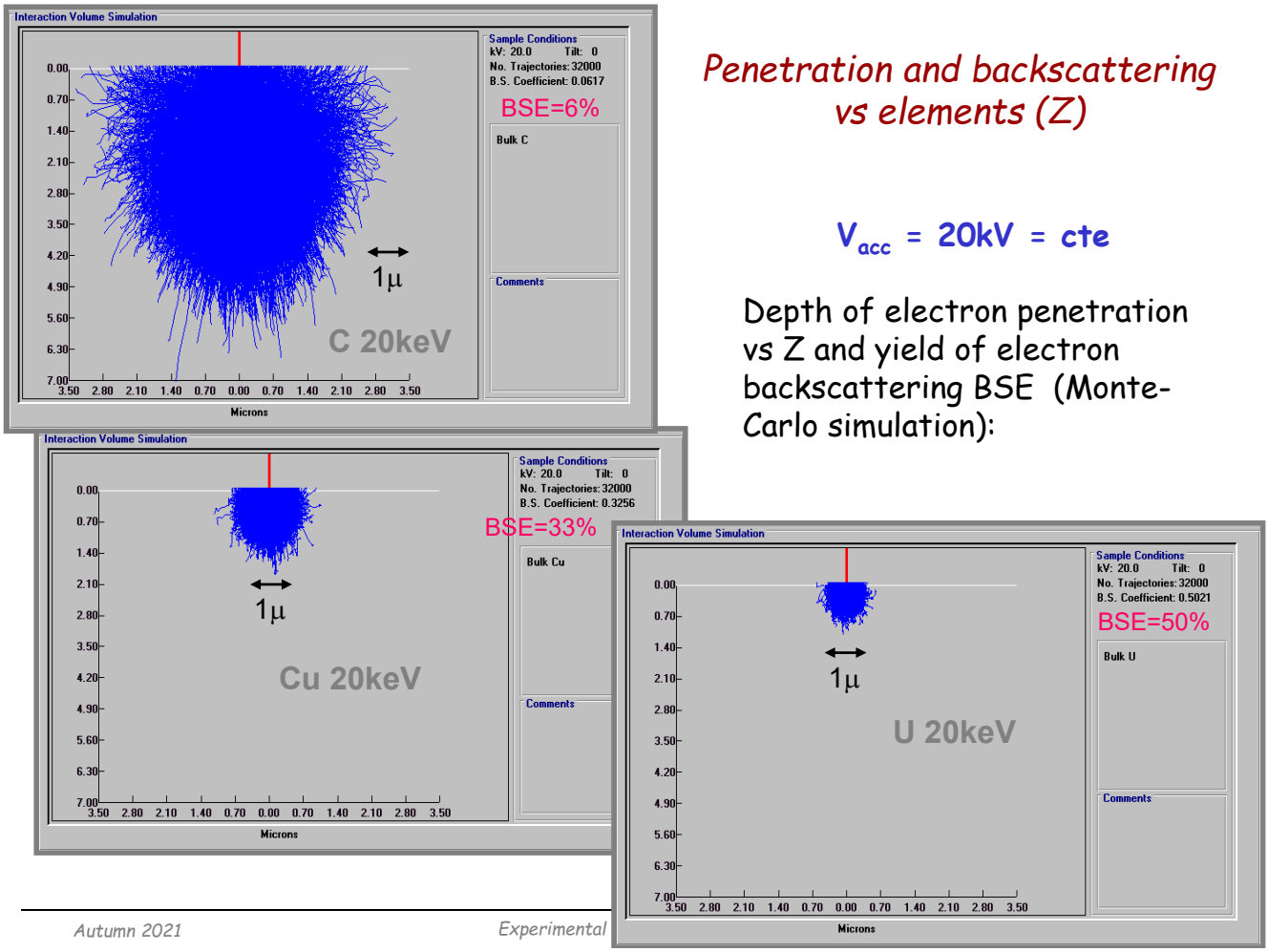
1kV: < 5nm

Interaction volume
Blue: scattered electron trajectory
Red: backscattered electrons
(leaving the sample surface)
Green: secondary electrons

Monte-Carlo Simulation CASINO v2.42

Number/Energy of backscattered electrons by Monte-Carlo simulations

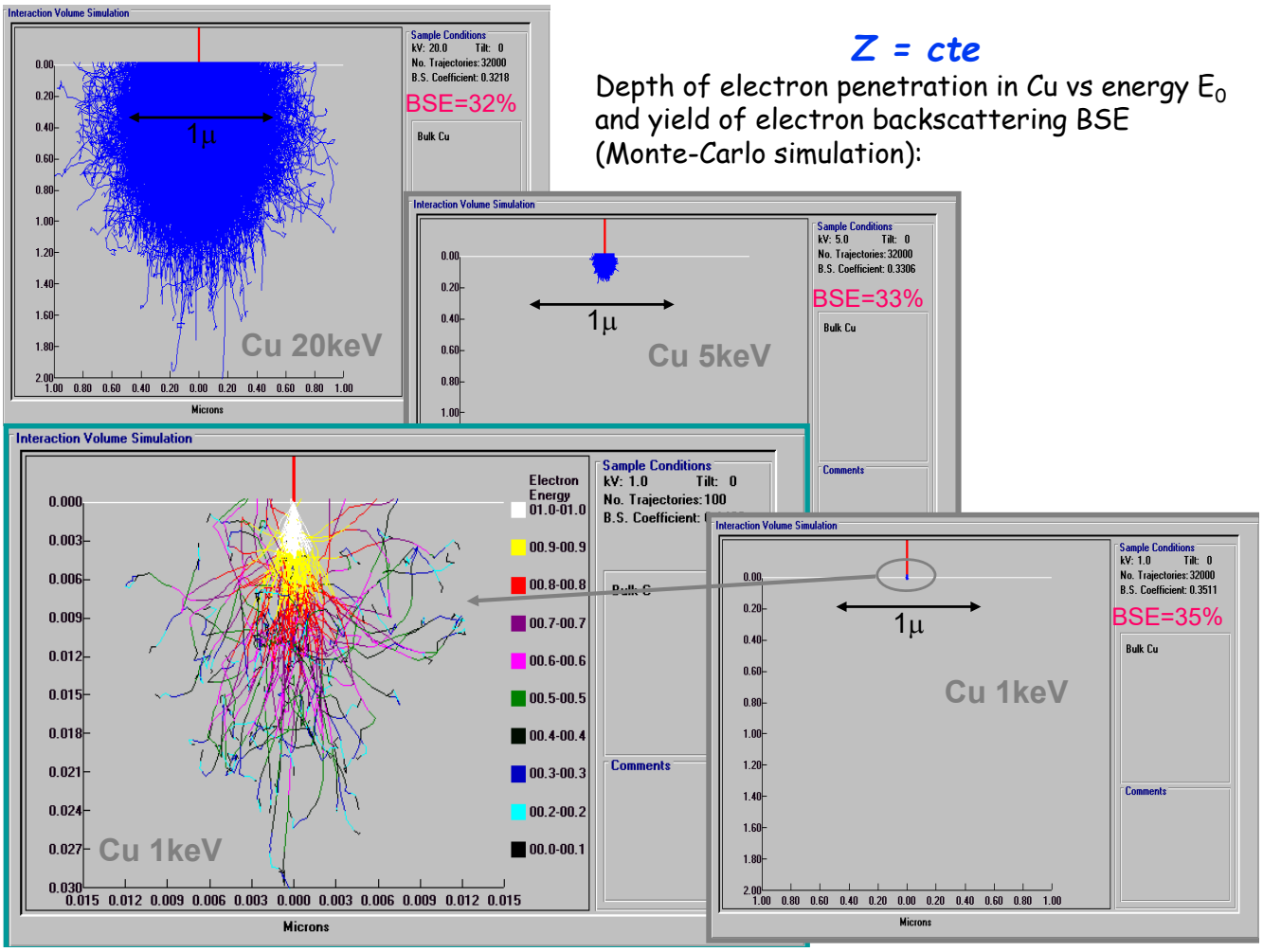




Penetration and backscattering vs elements (Z)

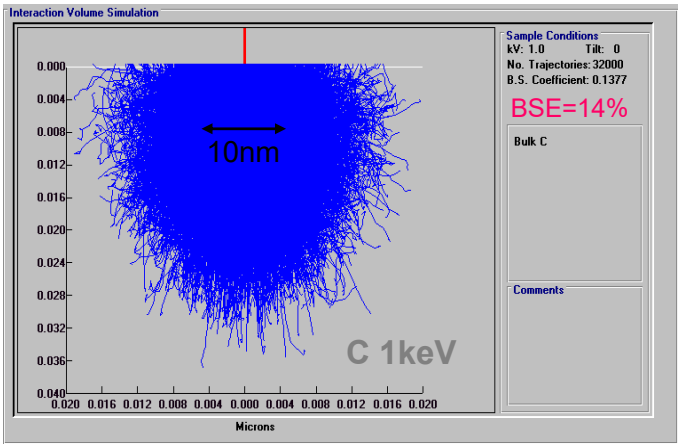
V_{acc} = 20kV = cte

Depth of electron penetration vs Z and yield of electron backscattering BSE (Monte-Carlo simulation):



Z = cte

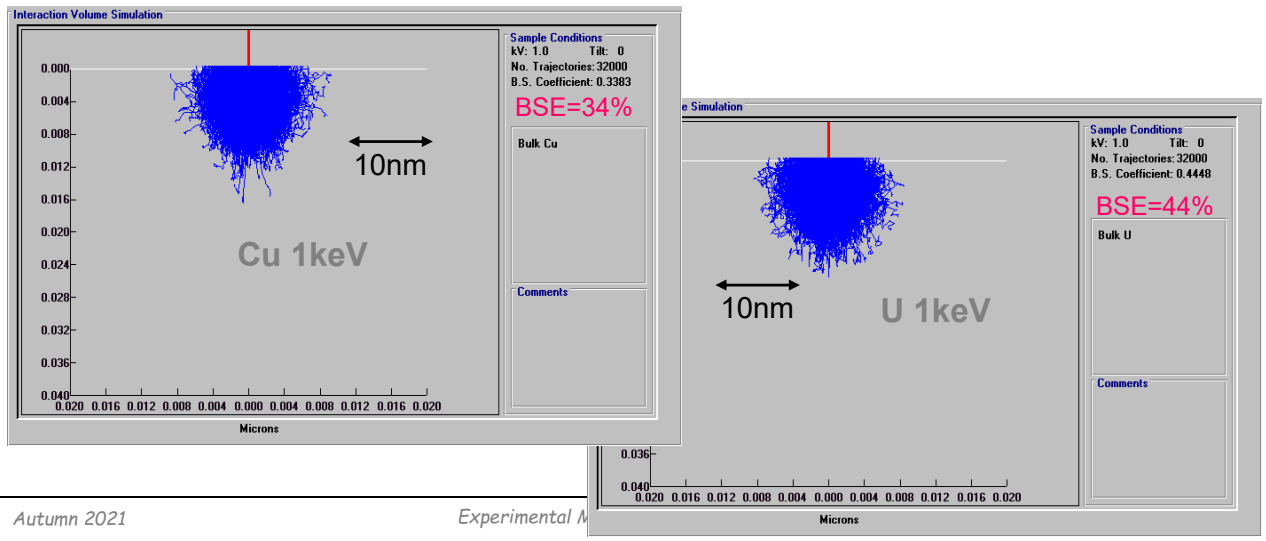
Depth of electron penetration in Cu vs energy E_0 and yield of electron backscattering BSE (Monte-Carlo simulation):

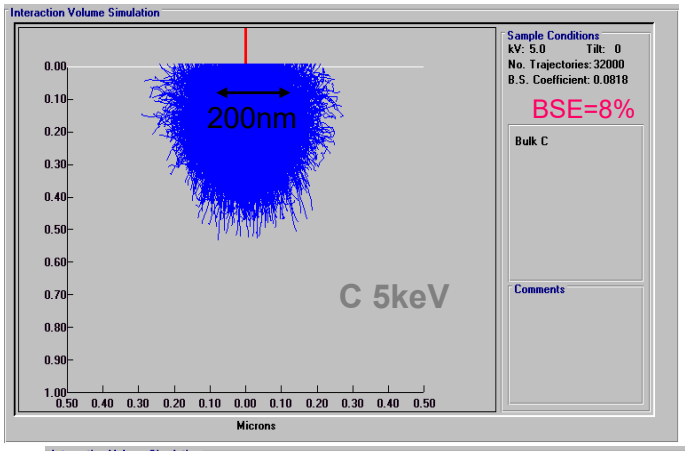


Penetration and backscattering

V_{acc} = 1kV = cte

Depth of electron penetration vs Z and yield of electron backscattering BSE (Monte-Carlo simulation):

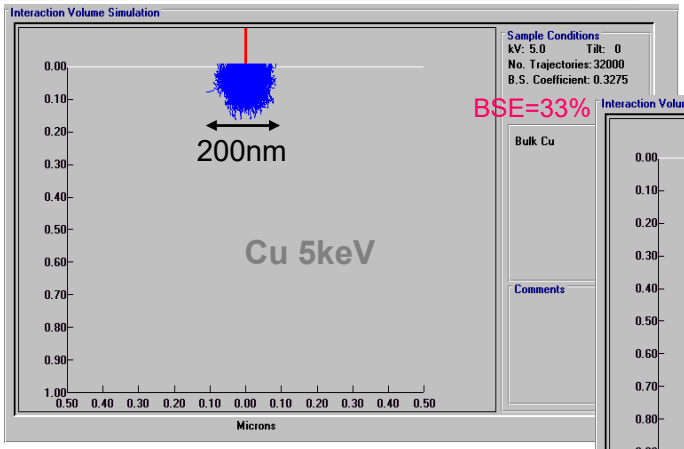


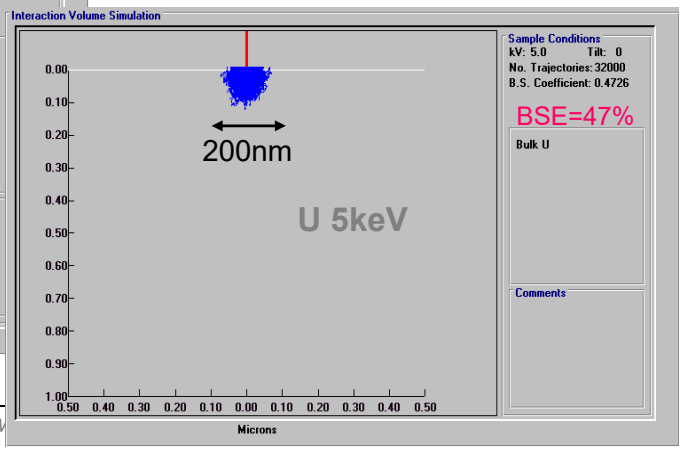


Penetration and backscattering

V_{acc} = 5kV = cte

Depth of electron penetration vs Z and yield of electron backscattering BSE (Monte-Carlo simulation):



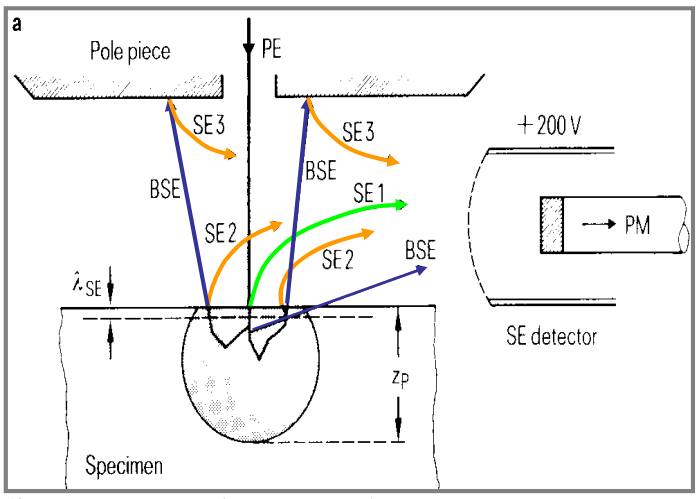


SEM: "true" secondary electrons *SE1* and "converted BSE" secondaries *SE2+SE3*

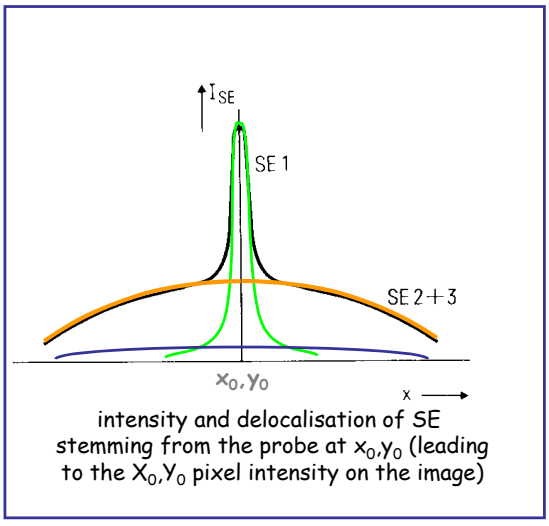
Different types of SE from

- SE1: incident probe
- SE2: BSE leaving the sample
- SE3: BSE hitting the surroundings

} although this signal is gathered around the probe, its intensity is only attributed to the pixel corresponding to the actual probe position



(from L. Reimer, Scanning Electron Microscopy)



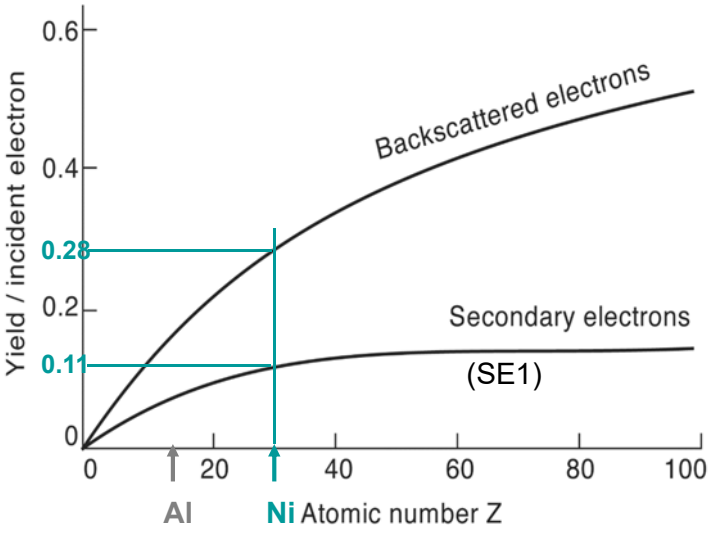
intensity and delocalisation of SE stemming from the probe at x_0,y_0 (leading to the X_0,Y_0 pixel intensity on the image)

The SE signal always contain a high resolution part (SE1 from the probe) and an average (low resolution) part from SE2+SE3!

