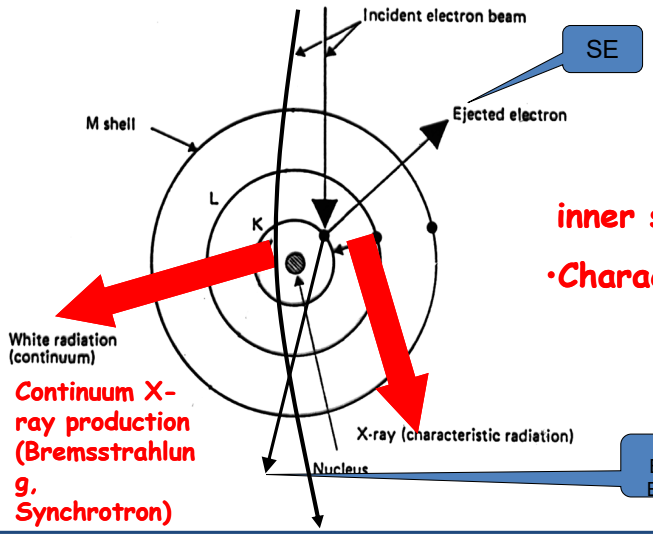
EDX Microanalysis in TEM

a) Review (brush-up) generation and detection of X-rays, SDD detectors

b) Quantification
- EDX in SEM, Interaction volume
- ZAF matrix corrections
- EDX in TEM (Cliff-Lorimer, thin film)

c) 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)**

Forbidden transitions !
quantum mechanics:
conservation of angular momentum

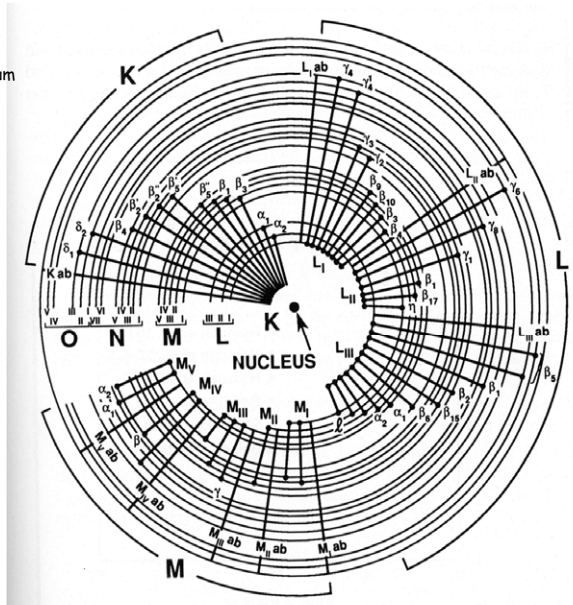
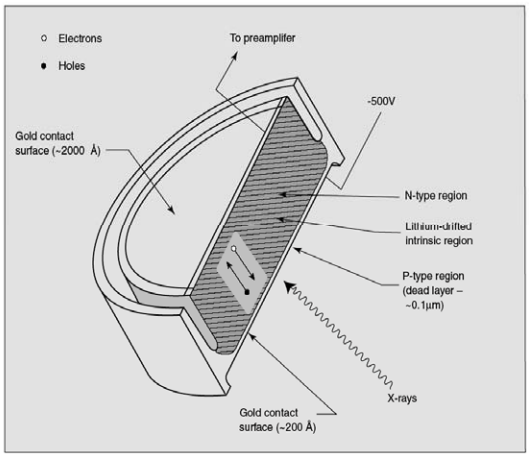
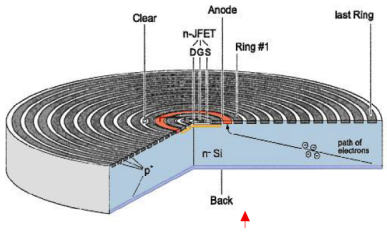


Figure 3.37. Comprehensive energy-level diagram showing all electron transitions which give rise to *K*, *L*, and *M* x rays (Woldseth, 1973).

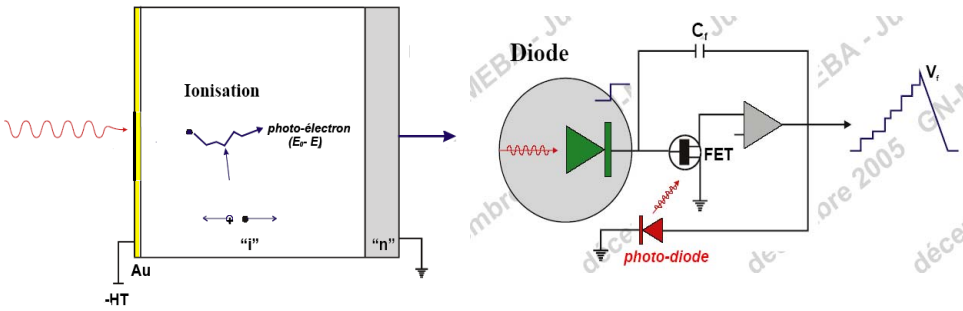
Figure 4-2. Cross section of a typical lithium-drifted silicon detector. X-rays create electron-hole pairs in the intrinsic region of the semiconductor; these charge carriers then migrate to the electrodes under the influence of an applied bias voltage.