Yield for SE and BSE emission per incident electron vs atomic number Z

sample ***surface polished*** (no topography) and perpendicular to the incident beam direction

(intermediate energy $E_0 \approx 15$ keV)



BSE: **chemical contrast** for all the elements (sensitivity $\approx \Delta Z=0.5$)

A fast way to phase mapping

$I_{BSE}=I_{pe}\cdot\eta$ with I_{pe} the intensity of the primary beam, η the BSE yield

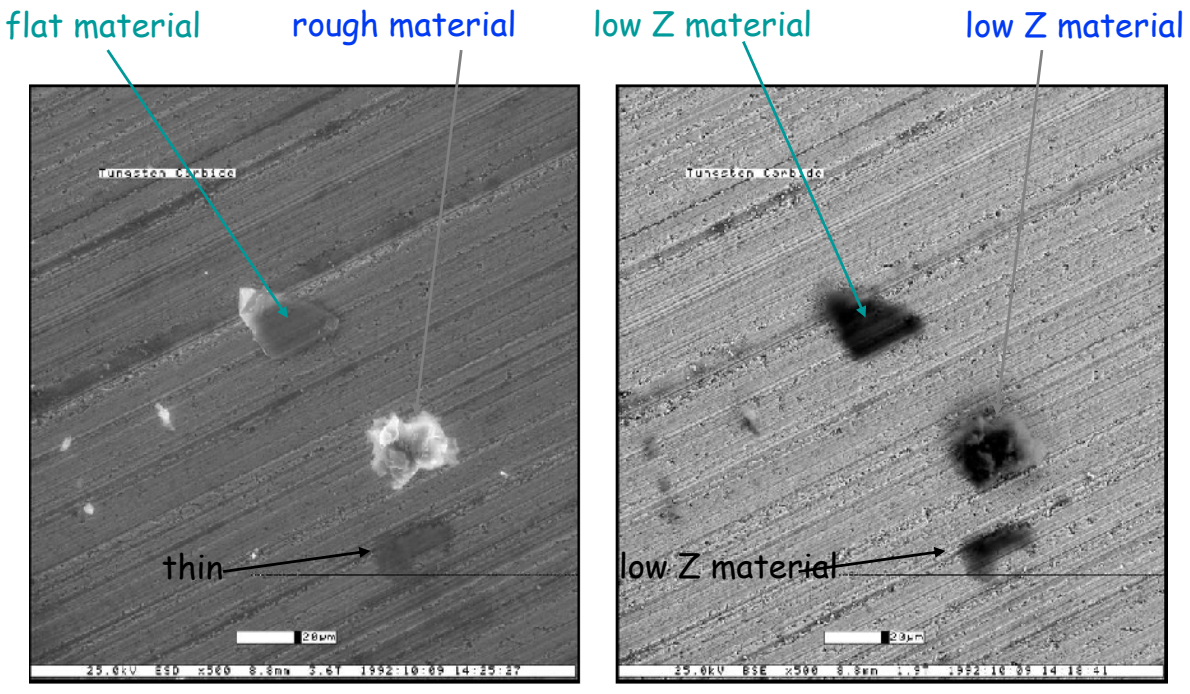
SE: **low or no chemical contrast** but for light elements

the topographical contrast will dominate on rough surfaces

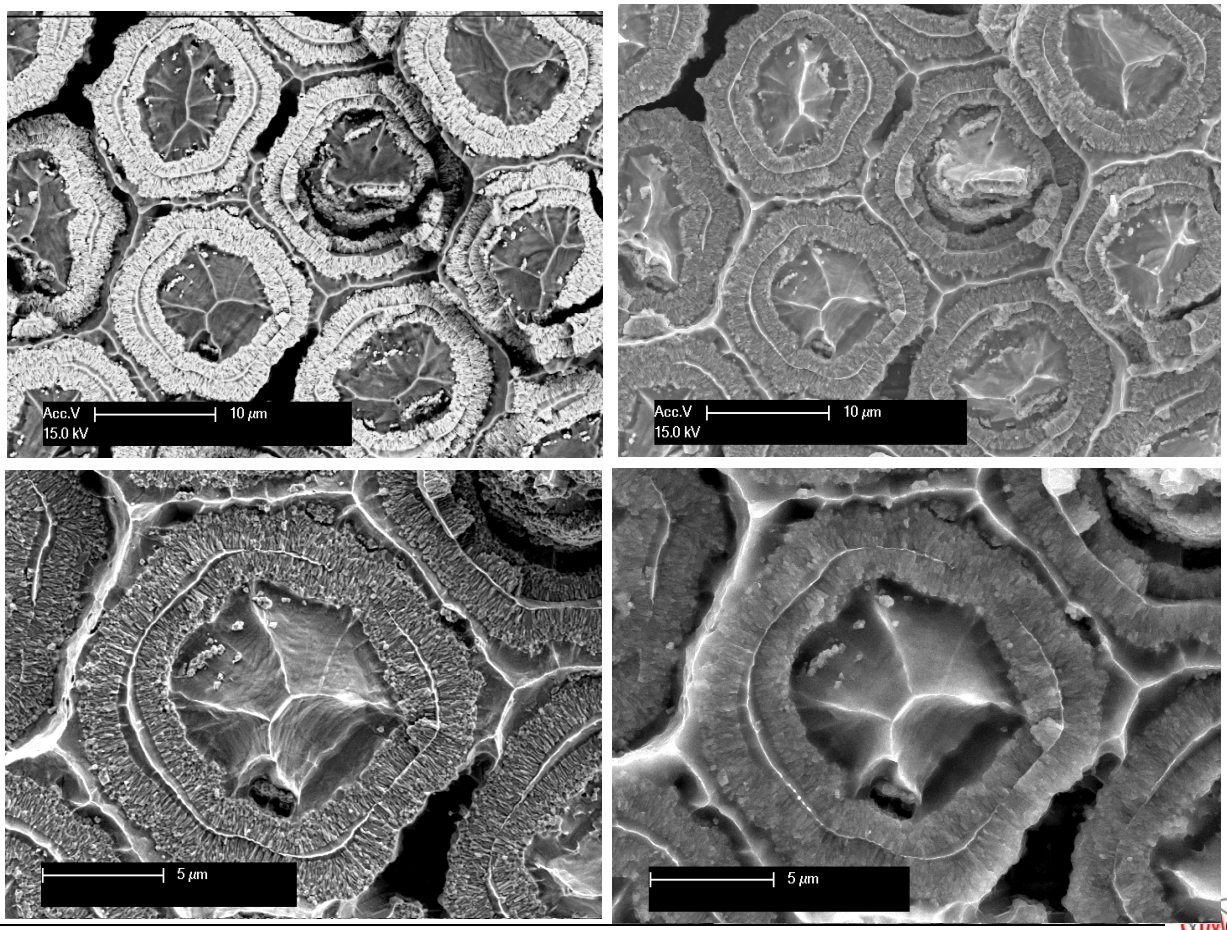
$$I_{SE}=I_{pe}\cdot\delta + I_{SE3}$$
$$=I_{pe}(\underbrace{\delta_{pe}}_{SE1}+\underbrace{\delta_{pe}\cdot\eta}_{SE2}+\underbrace{\delta_{sur}\cdot\eta}_{SE3})$$

with δ the total SE yield, δ_{pe} the yield for SE1 and δ_{sur} the SE3 yield for materials surrounding the sample (pole-pieces...)

Dust on WC (different Z materials

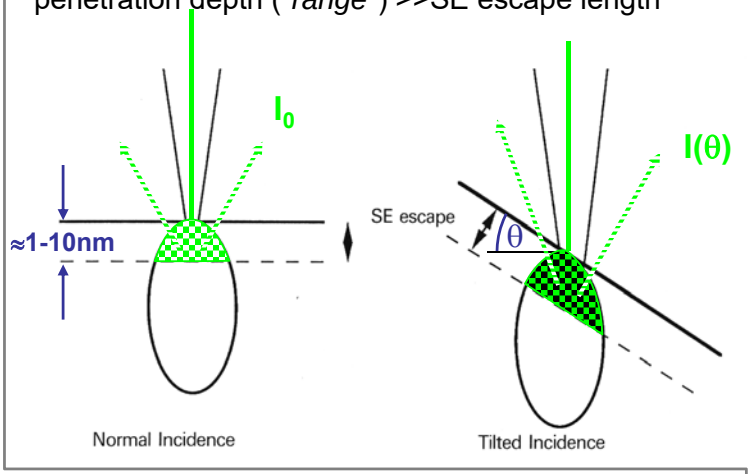


SE 25 kV BSE



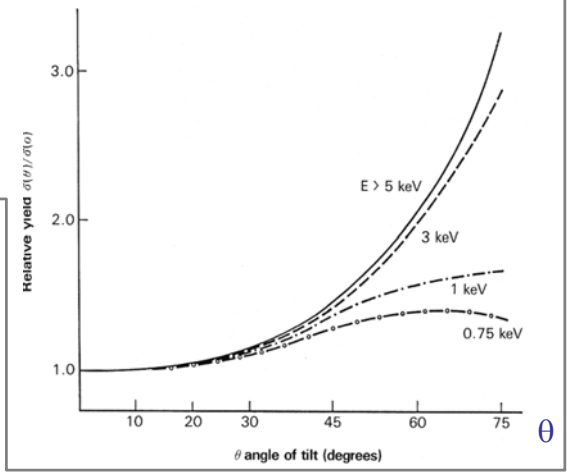
Topographic contrast in SE mode

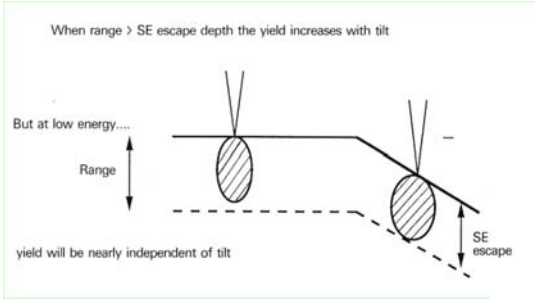
penetration depth (*"range"*) >>SE escape length



Relative yield of SE vs angle of incidence on the sample surface

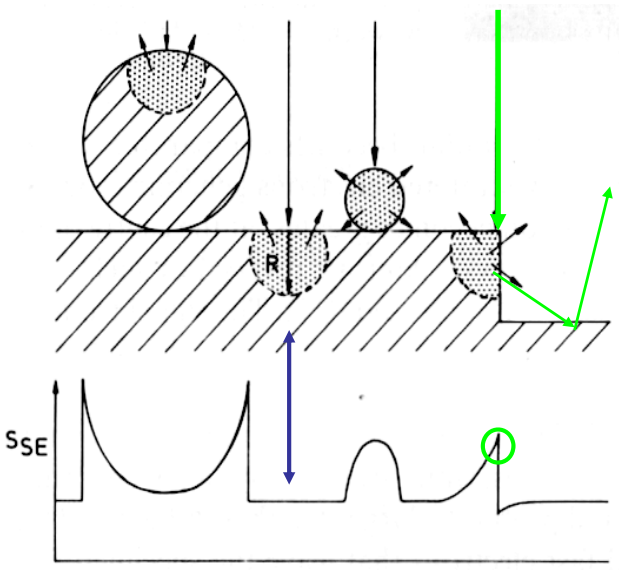
$$I(\theta) = I_{pe}\delta(\theta) \cong I(0)/\cos\theta$$





(adapted from D.C. Joy Hitachi News 16 1989)

Size and edge effects



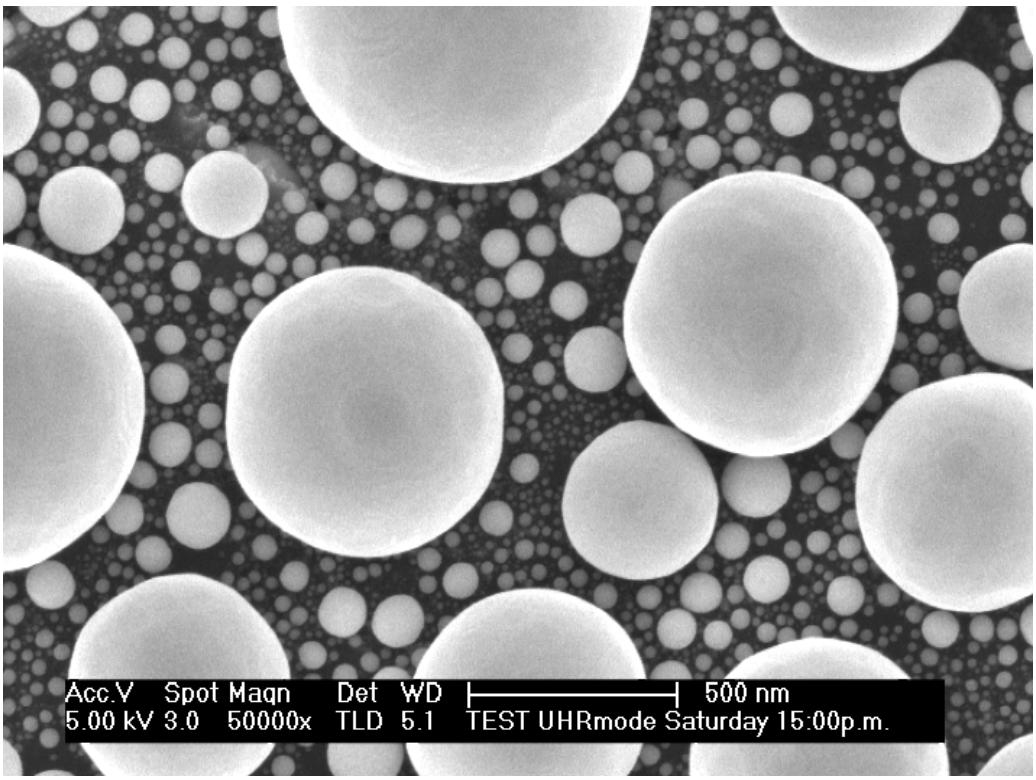
intensity profile on image

Fig. 6.6. SE signal intensity across spheres with diameters larger and smaller than the electron range R and increase of the SE signal at an edge caused by diffusion contrast

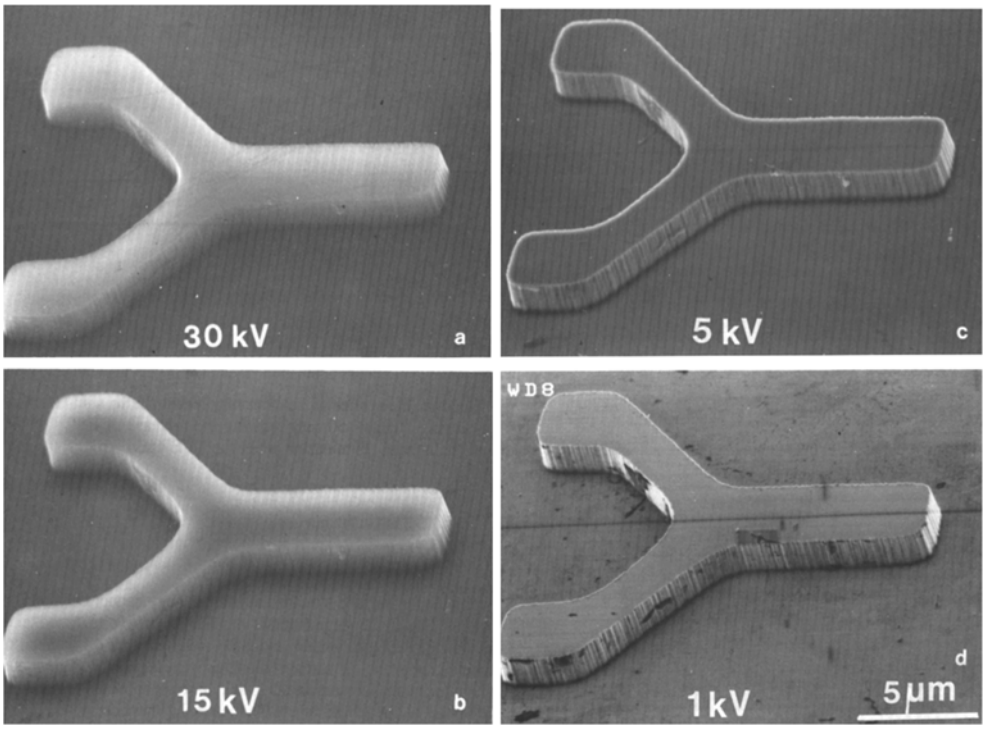
(adapted from L.Reimer, Scanning Electron Microscopy)

Do not forget, in SEM:
The signal is displayed at the probe position, not at the actual SE production position!!!

Tin balls

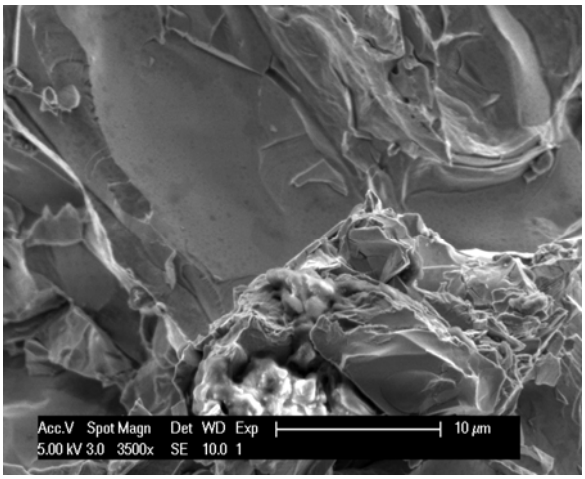


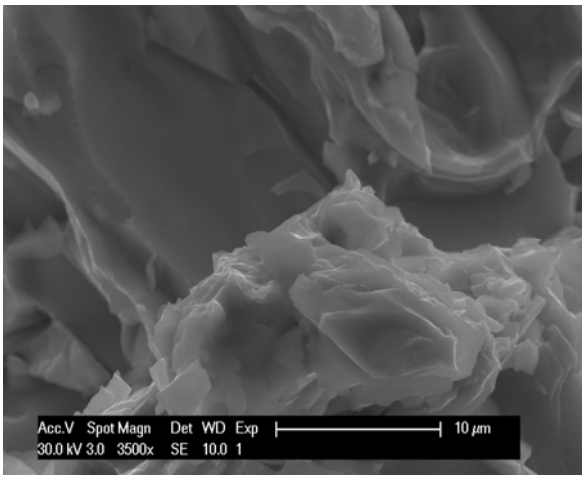
Change in secondary electron contrast with accelerating voltage



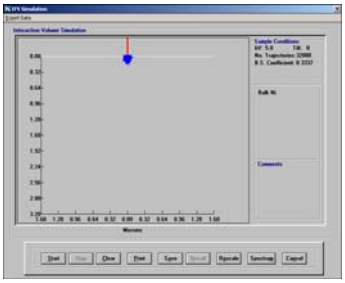
(from L.Reimer, Image formation in the low-voltage SEM)

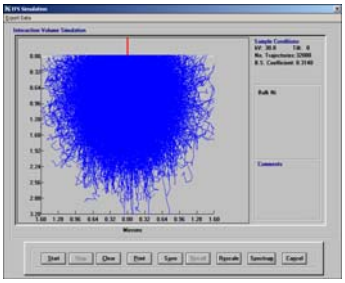
Contrast enhancement at low voltage: less delocalization by SE2. An example: a fracture in Ni-Cr alloy





SE, 5 kV

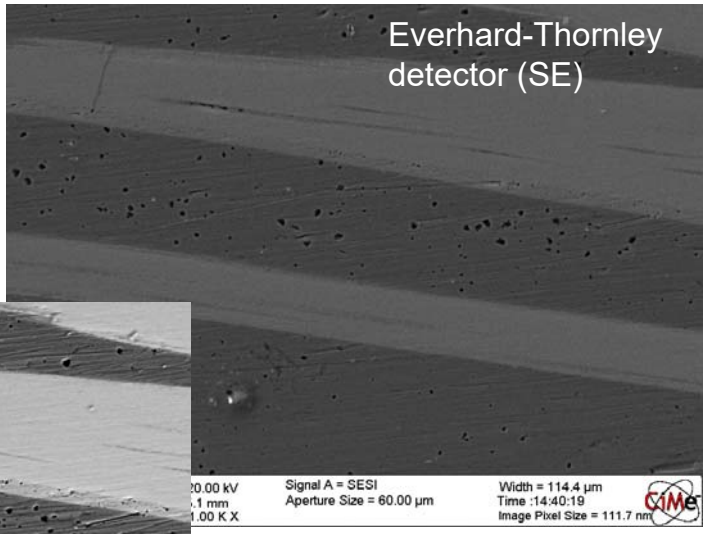


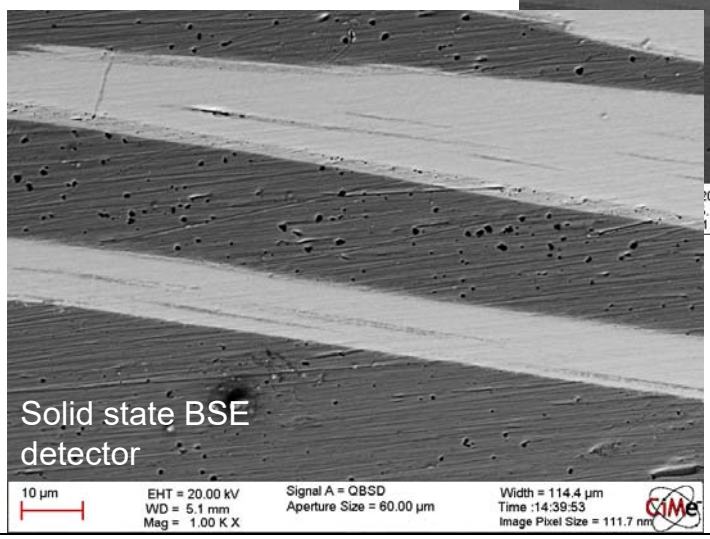


SE, 30 kV

SEM low kV imaging

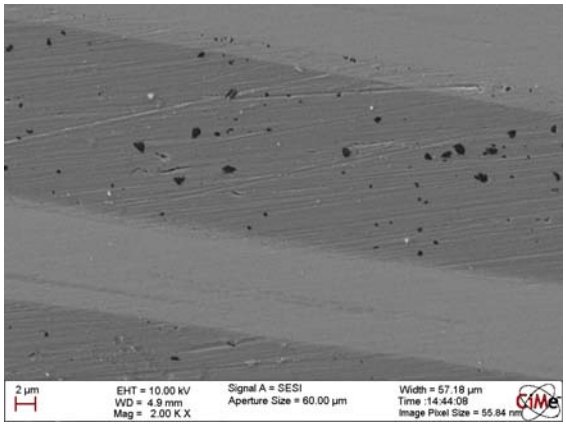
"classical" conditions: 20kV

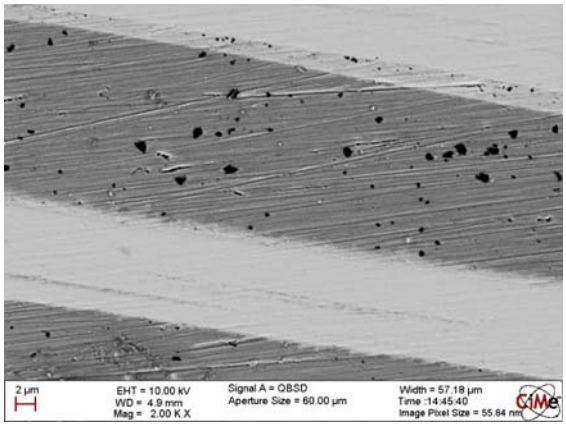


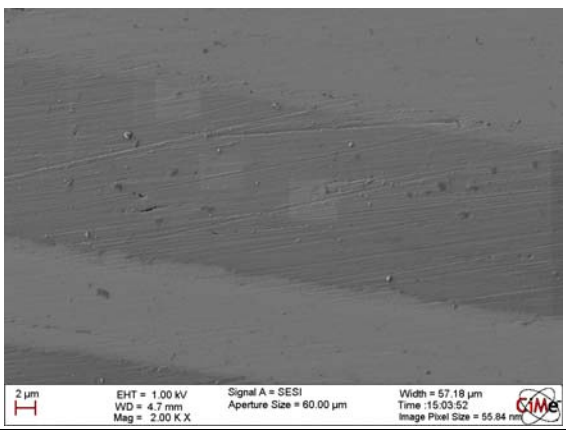


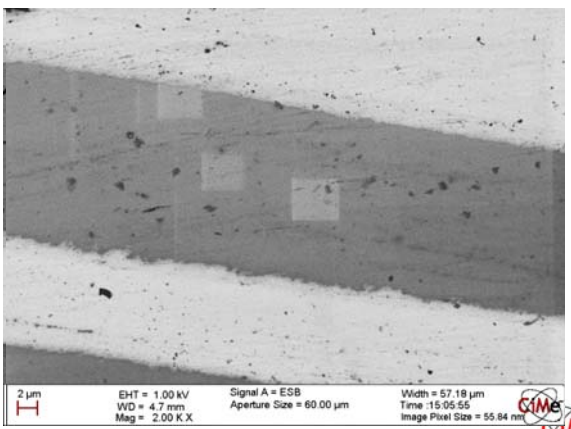
SEM low kV imaging

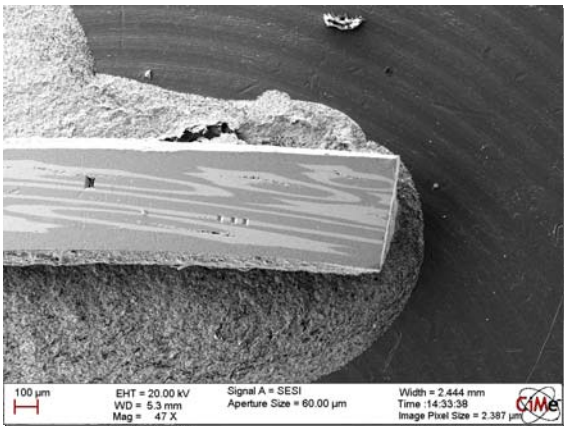
SE and BSE imaging

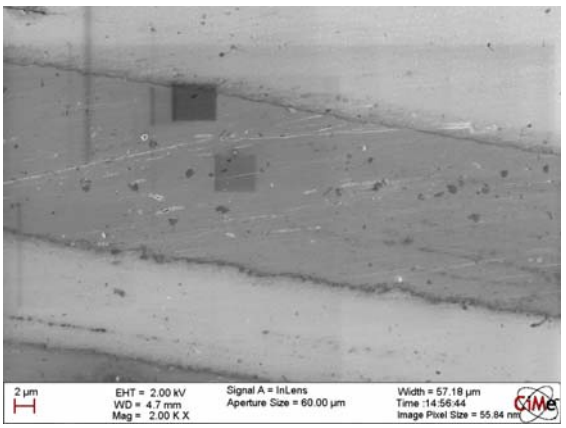


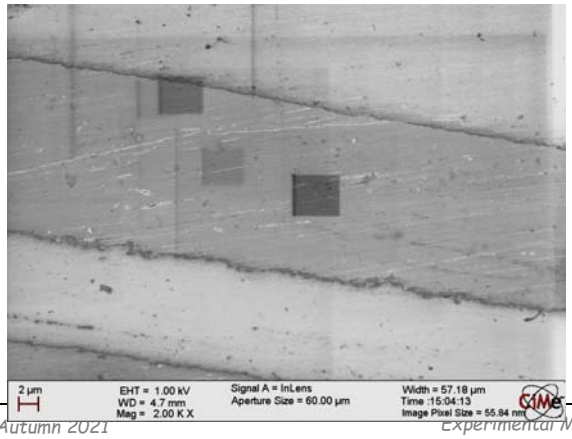


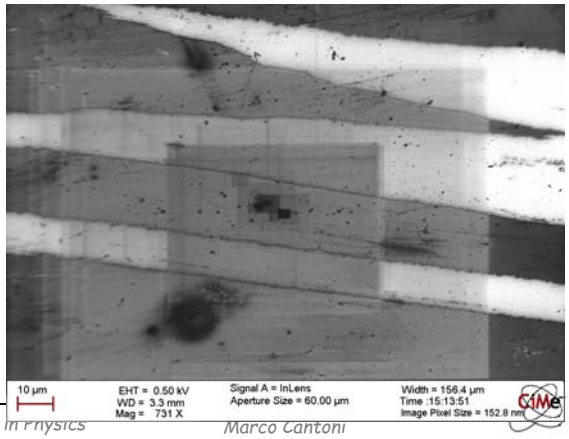


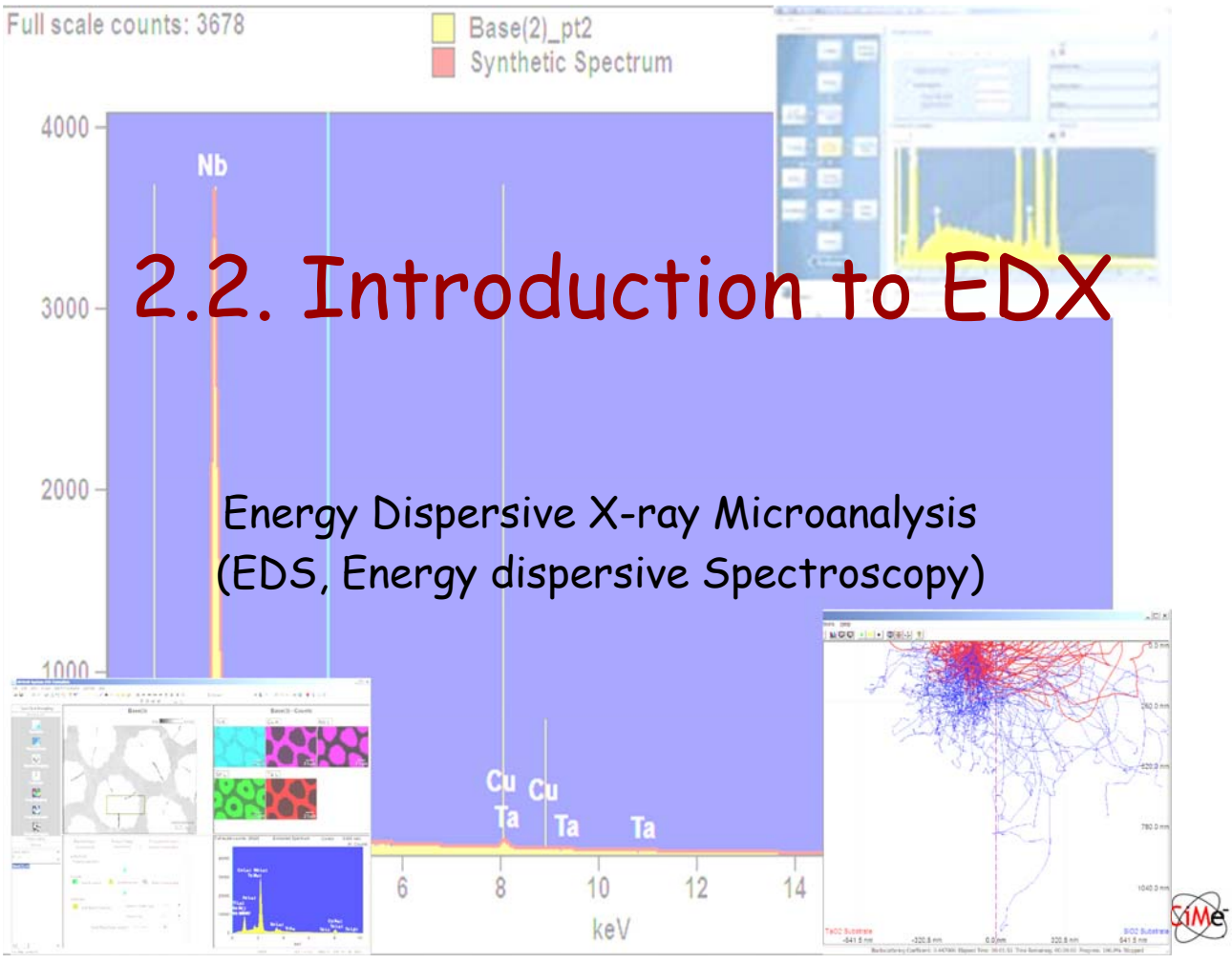












2.2. Introduction to EDX

Energy Dispersive X-ray Microanalysis
(EDS, Energy dispersive Spectroscopy)

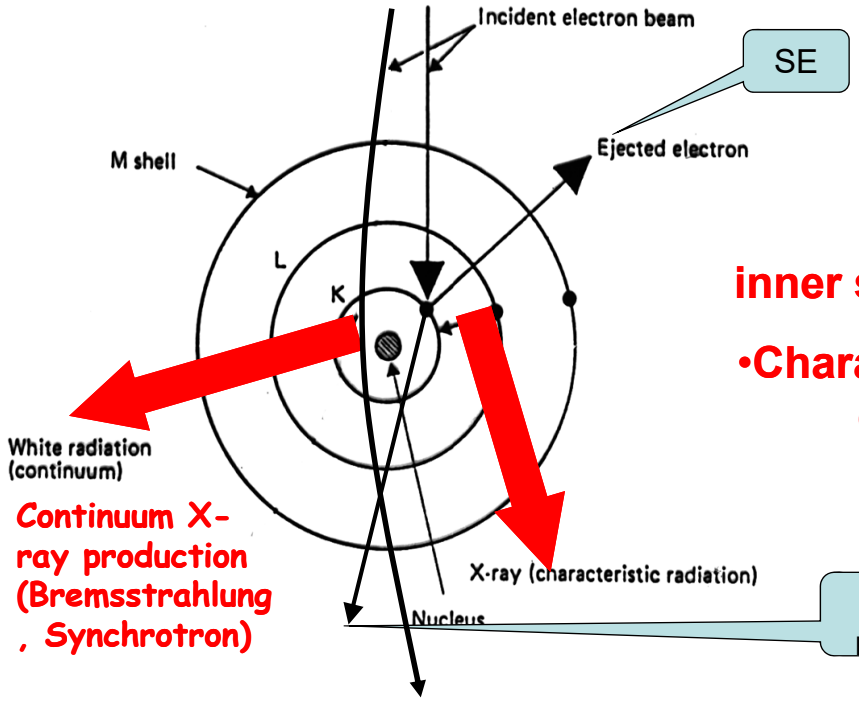
summary

- Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.
- To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

Basics of EDX

- a) Generation of X-rays
- b) Detection
- c) Quantification
  - EDX in SEM, Interaction volume
  - Monte-Carlo-Simulations
  - EDX in TEM
- d) Examples

X-ray generation:
Inelastic scattering of electrons at atoms
$E_{electron\_in} > E_{electron\_out}$