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

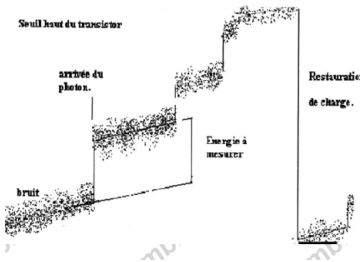




modern silicon drift (SDD) detector:
no LN cooling required



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 and artifacts

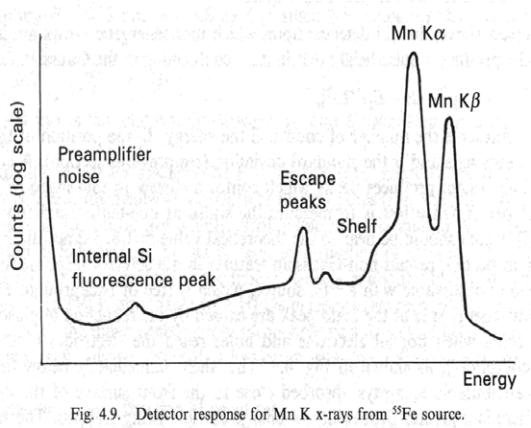
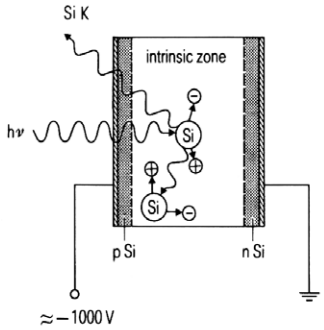


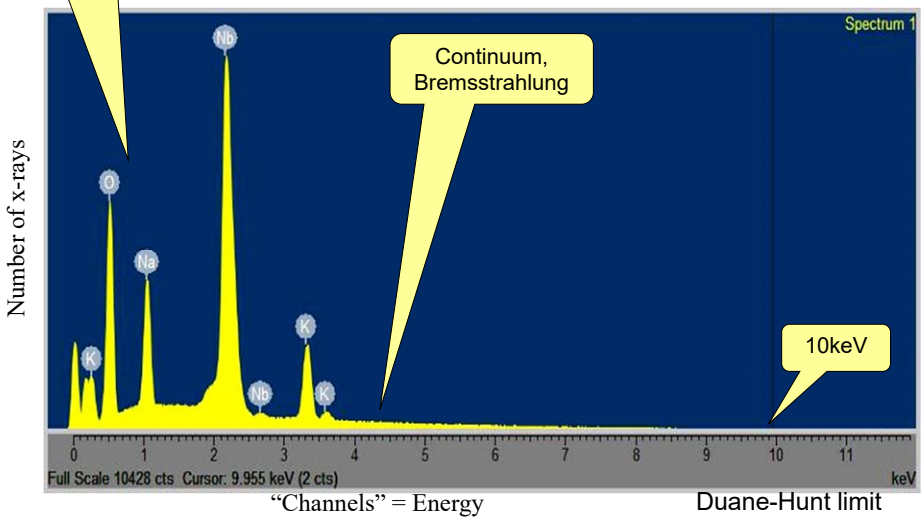
Fig. 4.9. Detector response for Mn K x-rays from ^{55}Fe source.



Take care when looking for "trace" elements (low concentrations). Don't confuse small peaks with escape peaks !

EDX spectrum in a SEM of $(K,Na)NbO_3$

Electron beam: 10keV



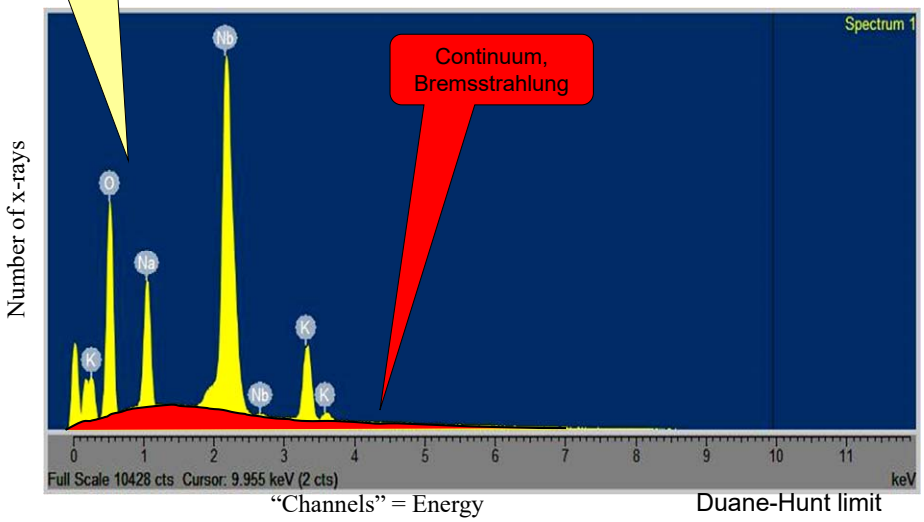
Number of x-rays

"Channels" = Energy

Duane-Hunt limit

Removal of Background...

Electron beam: 10keV



Number of x-rays

"Channels" = Energy

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

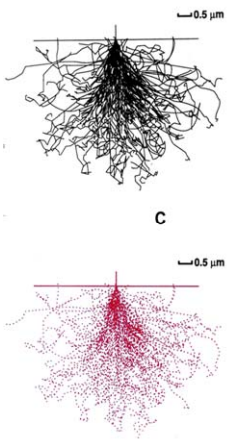
Yes, but…..

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

Quantification

When the going gets tough…..