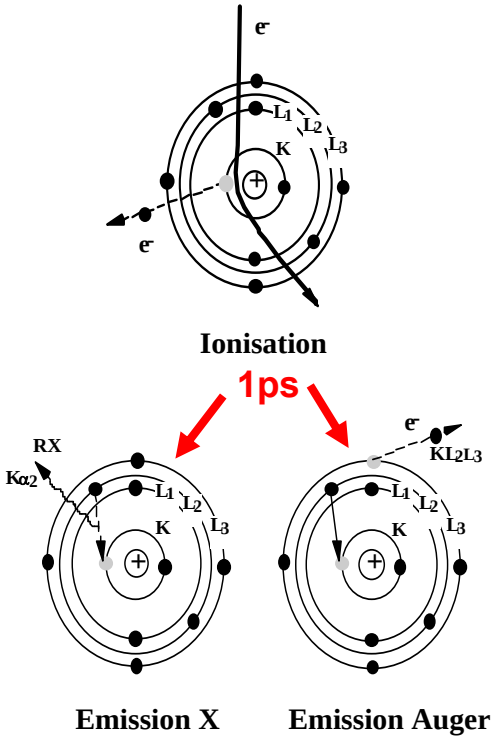


inner shell ionization

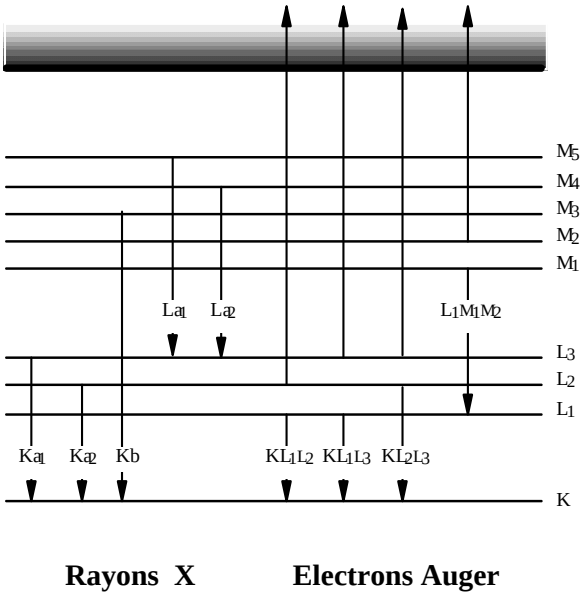
•Characteristic X-ray emission

- **Continuum X-ray production (Bremsstrahlung , Synchrotron)**

Core shell ionisation: chemical microanalysis by X-ray, Auger electron and Electron Energy Loss Spectrometries



Designation of x-ray emission lines



Forbidden transitions !
quantum mechanics:
conservation of angular momentum

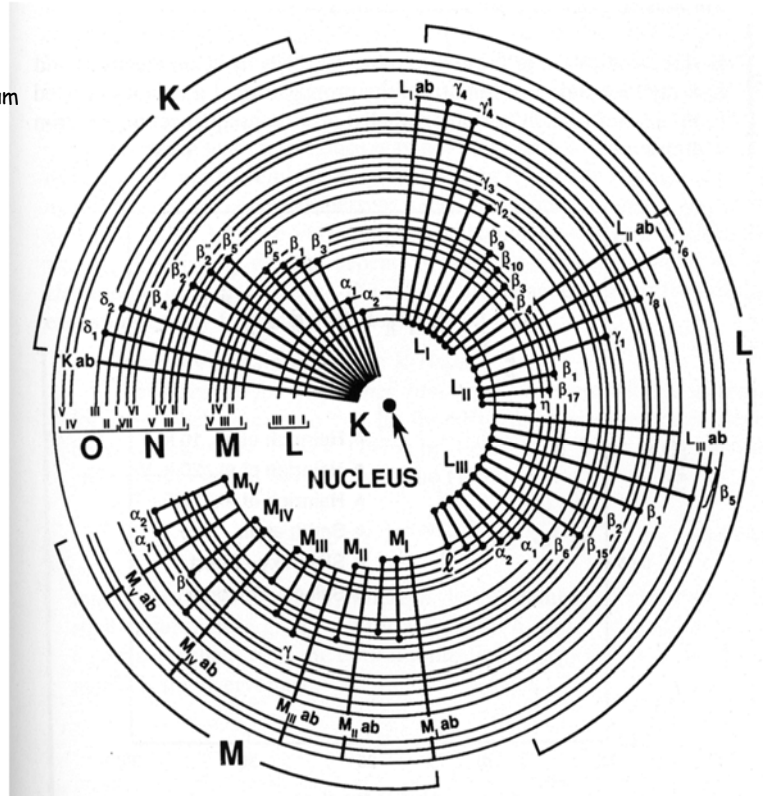
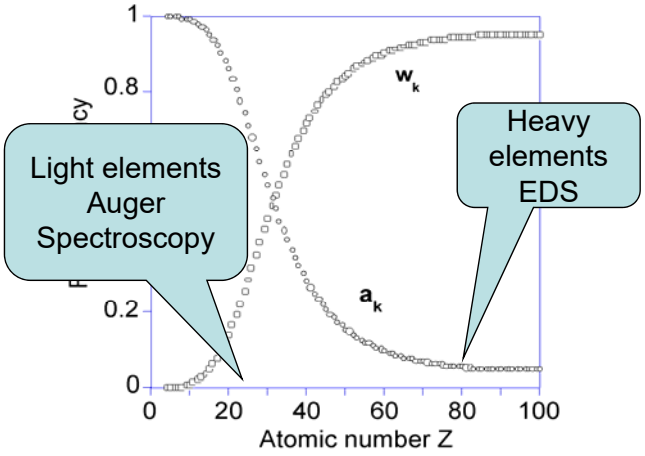


Figure 3.37. Comprehensive energy-level diagram showing all electron transitions which give rise to *K*, *L*, and *M* x rays (Woldseth, 1973).

Efficiency of X-ray generation

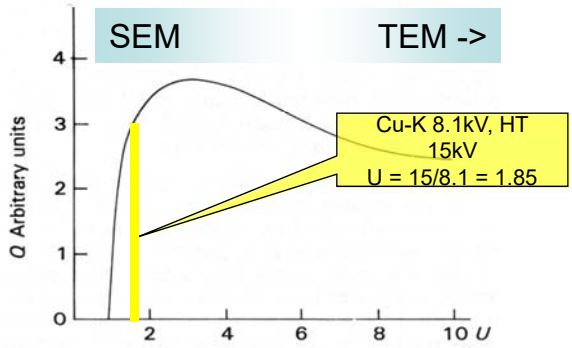
Relative efficiency of X-ray and Auger emission vs. atomic number for K lines



Light element atoms return to fundamental state mainly by Auger emission. For that reason, their K-lines are weak. In addition their low energy makes them easily absorbed.

Ionization cross-section vs. overvoltage U=Eo/Eedge

(electron in -> X-ray out)



To ionized the incident electron MUST have an energy larger than the core shell level U>1. To be efficient, it should have about twice the edge energy U>2.

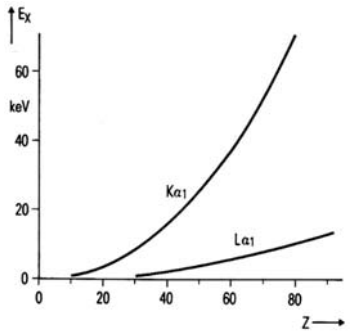
Characteristic lines: Moseley's Law

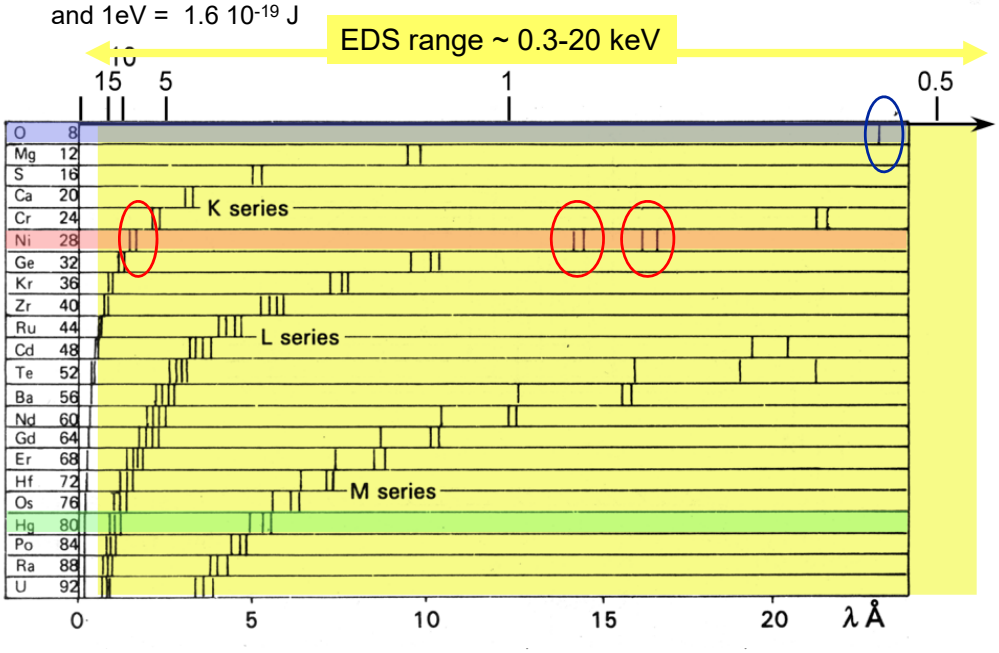
Frequency ν of X-rays emitted from K-level vs. atomic number

E= hν et λ=c/ν

$$\nu = 2.4810^{15}(Z-1)^2$$

with the Planck constant:h=6.626 068 76(52) × 10^{-34} J·s
and 1eV = 1.6 10^{-19} J



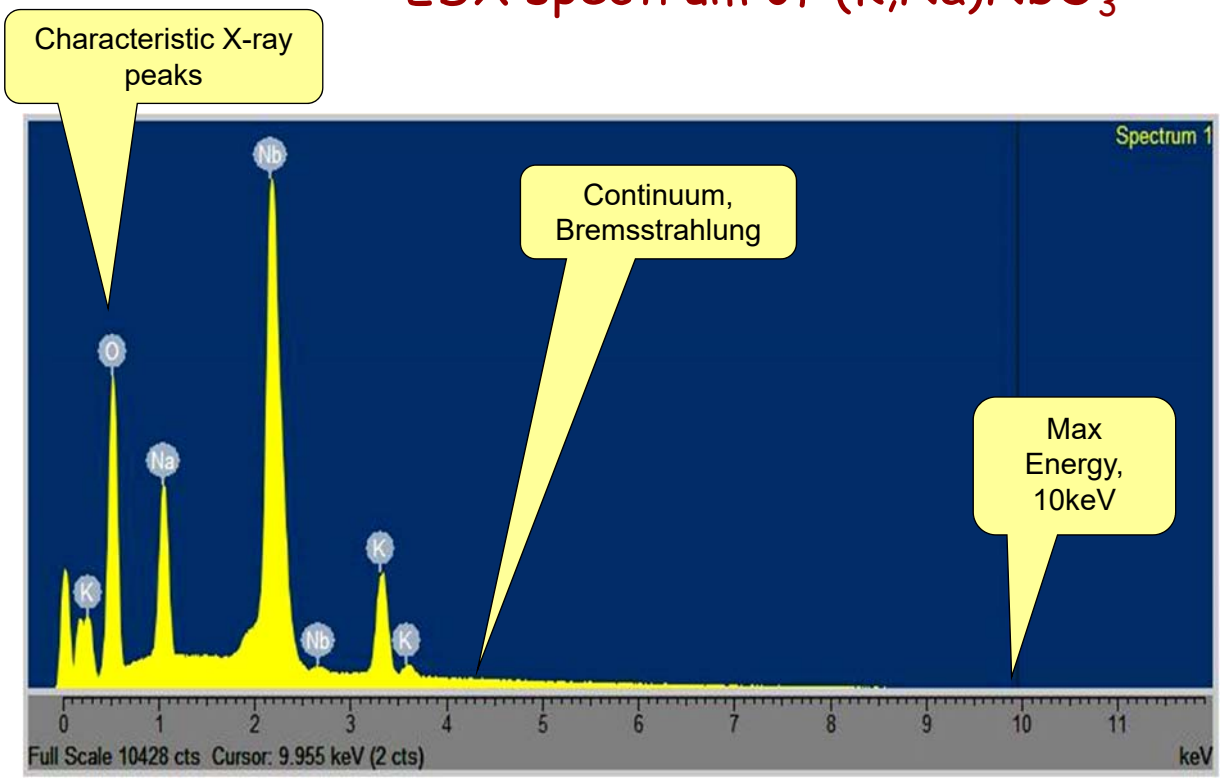


To assess an element all detectables lines MUST be present!!!

known ambiguities:

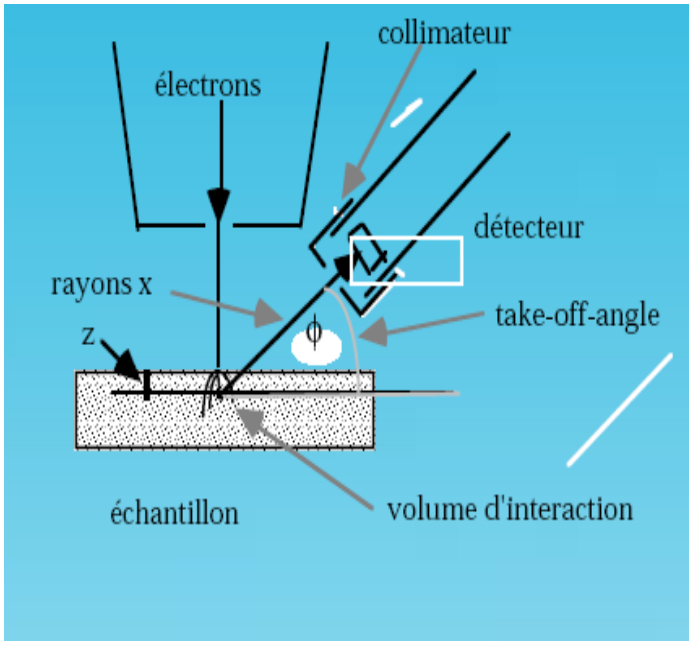
Al Kα = Br Ll
S Kα = Mo Ll

EDX spectrum of $(K,Na)NbO_3$



Electron beam: 10keV Duane-Hunt limit

b) Detection of X-rays (EDX)



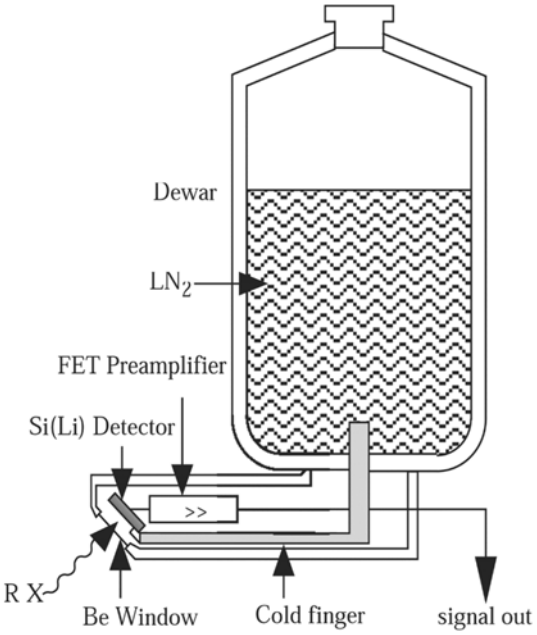
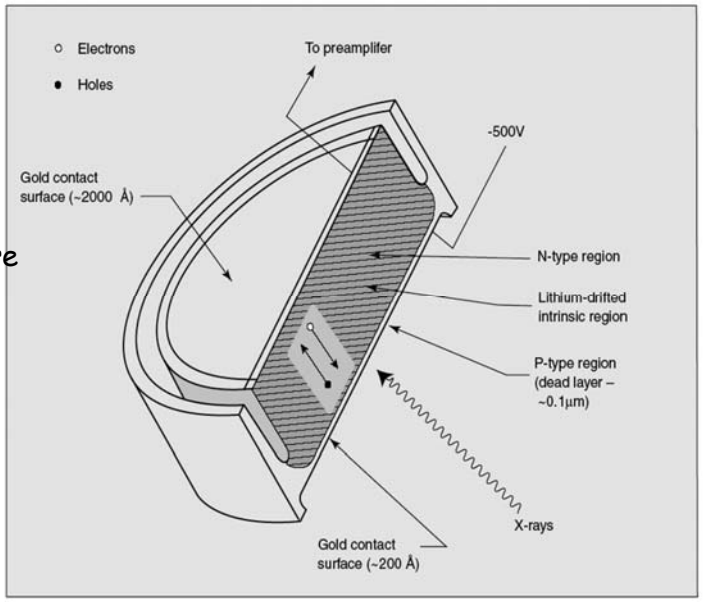
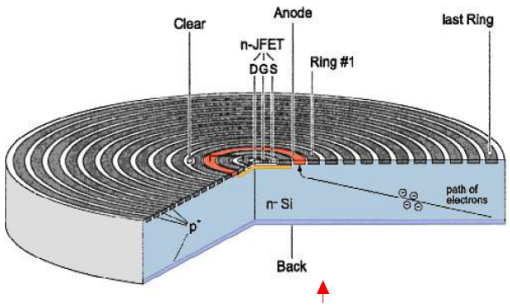


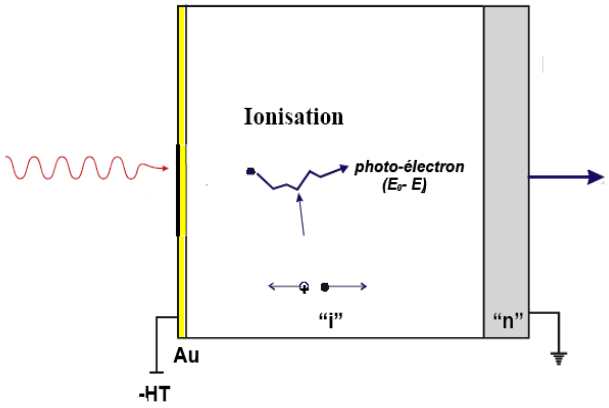
Figure 4-2. Cross section of a typical lithium-drifted silicon detector. X-rays create electron-hole pairs in the intrinsic region of the semiconductor; these charge carriers then migrate to the electrodes under the influence of an applied bias voltage.