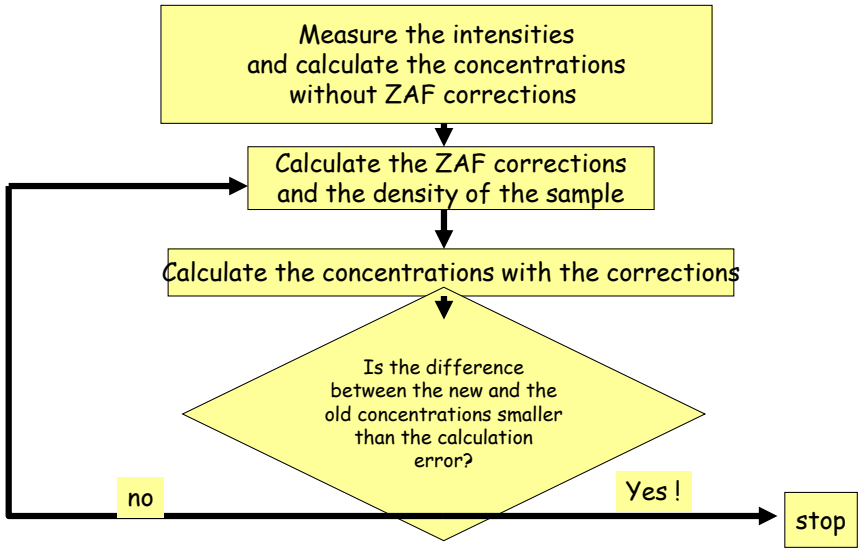
Correction matrix



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

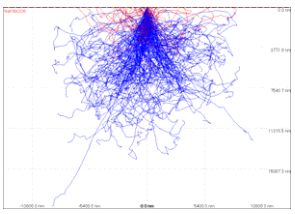
- "Z" describe how the electron beam penetrates in the sample (Z dependant and density dependant) and loose energy
- "A" takes in account the absorption of the X-rays photons along the path to sample surface
- "F" adds some photons when (secondary) fluorescence occurs

Flow chart of quantification



Correction methods for EDX in SEM

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

$$\frac{C_i}{C_{(i)}} = K \frac{I_i}{I_{(i)}}$$

K is the *sensitivity factor* (not constant), determined (inversely) by:

- Z the atomic number
- A absorption of X-rays within the specimen
- F fluorescence of X-rays within the specimen

The correction factor for bulk analysis is referred to as *ZAF correction*

Cliff and Lorimer 1972

- HOWEVER…for thin samples A and F are very small and can be ignored
  - Sensitivity factor proportional only to Z!
- In 1975 Cliff and Lorimer showed that a standard is not needed if intensities for two elements are gathered simultaneously and compared…

The weight percent of each element analysed can be related to the measured intensities

For a binary system this gives:

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B}$$ Cliff-Lorimer equation

$$C_A + C_B = 100\%$$

The convention is to use wt%

k_{AB} is another sensitivity factor, called the Cliff-Lorimer factor

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B}$$

$$\frac{C_B}{C_C} = k_{BC}\frac{I_B}{I_C}$$

$$C_A + C_B + C_C = 100\%$$

Ternary systems

$$k_{AB} = \frac{k_{AD}}{k_{BD}} \qquad k_{BC} = \frac{k_{BD}}{k_{CD}}$$

k_{AB} can be calculated from k_{AD} and k_{BD}

If the specimen is thin enough to assume no absorption and no fluorescence then k_{AB} is only related to the atomic number, Z.

This is often true in TEM/XEDS

For bulk specimens ZAF correction is necessary

- k-factors can be determined experimentally (using standards) or calculated from first principles
- Remember this is not a constant, but a sensitivity factor that depends on the detector, microscope, analysis conditions…

depends on your detector, your microscope

- We only need to determine k_{AB} in relation to one element. Then all other *k*-values can be calculated:

$$k_{AB} = \frac{k_{AC}}{k_{BC}}$$

Typically Si as reference element

- Experimental k-values can be obtained from single-phase compounds
- Standard spectra must be recorded for each instrument setup

In case of non neglectable absorption:

$$k'_{AB} = k_{AB}\left[\frac{(\mu/\rho)^{A}_{sp}}{(\mu/\rho)^{B}_{sp}}\right]\times\left\{\frac{1-\exp\left[-(\mu/\rho)^{B}_{sp}\rho t\cos ec\theta\right]}{1-\exp\left[-(\mu/\rho)^{A}_{sp}\rho t\cos ec\theta\right]}\right\}$$

$(\mu\rho)^{A}_{sp}$ and $(\mu\rho)^{B}_{sp}$-- The mass absorption coefficients of the characteristic X-ray lines A and B
k_{AB}: zero thickness k-factor
ρ: density
t: thickness
θ : take off angle

The quantitative analysis of thin specimens: a review of progress from the Cliff-Lorimer to the new ζ-factor methods

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Department of Materials Science and Engineering/Center for Advanced Materials and Nanotechnology, Lehigh University, Bethlehem, PA 18015, U.S.A.

Alternative to Cliff Lorimer
Not implemented in CIME

Comparison with the Cliff-Lorimer ratio method

The advantages of the ζ-factor method over the traditional Cliff-Lorimer ratio method were described in the previous sections. These advantages are summarized as: (1) use of PE thin film standards; (2) built-in absorption correction; (3) calculation of the spatial resolution; (4) mapping of composition in terms of the absolute number of atoms and (5) determination of the MDM values. Compared with the previously proposed absorption-correction procedures, the absorption correction in the ζ-factor method is performed for individual measurements only using X-ray intensities and this is the most flexible and easy approach. In addition, the ζ-factor can also be used for diagnosis of problems with the AEM–XEDS interface in combination with the NIST SRM 2063a universal, standard, thin specimen. There are two major disadvantages to the new ζ-factor method: (1) the need for specimen-thickness information and (2) the requirement for measurement of the beam current. The former limitation can be simplified if PE thin films are used. Therefore, the capability for *in-situ* beam current measurement is a minimum requirement if the ζ-factor method is to be used.