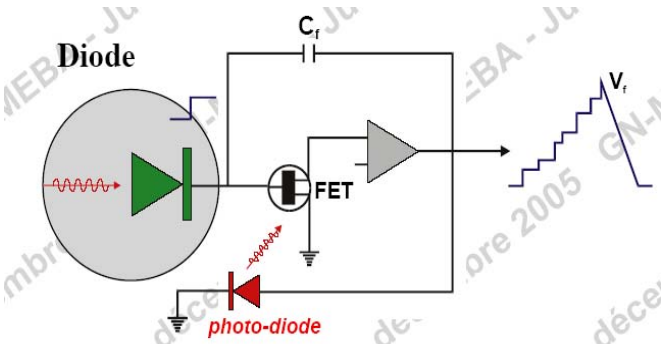
Right: Si(Li) detector
Cooled down to liquid nitrogen temperature



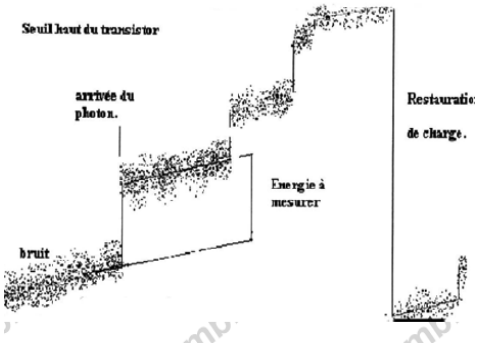


modern silicon drift (SDD) detector:
no LN cooling required





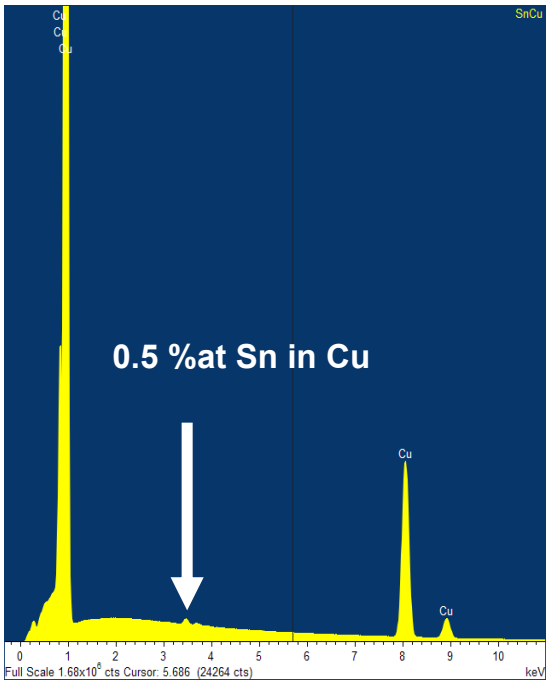
X-Ray energy conversion to electrical charges:
3.8eV / electron-hole pair in average
electronic noise+ imperfect charge collection:
130 eV resolution / Mn Ka line



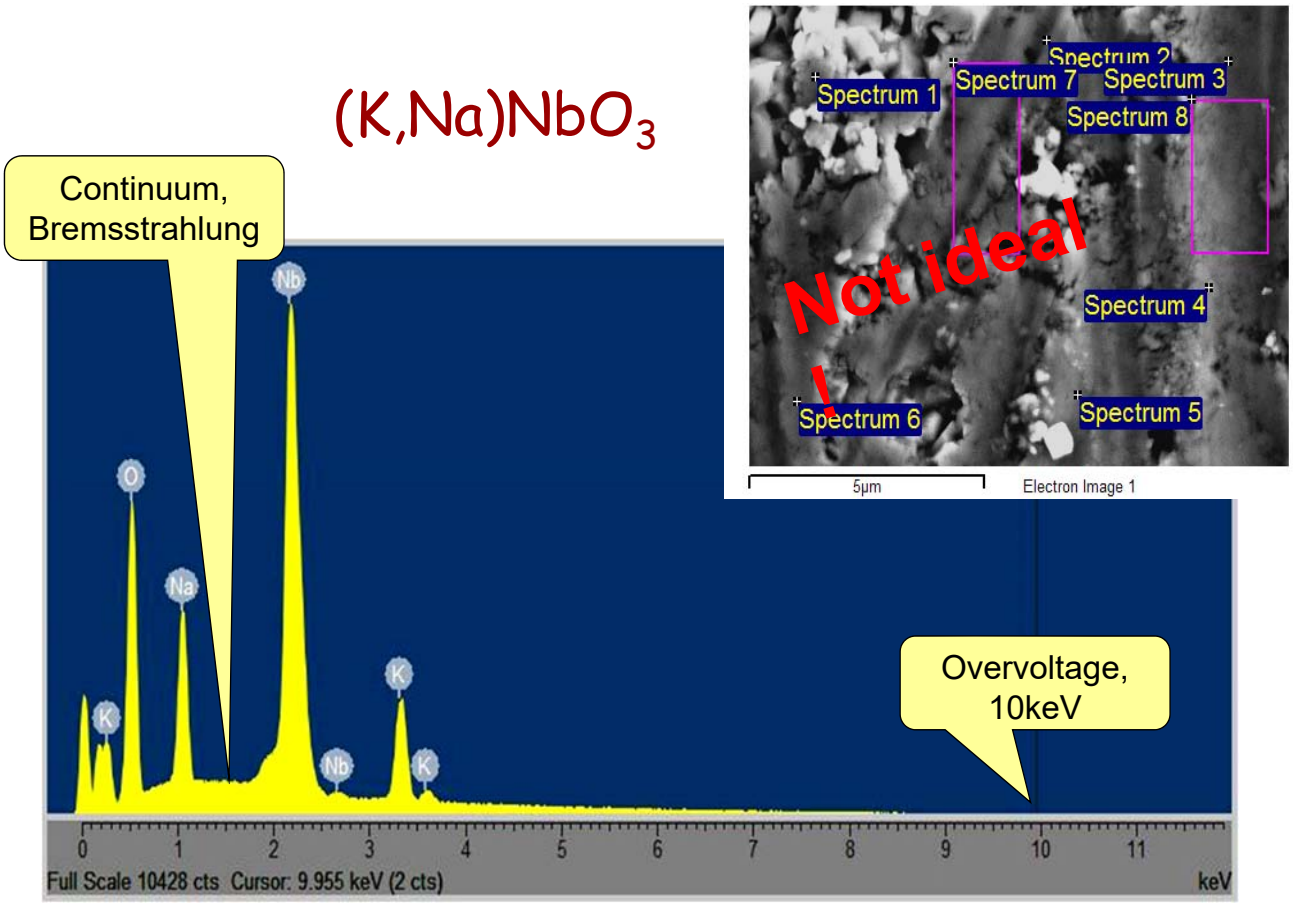
- Detector acts like a diode: at room temperature the leak current for 1000V would be too high !
- The FET produces less noise if cooled !
- Li migration at room temperature !
- ->Detector cooling by L-N

Detection limit EDS in SEM

- Acquisition under best conditions
  - Flat surface without contamination (no Au coating, use C instead)
  - Sample must be homogenous at the place of analysis (interaction volume !!)
  - Horizontal orientation of the surface
  - High count rate
  - Overvoltage U=Eo/Ec >1.5-2
- For acquisition times of 100sec. : detection of ~0.5at% for almost all elements



$(K,Na)NbO_3$



Duane-Hunt limit

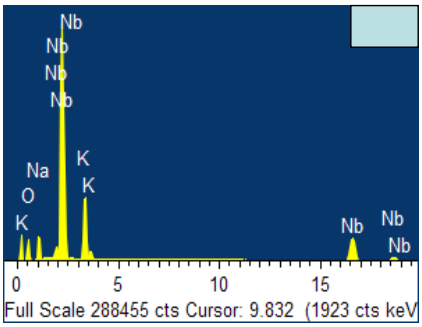
c) Quantification

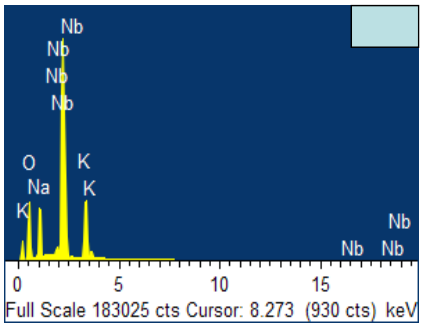
- First approach: compare X-ray intensity with a standard (sample with known concentration, same beam current of the electron beam)
- c_i: wt concentration of element i
- I_i: X-ray intensity of char. Line
- k_i: concentration ratio

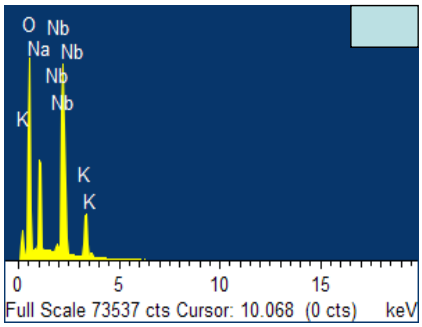
Yes, but....

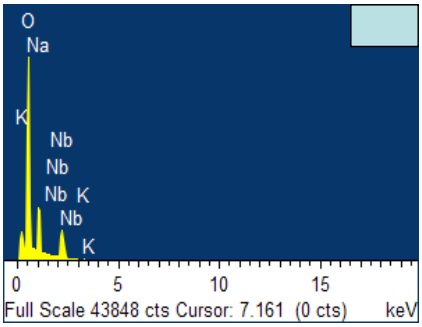
$$\frac{c_i}{c_i^{std}} = \frac{I_i}{I_i^{std}} = k_i$$

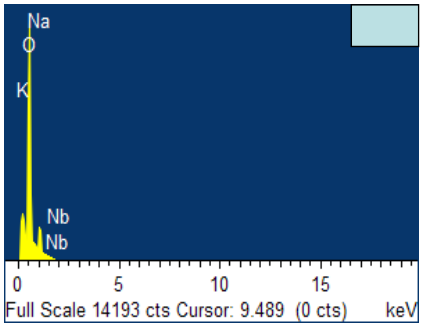
Intensity ~ Concentration…?



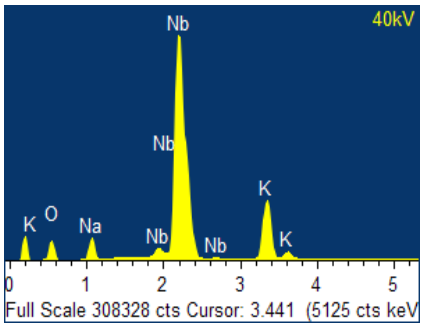


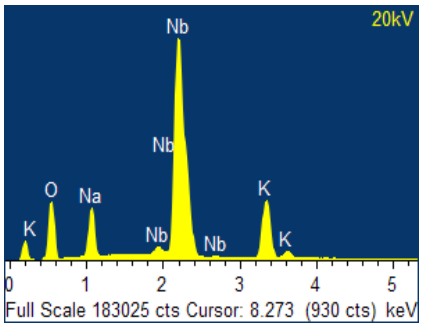


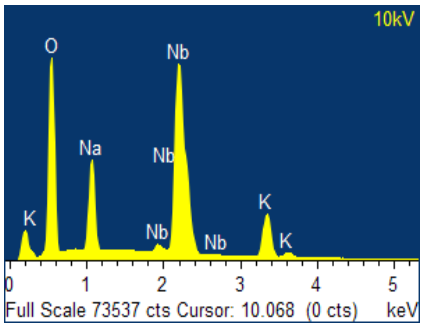


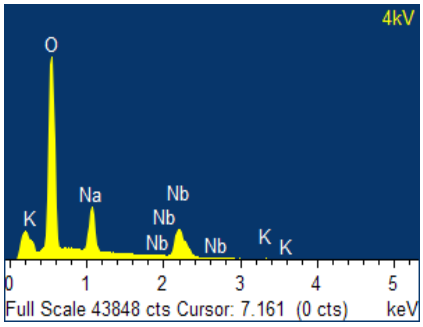


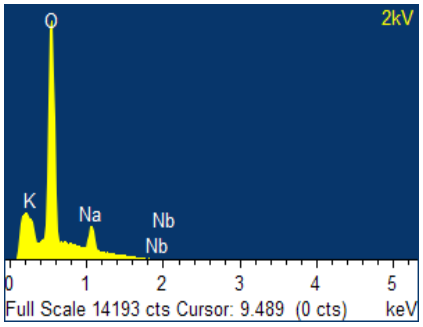
How many different samples…?