If we take a ratio between Eqs (2) and (6) and rearrange it as

$$\frac{C_A}{C_B} = \frac{\zeta_A I_A}{\zeta_B I_B} \qquad (25)$$

by comparing the above equation with the original Cliff-Lorimer ratio equation [Eq. (1)], the following relationship holds between the Cliff-Lorimer k-factor and the ζ-factor

$$k_{AB} = \frac{\zeta_A}{\zeta_B} \qquad (26)$$

Quantification procedure in ζ-factor method

Measured X-ray intensities: I_A, I_B, ..., I_j, ..., I_N
Acquisition parameters: $D_e = N_e I_p \tau$

Calculate initial mass thickness and compositions:

$$\rho t = \sum_j^N \frac{\zeta_j I_j}{D_e},\ C_A = \frac{\zeta_A I_A}{\sum_j^N \zeta_j I_j},\ \cdots,\ C_N = \frac{\zeta_N I_N}{\sum_j^N \zeta_j I_j}$$

Calculate corrections terms:

$$A_j = \frac{(\mu/\rho)_j^{sp}\ \rho t \operatorname{cosec}\alpha}{1-\exp[-(\mu/\rho)_j^{sp}\ \rho t \operatorname{cosec}\alpha]}$$

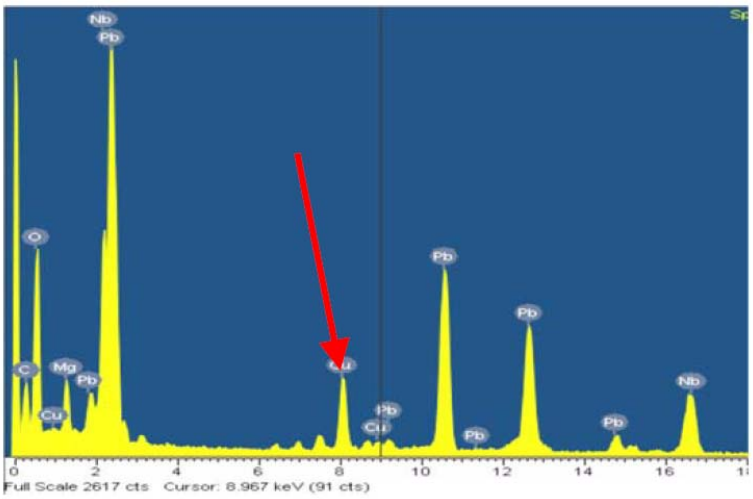
Calculate mass thickness and compositions:

$$\rho t = \sum_j^N \frac{\zeta_j I_j A_j}{D_e},\ C_A = \frac{\zeta_A I_A A_A}{\sum_j^N \zeta_j I_j A_j},\ \cdots,\ C_N = \frac{\zeta_N I_N A_N}{\sum_j^N \zeta_j I_j A_j}$$

Check convergence — No → (back to corrections terms)
Yes → Final mass thickness and compositions: ρt, C_j

Artifacts

how to recognize/minimize them

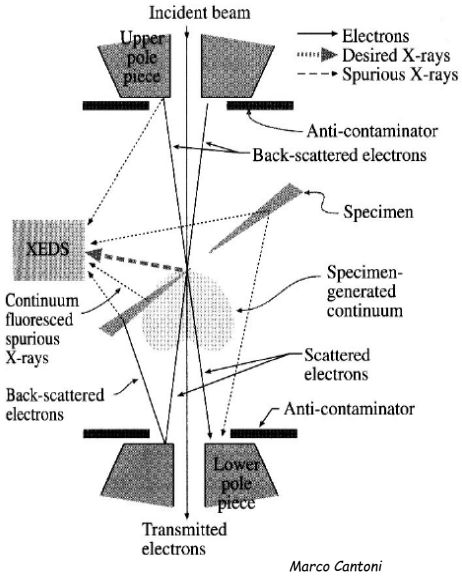


EDS in TEM

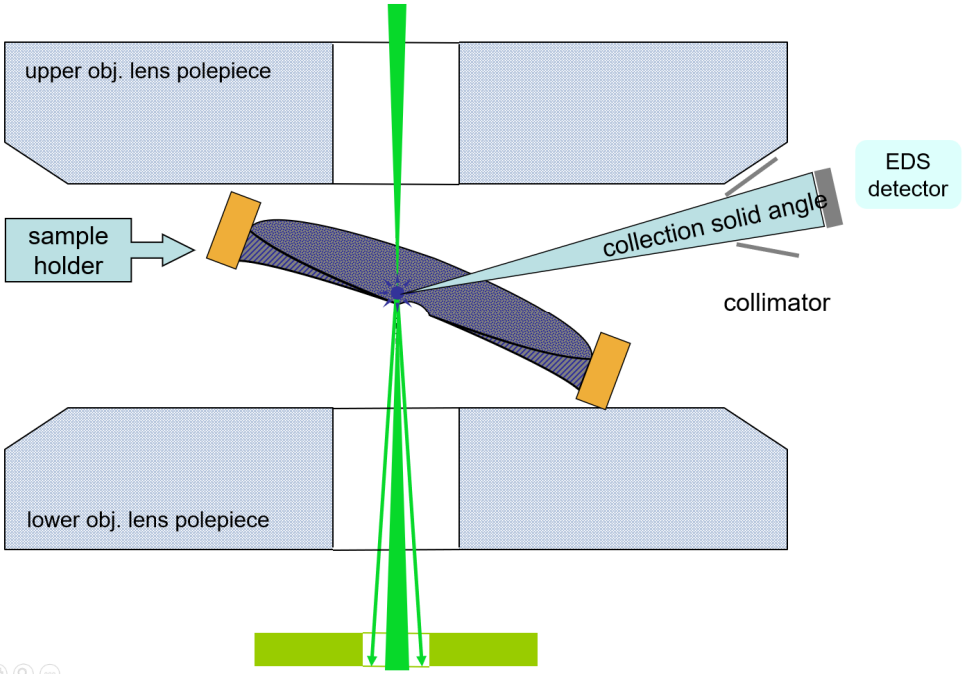
Thin samples -> correction factors weak (A and F can be neglected)

Very weak beam broadening -> high spatial resolution ~ beam diameter (~nm)

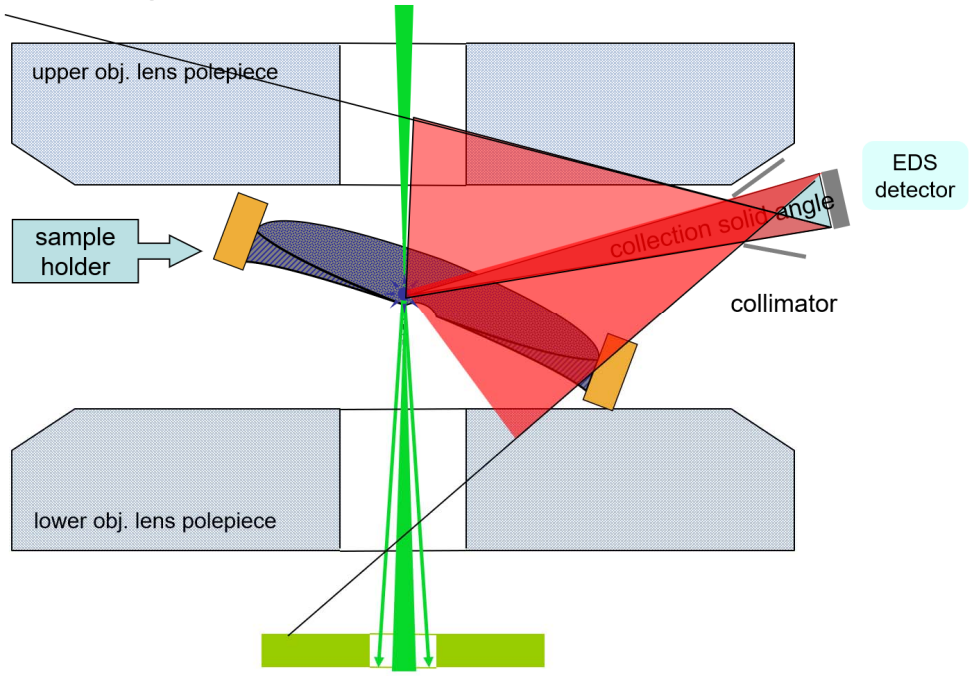
High energy: artifacts !