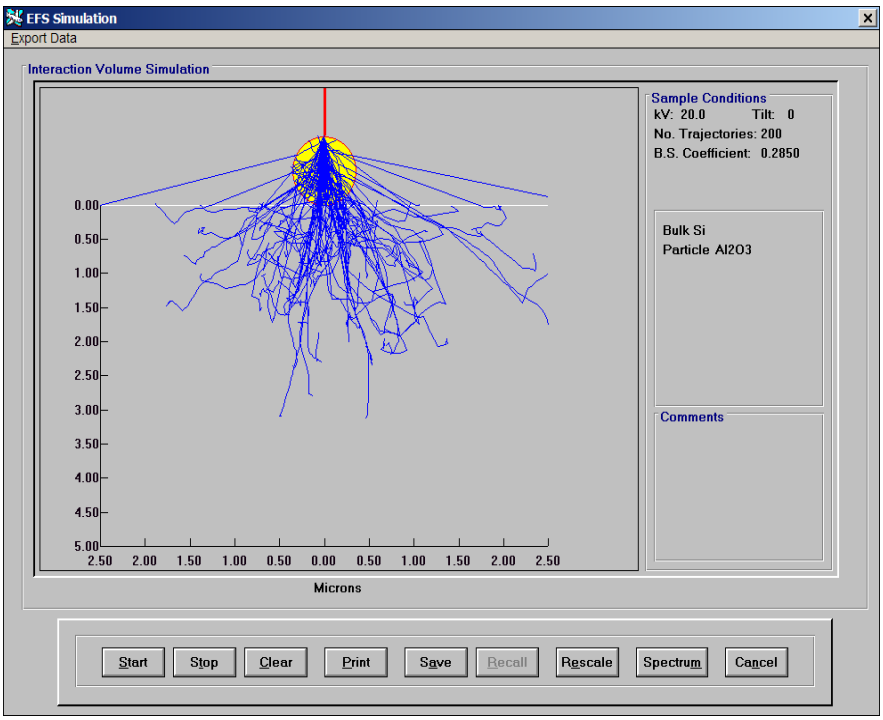




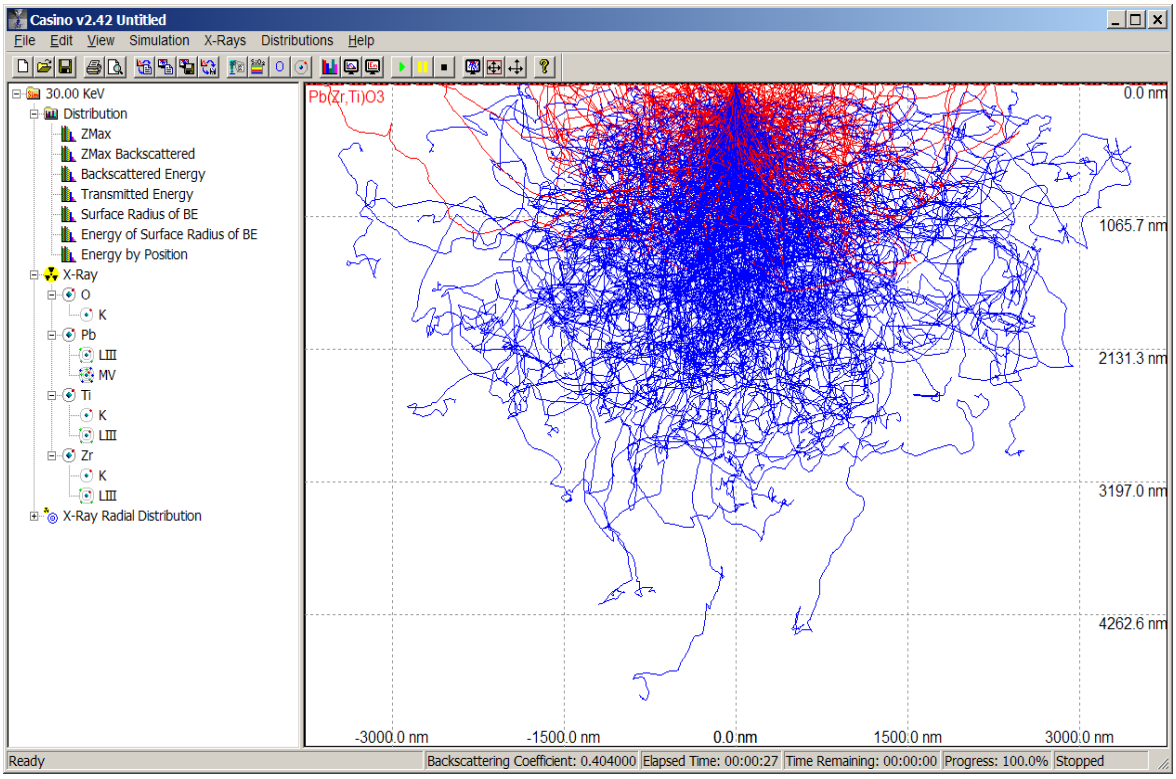


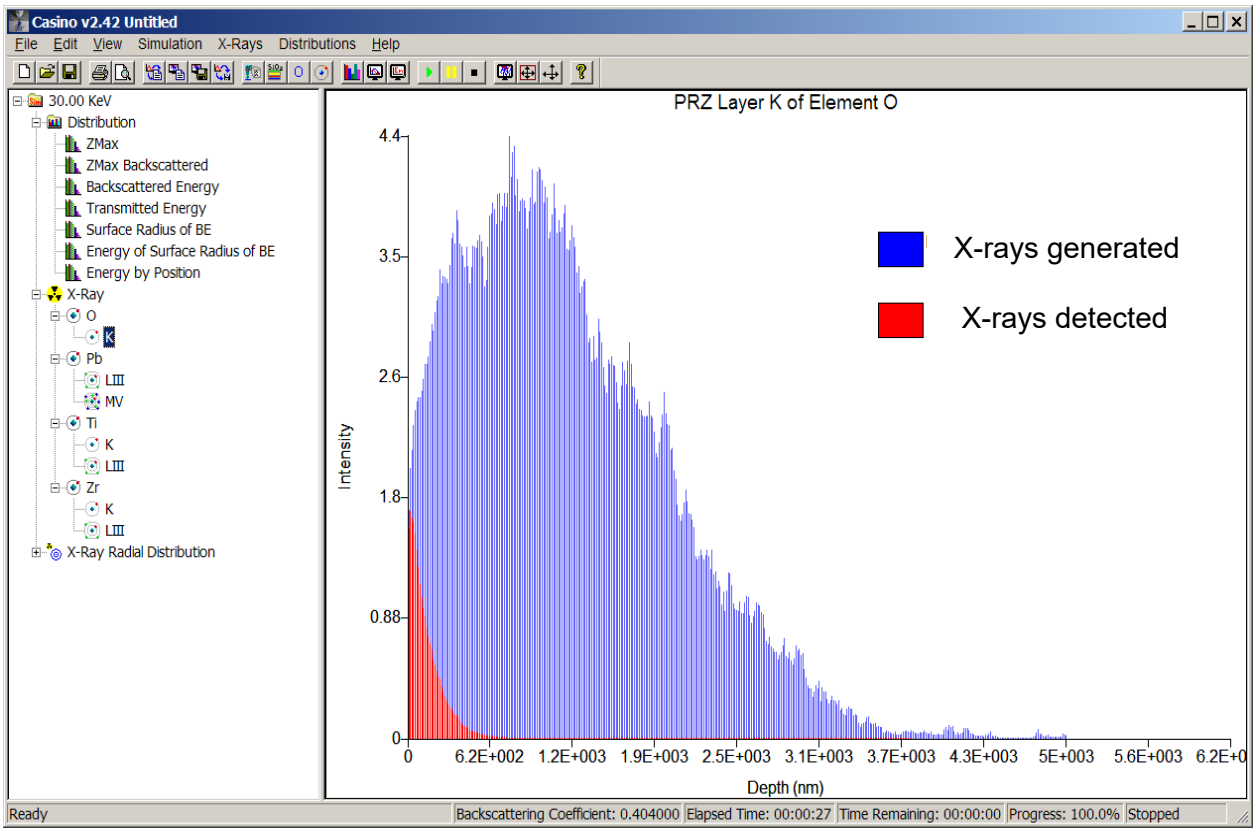


Electron Flight Simulator

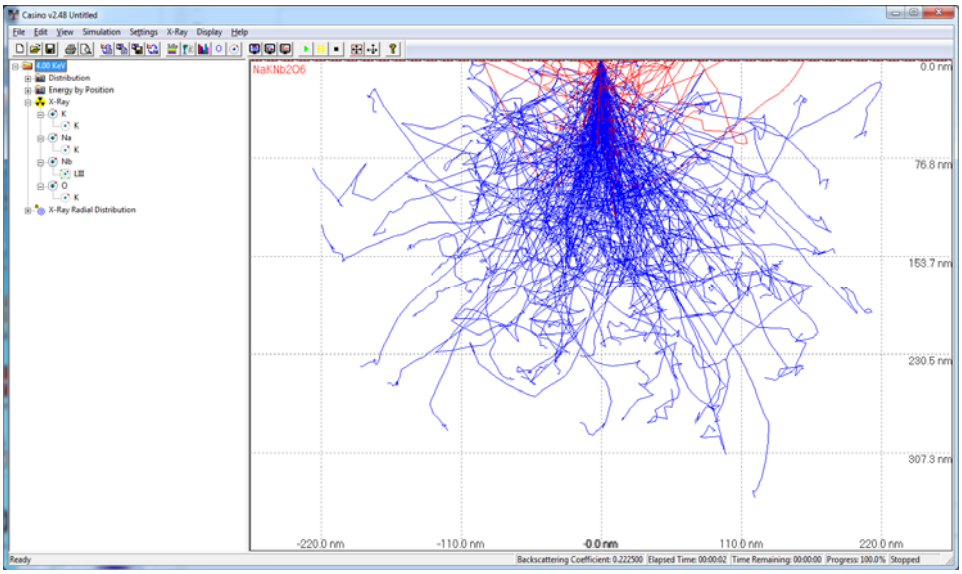


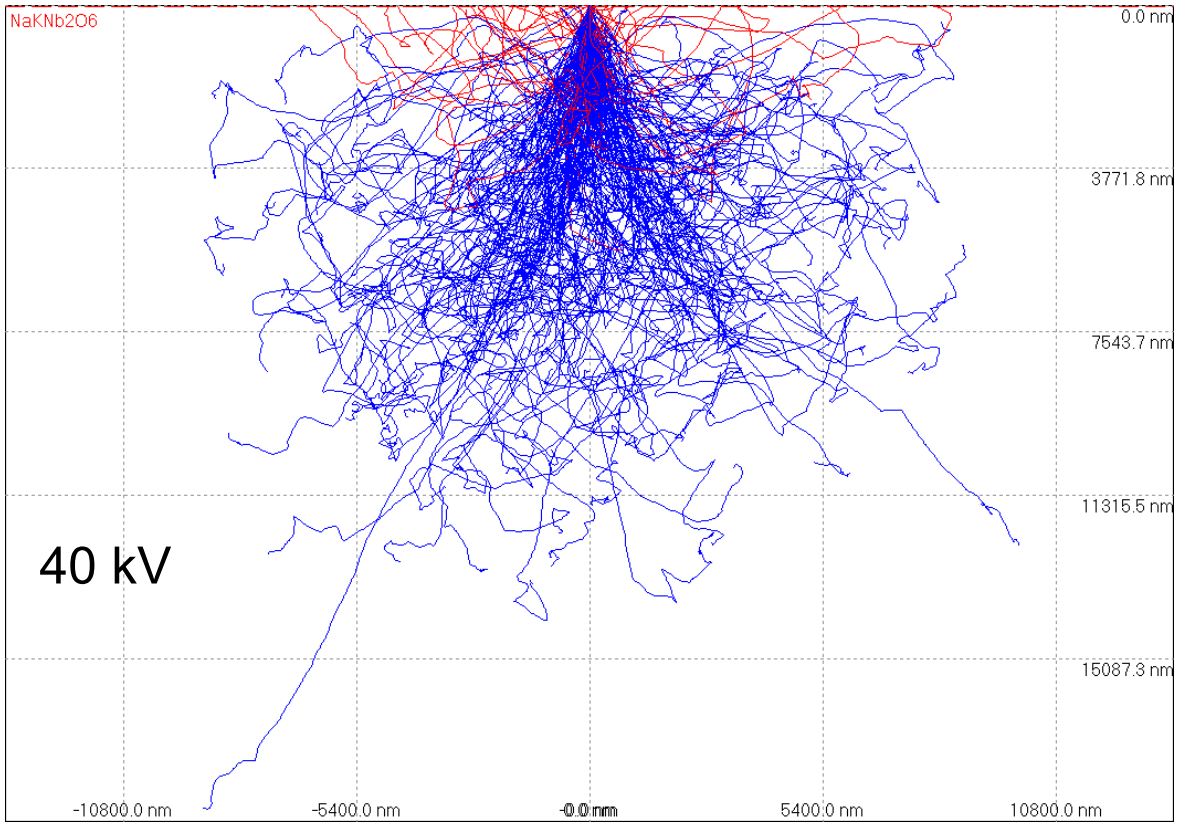
Casino

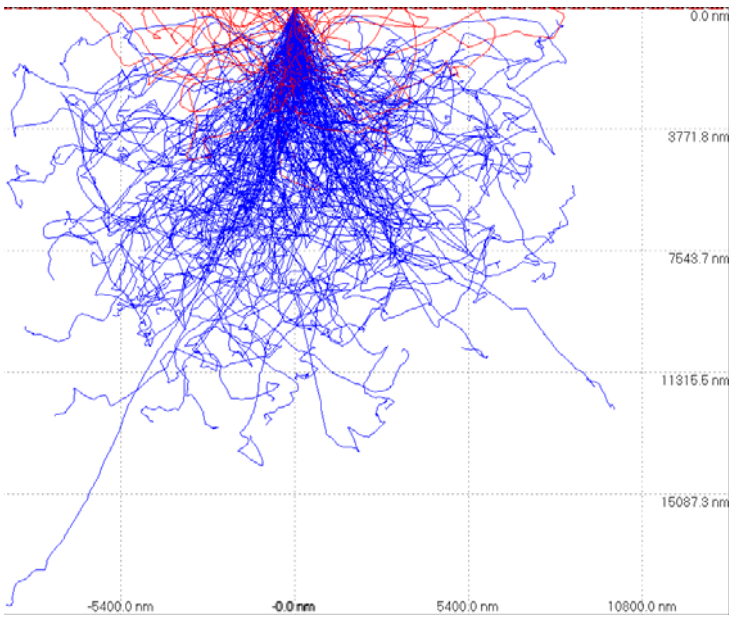




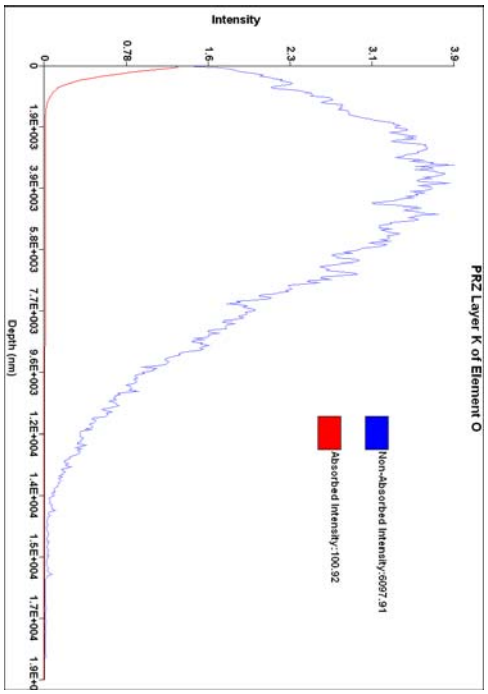
Monte-Carlo Simulation with CASINO

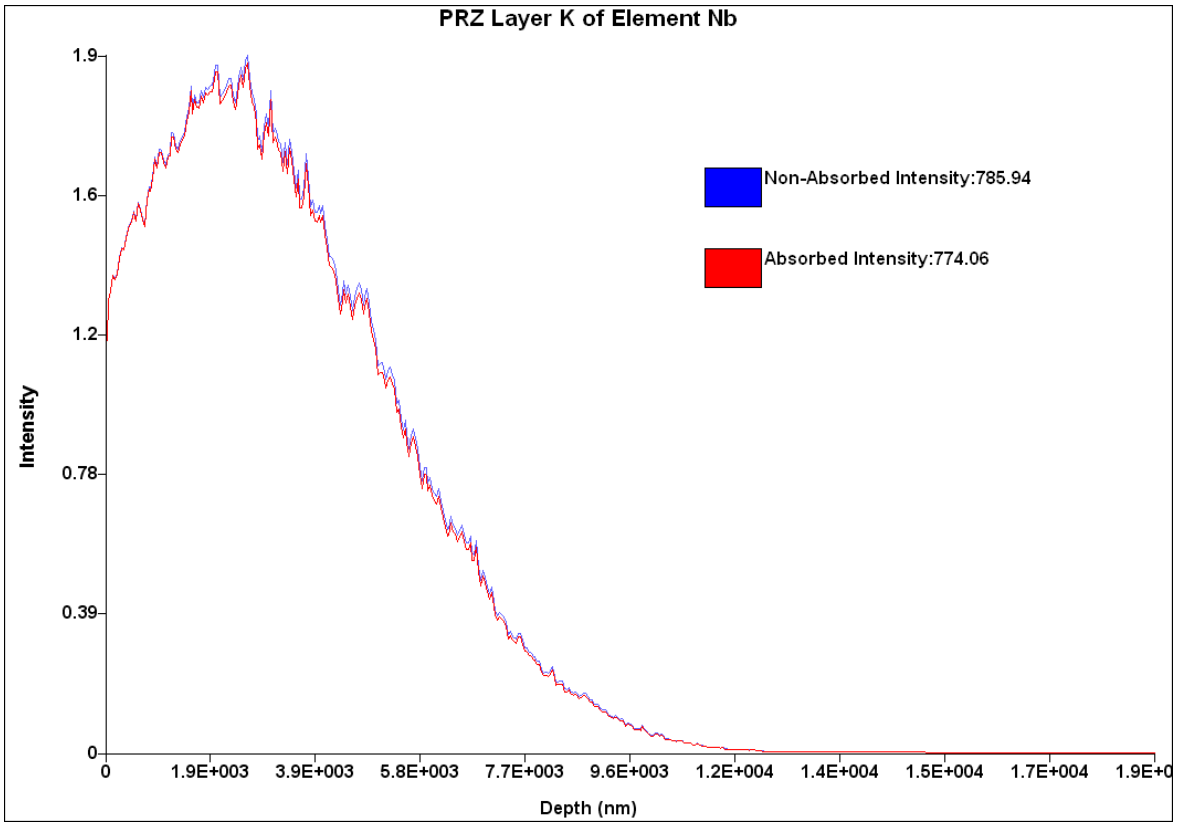


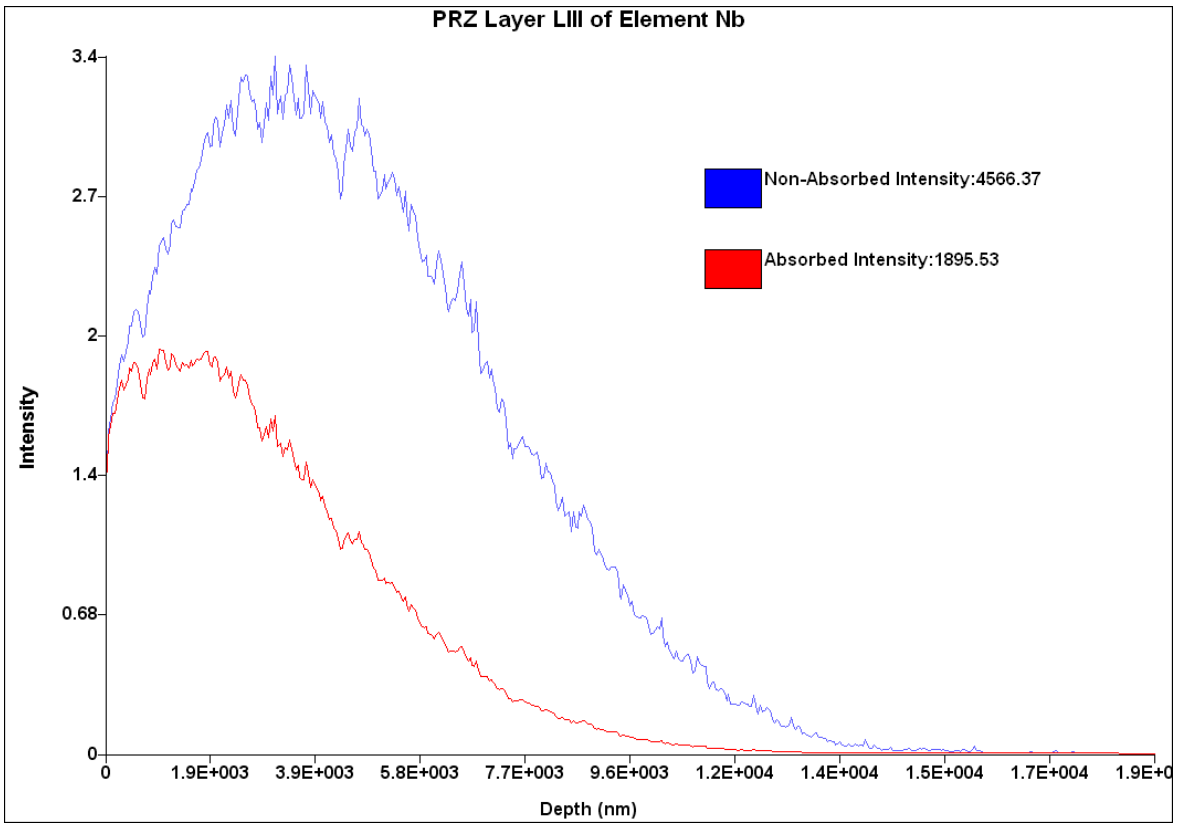

NaKNb2O6
0.0 nm
3771.8 nm
7543.7 nm
11315.5 nm
15087.3 nm
40 kV
-10800.0 nm
-5400.0 nm
-0.0 nm
5400.0 nm
10800.0 nm

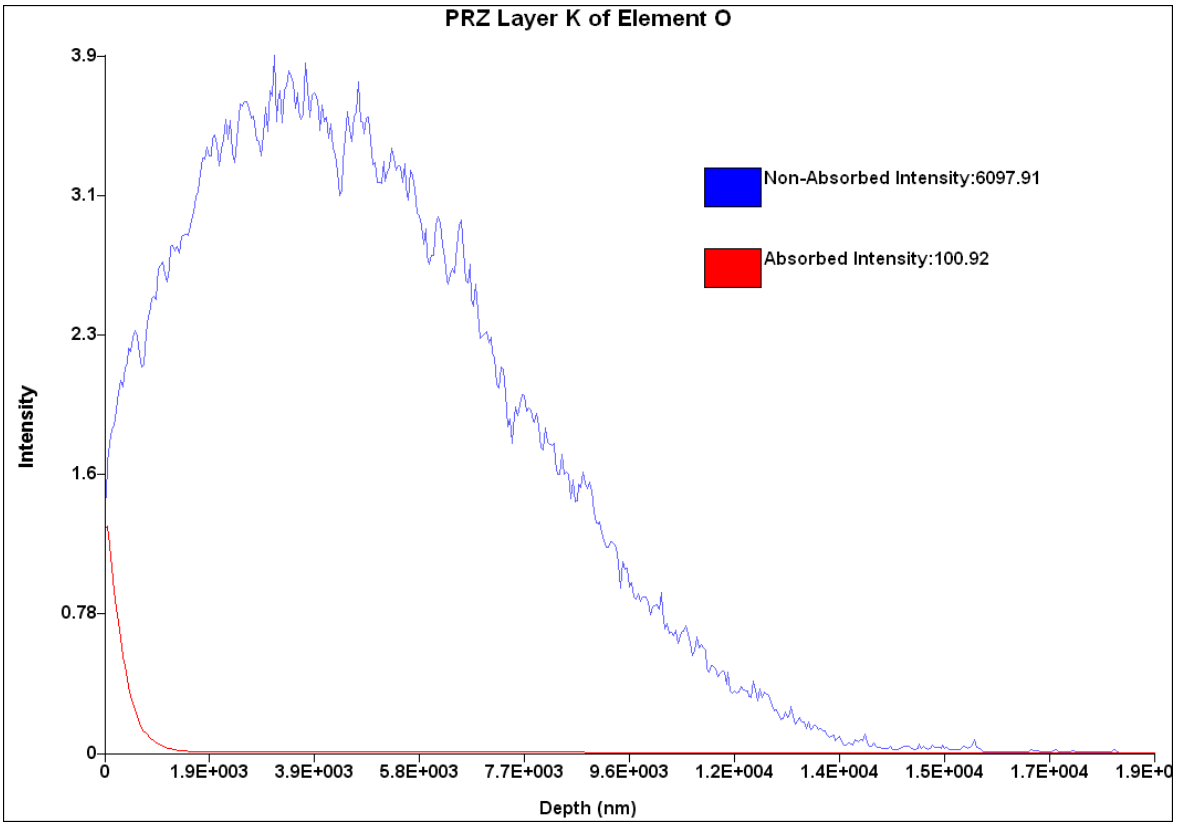

0.0 nm
3771.8 nm
7543.7 nm
11315.5 nm
15087.3 nm
-5400.0 nm
-0.0 nm
5400.0 nm
10800.0 nm