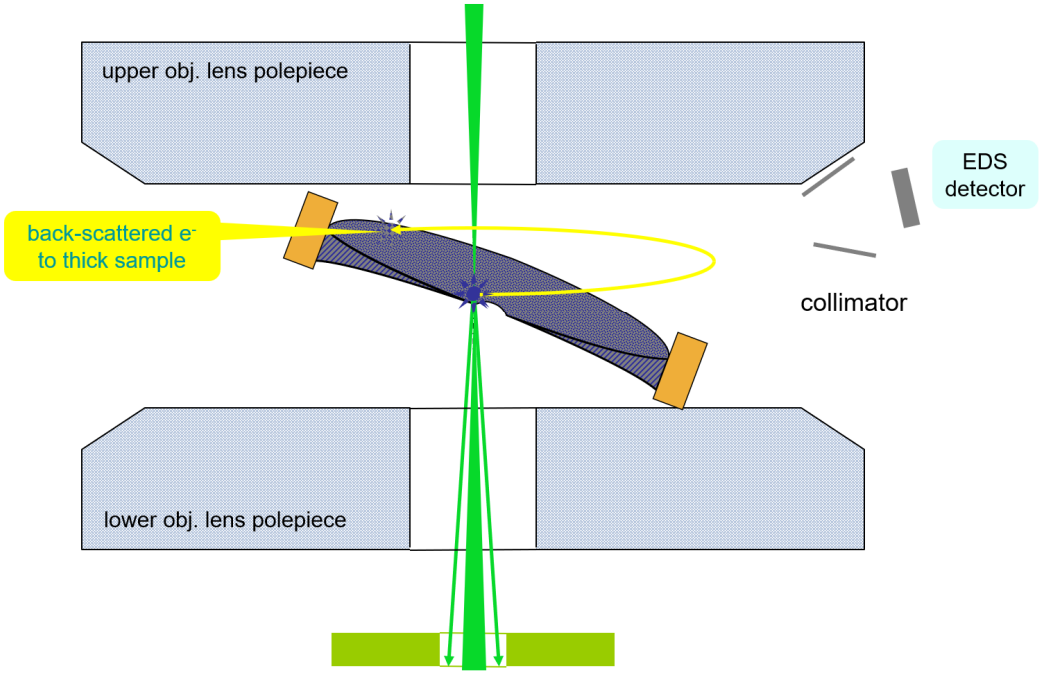
X-Ray collection in TEM EDS



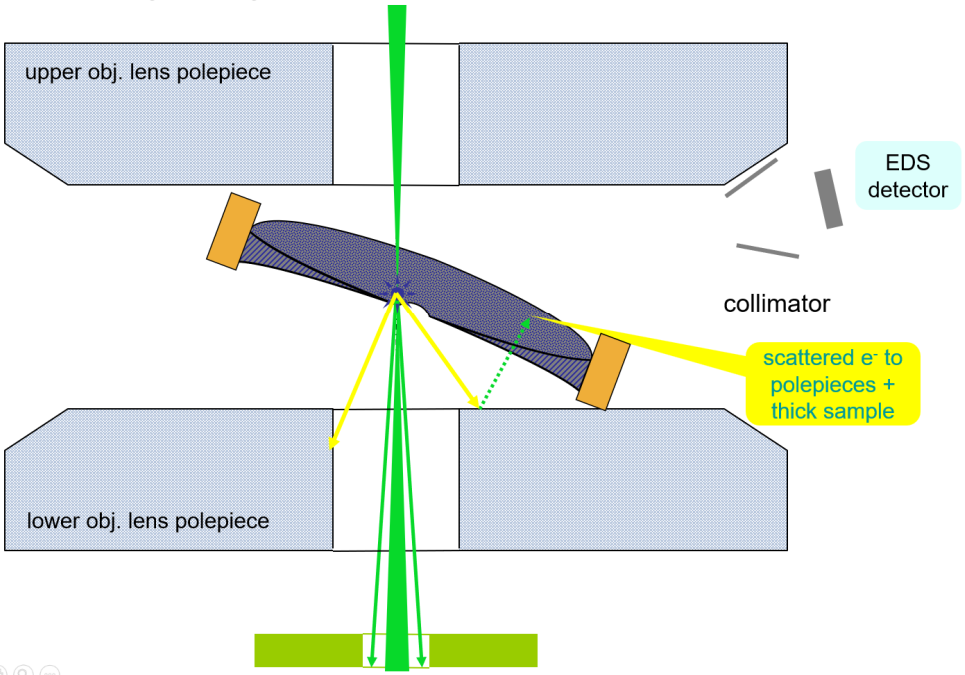
X-Ray collection in TEM EDS



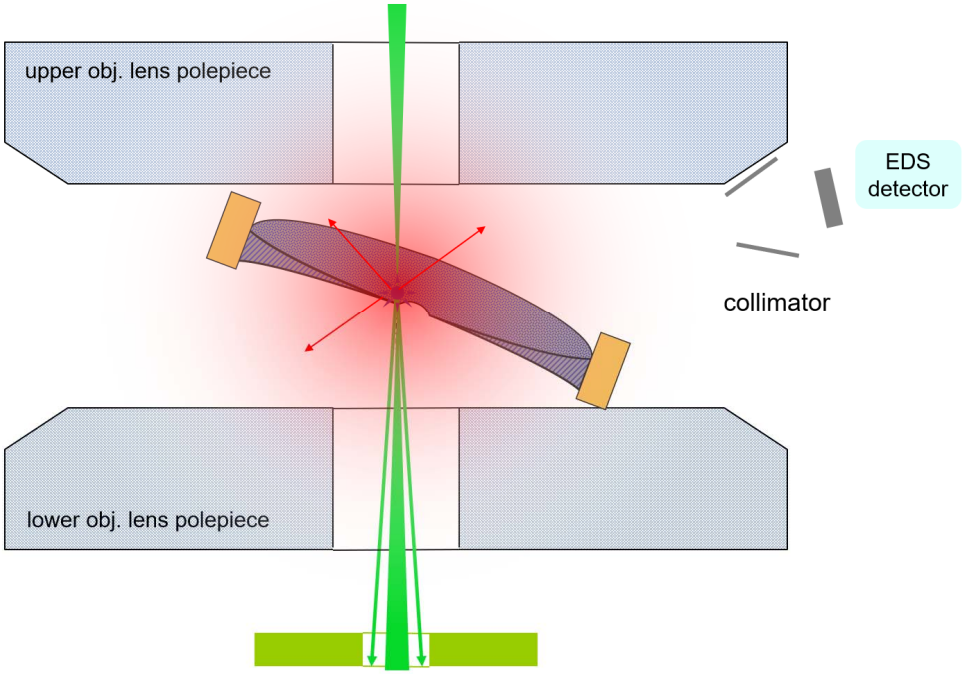
Stray X-Rays in TEM EDS



Stray X-Rays in TEM EDS



Stray X-Rays in TEM EDS: characteristic x-rays



Analytical TEM
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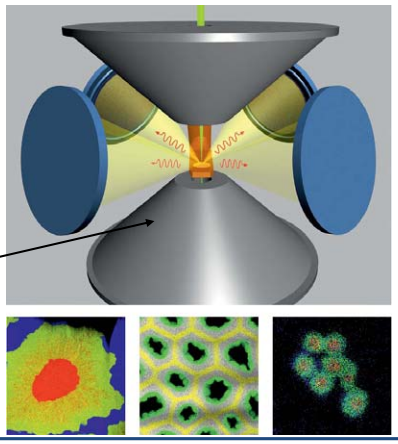
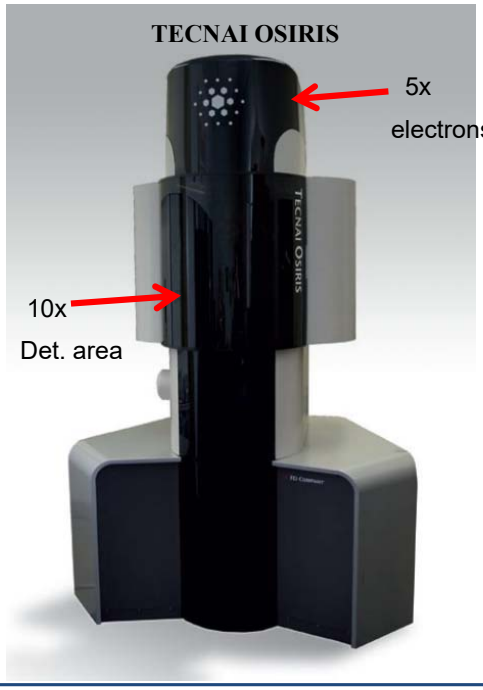
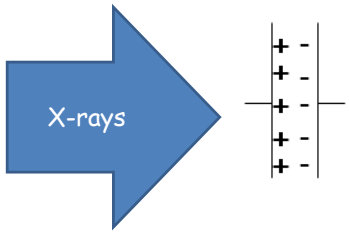
ChemiSTEM™ Technology
A revolution in EDX analytics

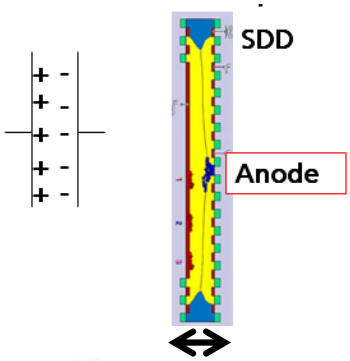


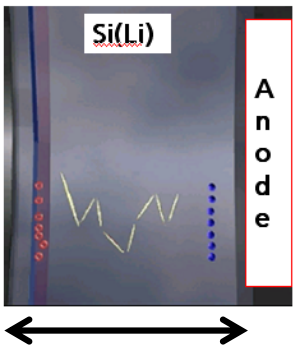
Be coated
pole-pieces

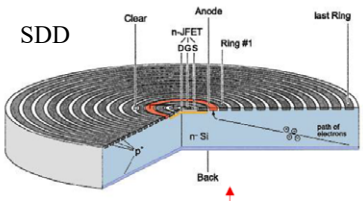


New possibilities due to SDD (silicon drift detector) technology









	SDD	Si(Li)
Thickness	300-400µm	3mm
Area	30,50,80mm^2	30mm^2
Det. Interval	4-10µsec.	50-100µsec.
Speed:	100'000cps	10'000cps
Cooling	Peltier	Liq. N

SUPER-X

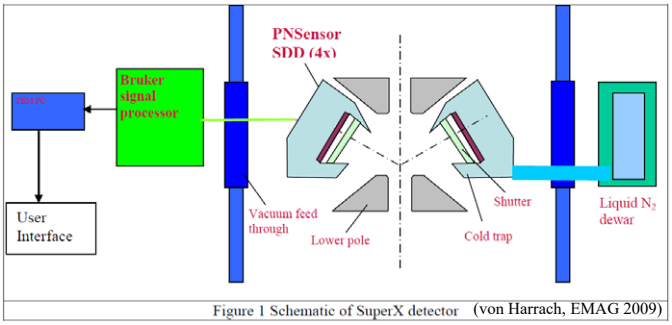
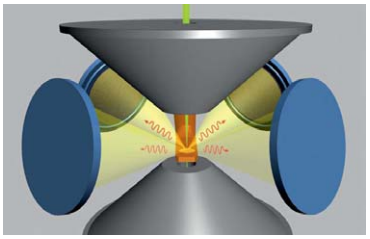
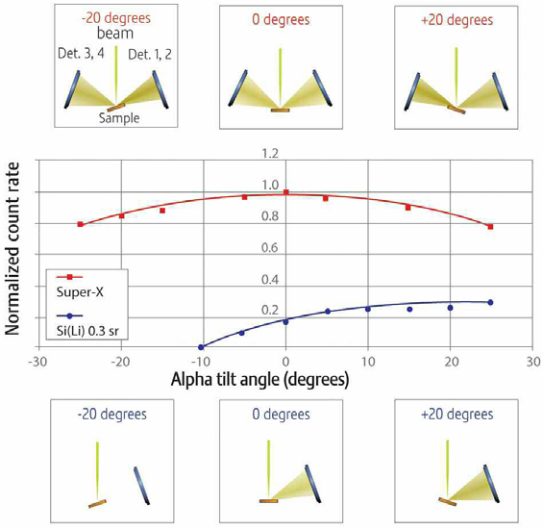
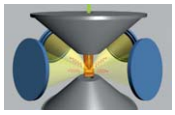


Figure 1 Schematic of SuperX detector (von Harrach, EMAG 2009)

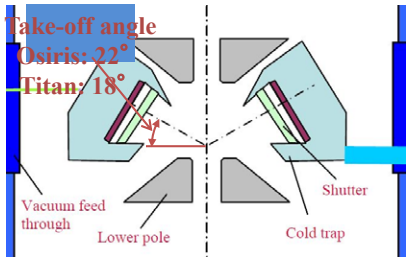


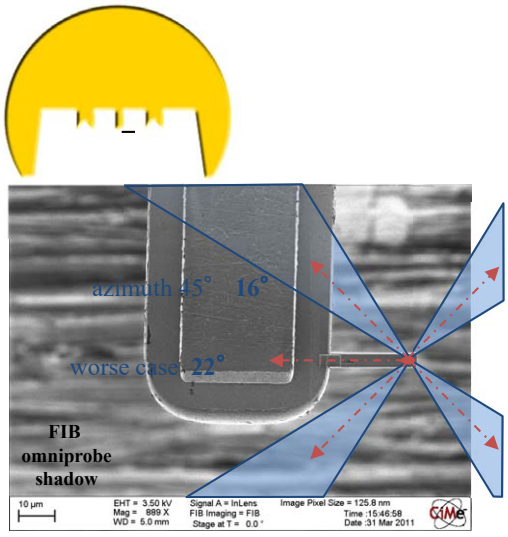
(from FEI ChemiSTEM Application note)