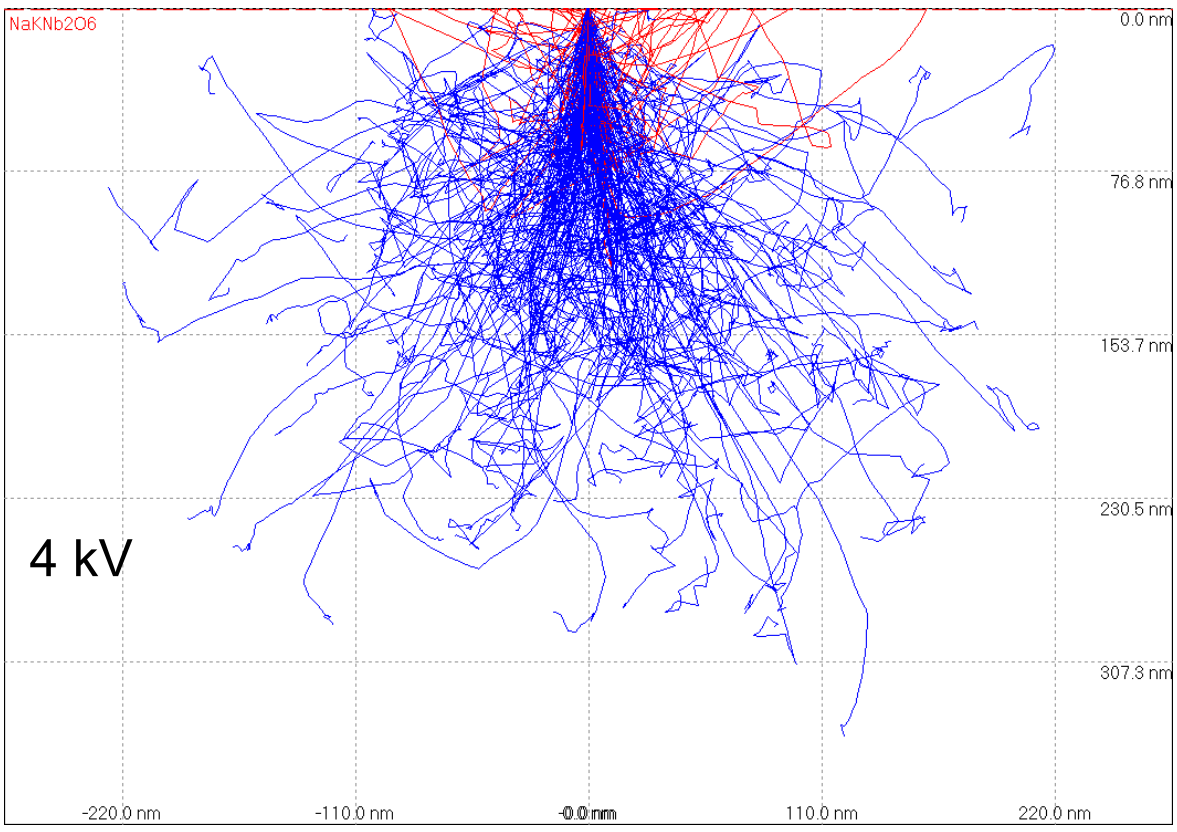
40 kV

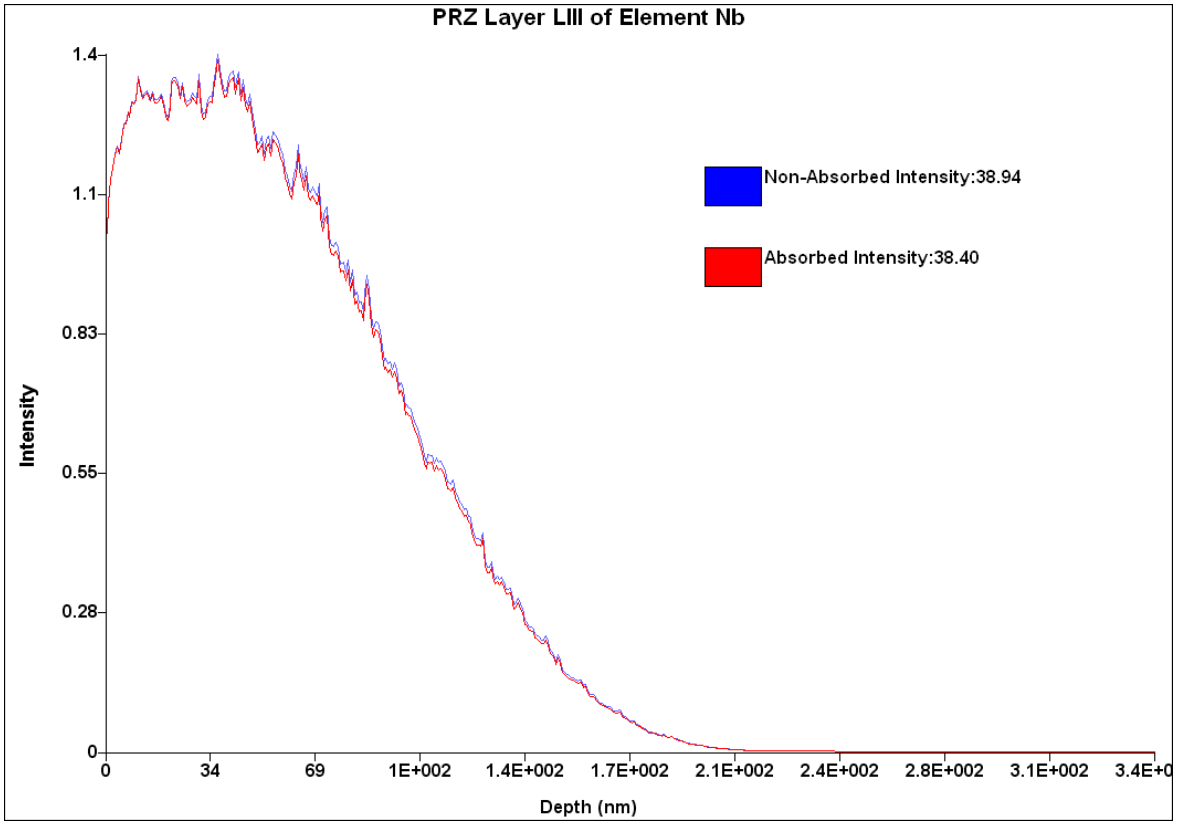

Intensity
Depth (nm)
PRZ Layer K of Element O
Absorbed Intensity:100.92
Non-Absorbed Intensity:6997.91

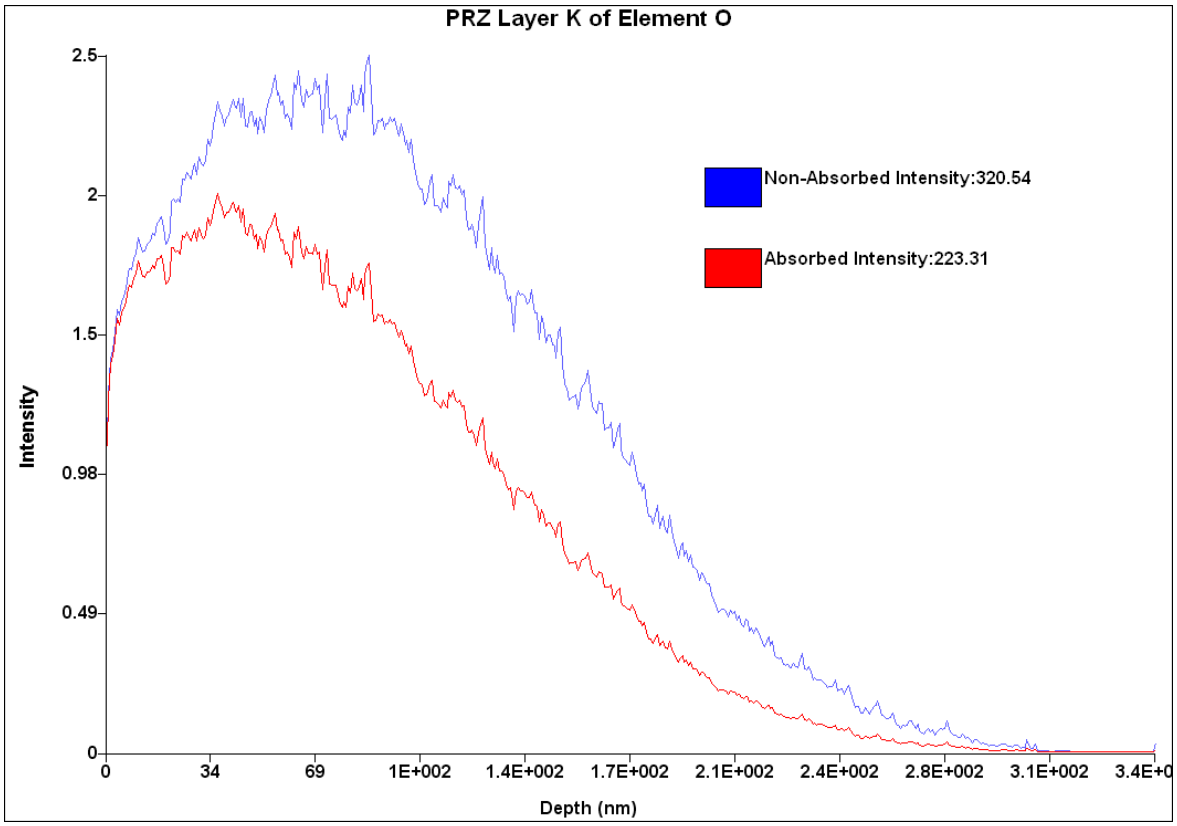

PRZ Layer K of Element Nb
Non-Absorbed Intensity:785.94
Absorbed Intensity:774.06
Intensity
1.9
1.6
1.2
0.78
0.39
0
0
1.9E+003
3.9E+003
5.8E+003
7.7E+003
9.6E+003
1.2E+004
1.4E+004
1.5E+004
1.7E+004
1.9E+0
Depth (nm)


PRZ Layer LIII of Element Nb
Non-Absorbed Intensity:4566.37
Absorbed Intensity:1895.53
Intensity
3.4
2.7
2
1.4
0.68
0
0
1.9E+003
3.9E+003
5.8E+003
7.7E+003
9.6E+003
1.2E+004
1.4E+004
1.5E+004
1.7E+004
1.9E+0
Depth (nm)


PRZ Layer K of Element O
Non-Absorbed Intensity:6097.91
Absorbed Intensity:100.92
Intensity
3.9
3.1
2.3
1.6
0.78
0
0
1.9E+003
3.9E+003
5.8E+003
7.7E+003
9.6E+003
1.2E+004
1.4E+004
1.5E+004
1.7E+004
Depth (nm)


NaKNb2O6
0.0 nm
76.8 nm
153.7 nm
230.5 nm
307.3 nm
4 kV
-220.0 nm
-110.0 nm
110.0 nm
220.0 nm

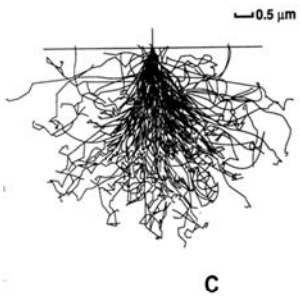

PRZ Layer LIII of Element Nb
Non-Absorbed Intensity:38.94
Absorbed Intensity:38.40
Intensity
1.4
1.1
0.83
0.55
0.28
0
0
34
69
1E+002
1.4E+002
1.7E+002
2.1E+002
2.4E+002
2.8E+002
3.1E+002
3.4E+0
Depth (nm)


PRZ Layer K of Element O
Non-Absorbed Intensity:320.54
Absorbed Intensity:223.31
Intensity
2.5
2
1.5
0.98
0.49
0
0
34
69
1E+002
1.4E+002
1.7E+002
2.1E+002
2.4E+002
2.8E+002
3.1E+002
3.4E+0
Depth (nm)

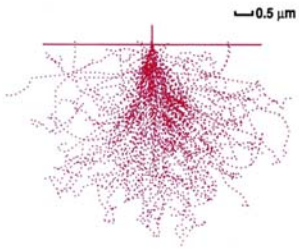
Quantification

When the going gets tough.....

Correction matrix



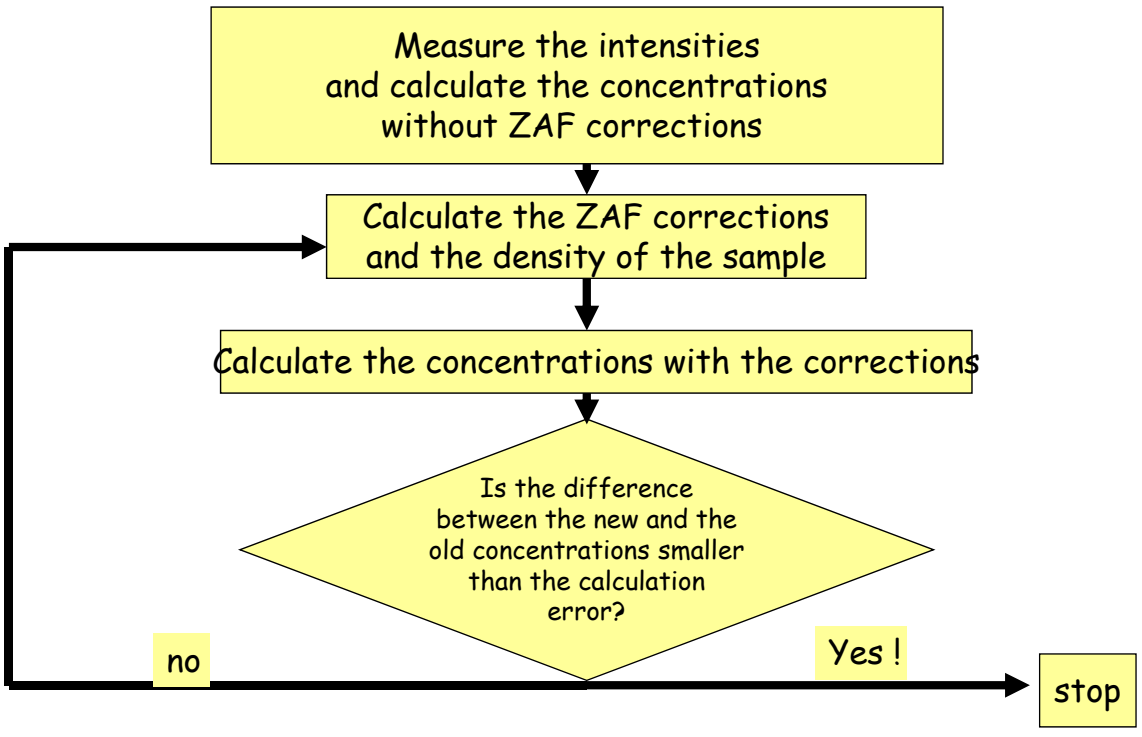
C



$$[Z \times A \times F]\frac{c_i}{c_i^{std}} = \frac{I_i}{I_i^{std}} = k_i$$

- "Z" describe how the electron beam penetrates in the sample (Zdependant and density dependant) and loose energy
- "A" takes in account the absorption of the X-rays photons along the path to sample surface
- "F" adds some photons when (secondary) fluorescence occurs

Flow chart of quantification



Correction methods:

- ZAF (purely theoretical)
- PROZA Phi-Rho-Z
- PaP (Pouchou and Pichoir)
- XPP (extended Puchou/Pichoir)

- with standards (same HT, current, detector settings)
- Standardless: theoretical calculation of I_{std}
- Standardless optimized: « hidden » standards, user defined peak profiles

Quantitative EDX in SEM

•Acquisition under best conditions

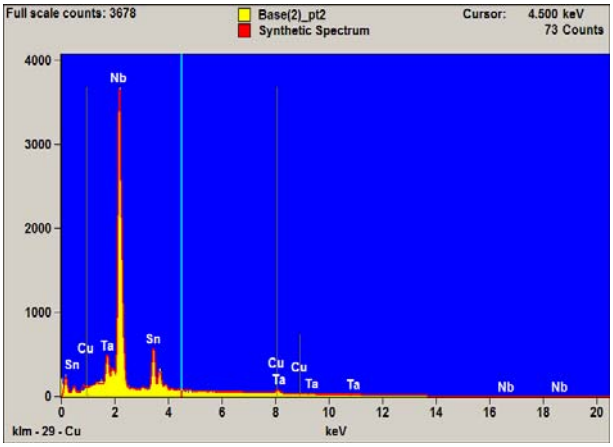
- –Flat surface without contamination, horizontal orientation of the surface (no Au coating, use C instead)
- –Sample must be homogenous at the place of analysis (interaction volume !!)
- –High count rate (but dead time below 30%)
- –Overvoltage U=Eo/Ec >1.5-2

•For acquisition times of 100sec. :
detection of ~0.5at% possible for almost all elements

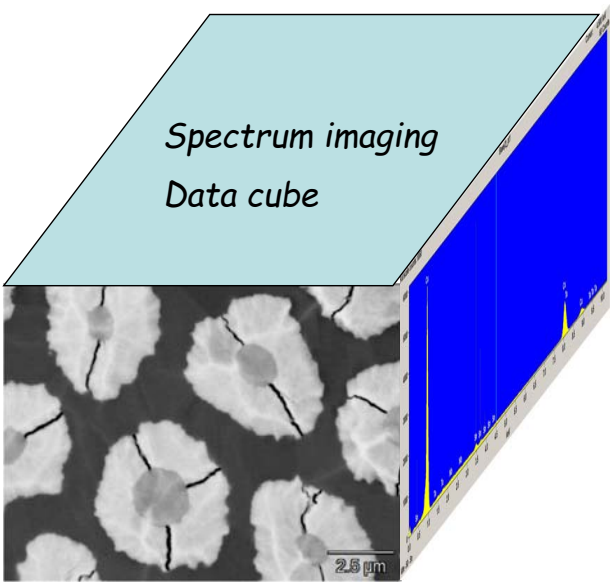
•Standardless quantification

•possible with high accuracy (intensities of references under the given conditions can be calculated for a great range of elements), test with samples of known composition, light elements (like O) are critical…

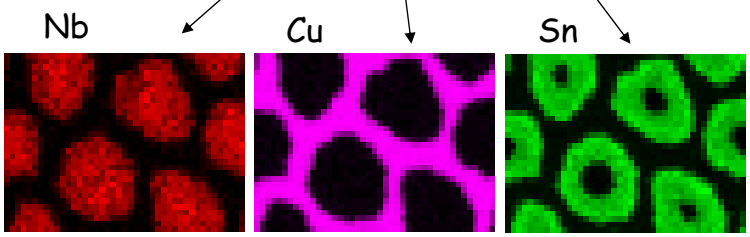
•Spatial resolution depends strongly on HT and the density of the sample



Synthesized spectrum



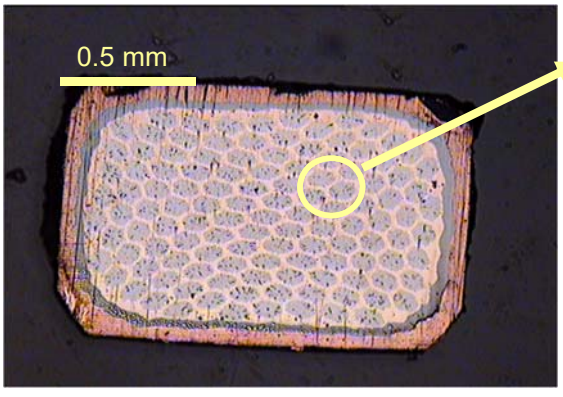
Extraction of element maps

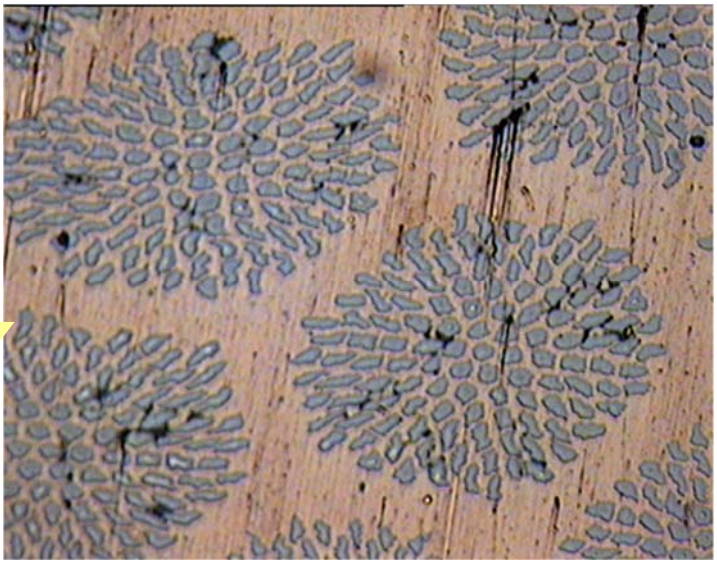


Nb_3Sn multifilament superconducting cables

Superconducting Nb_3Sn cables for high magnetic fields 10-20T:
increase current density, lower cost
Potential Applications:
NMR, Tokamak fusion reactors
Large Hadron Collider (LHC), CERN

Typical cable:
1 x 1.5mm cross-section
121x121 filaments of Nb_3Sn
in a bronze (Cu/Sn) matrix





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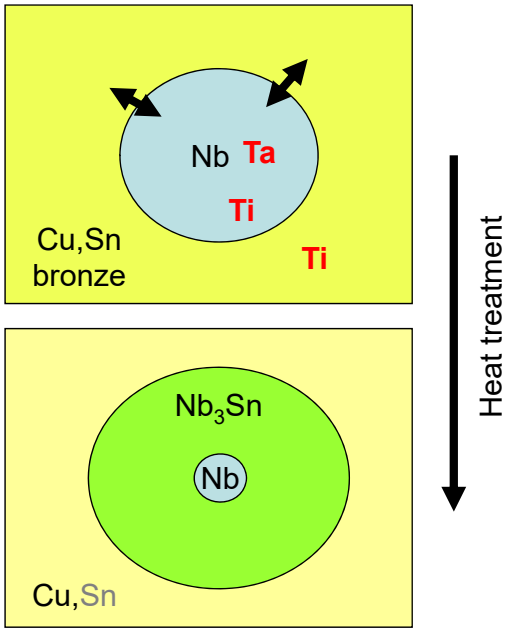
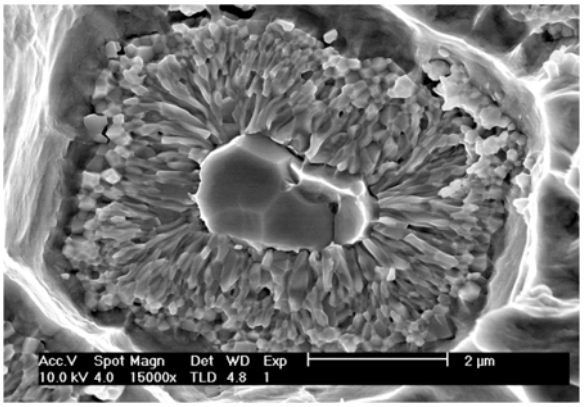
Dept. Condensed Matter Physics (DPMC),
University of Geneva

Processing
„bronze route"

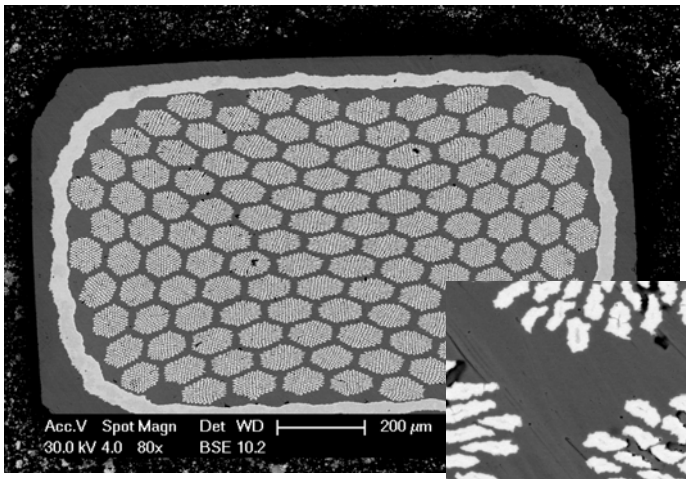


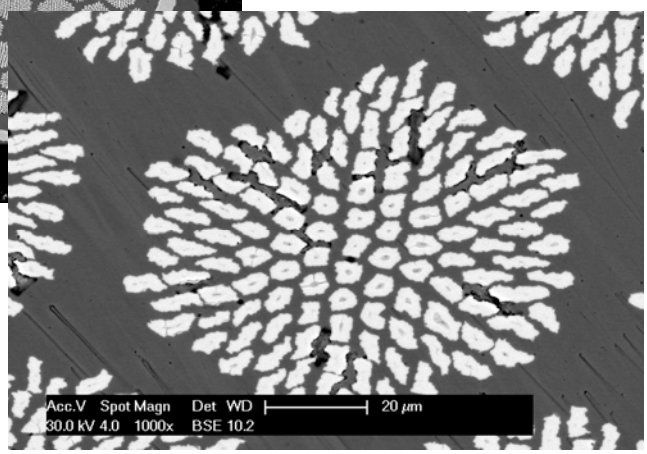
Cu and Ti are believed to play an important role at the grain boundaries (pinning)

- Is the Nb3Sn phase homogenous?
- Is it possible to detect Cu and Ti at the grain boundaries ?



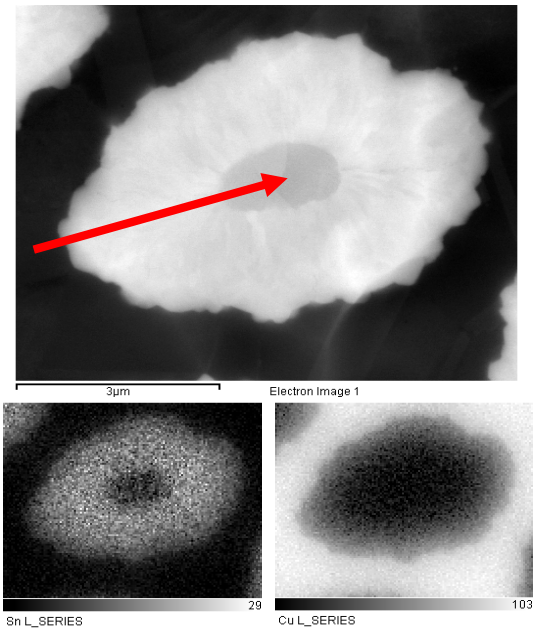
SEM: reacted filament

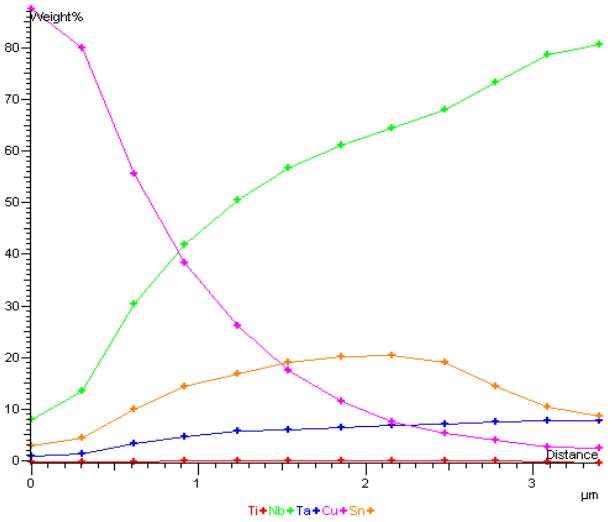




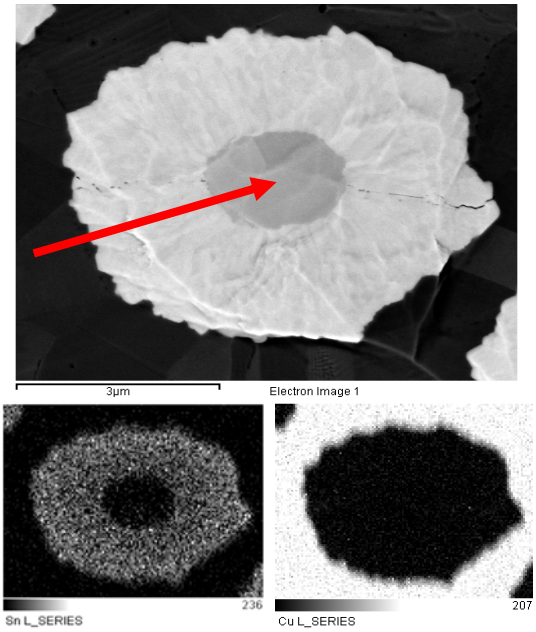
SEM BSE images

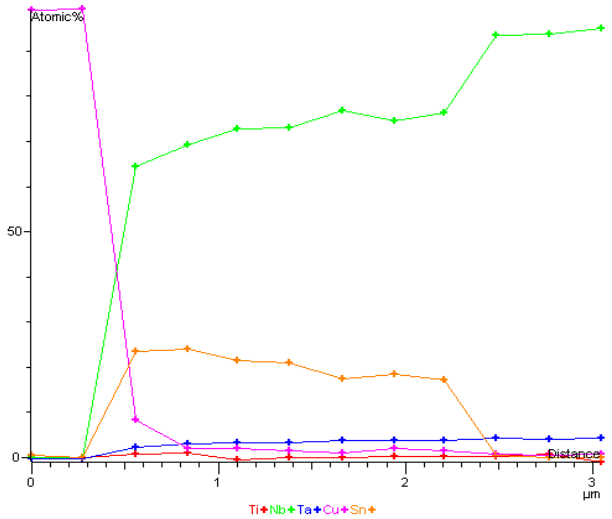
Spatial resolution @ 30kV



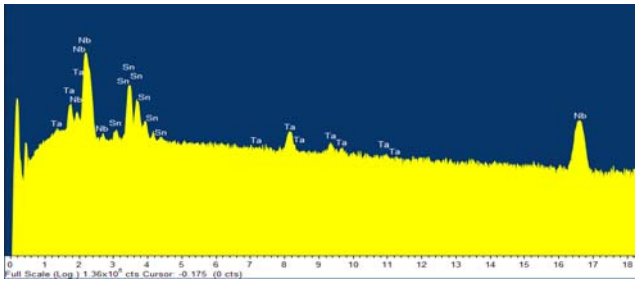


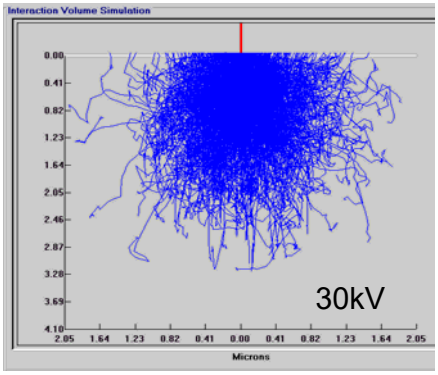
Spatial resolution @ 7kV

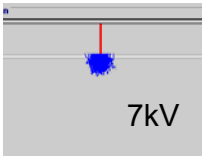


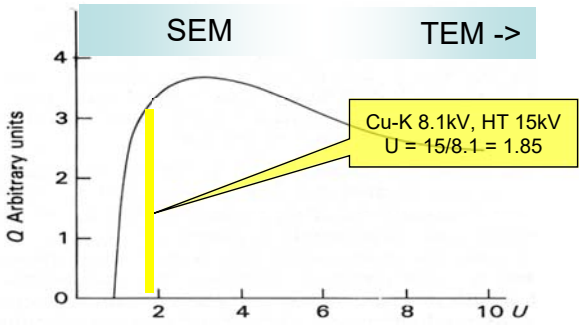


Overvoltage and penetration depth !



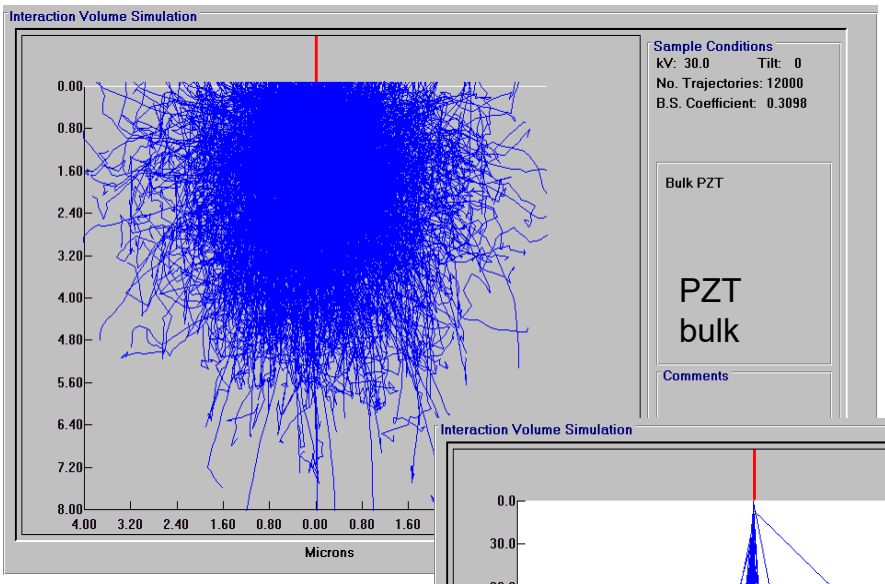




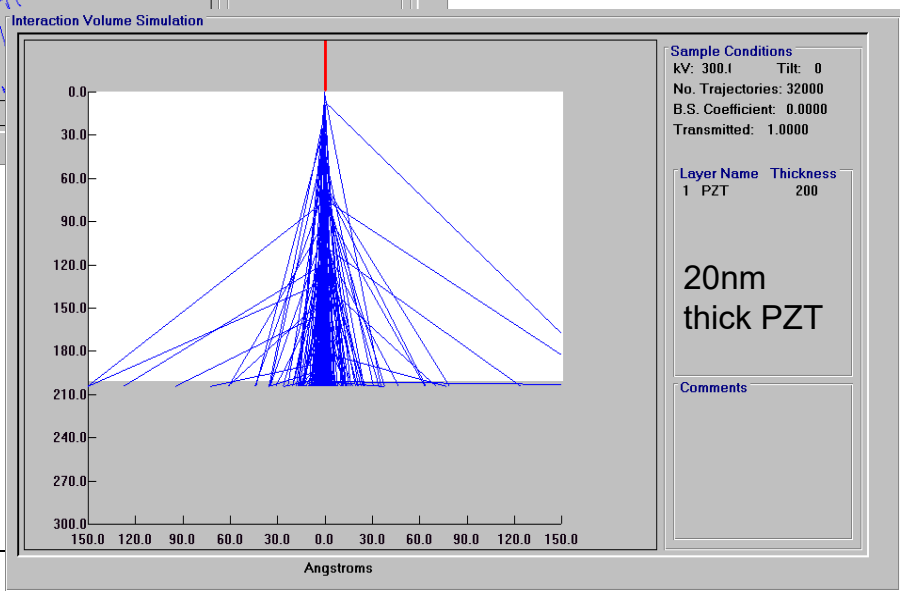


To ionized the incident electron MUST have an energy larger than the core shell level U>1. To be efficient, it should have about twice the edge energy U>2.

- *Nb Ka1 16.6 keV*
  Nb La1 2.14 keV *Ta La1 8.14 keV*
- *Cu Ka1 8.1 keV* *Ta Ma1 1.71 keV*
  Cu La1 0.93 keV *Ti Ka1 4.51 keV*
- *Sn Ka1 25.2 keV* *Ti La1 0.45 keV*
  Sn La1 3.44 keV



EDS in TEM



High spatial resolution !