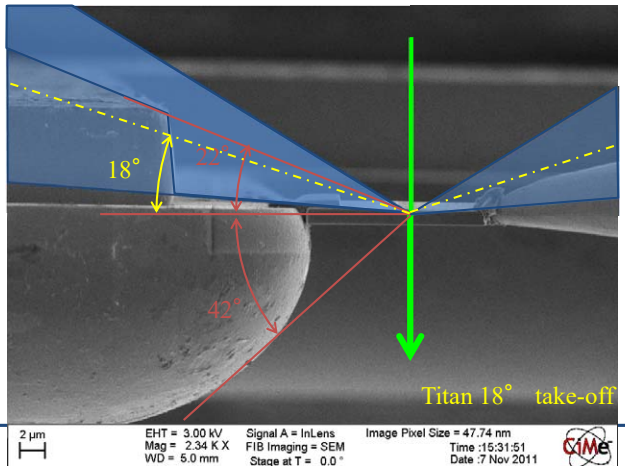




SUPER-X: take-off

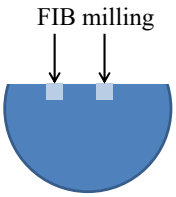


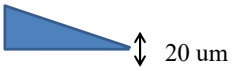


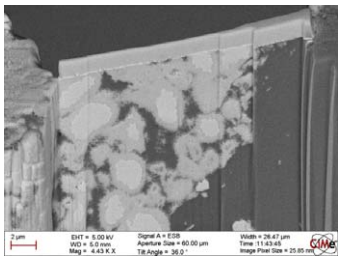


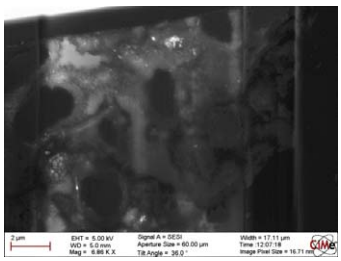
TEM sample preparation

Cement sample
Resin embedding G2, hardening 1h at 80° C
Cutting 3 mm disc with an ultrasonic cutting machine
Mechanical polishing 3 faces
Bevelled edge polishing until 20 um
FIB milling



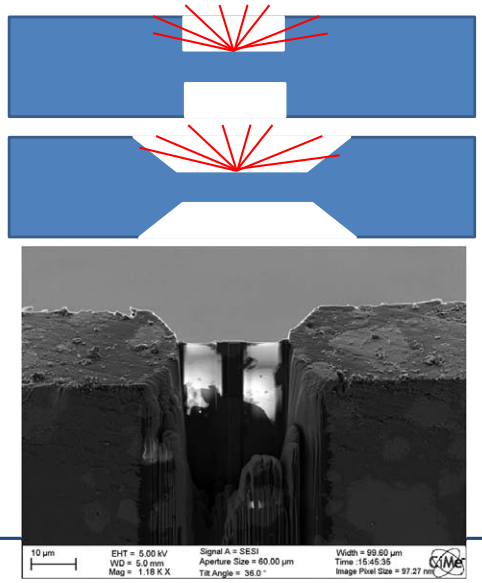




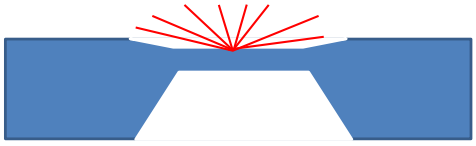


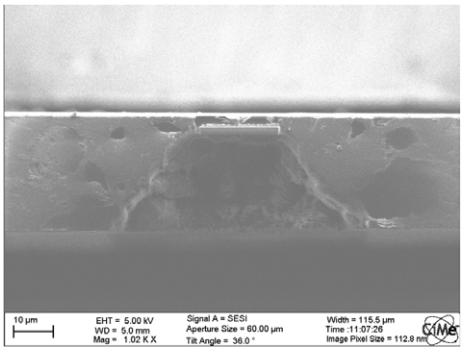
Position of the lamella on H-Bar

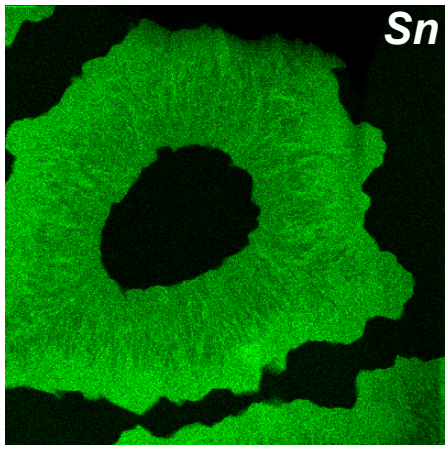
Not OK for EDX

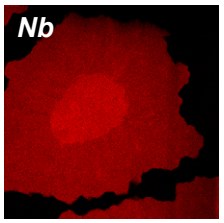


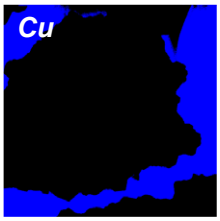
OK for EDX

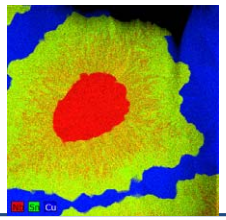




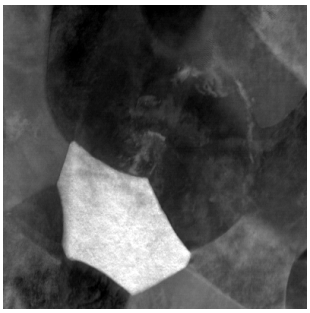


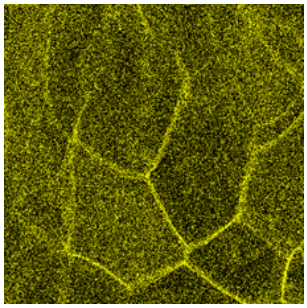


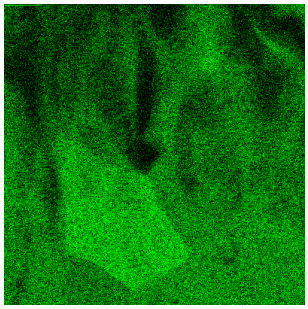




400x400 pixels (5umx5um)
160'000 spectra
4msec., (10min.)
2.5nA





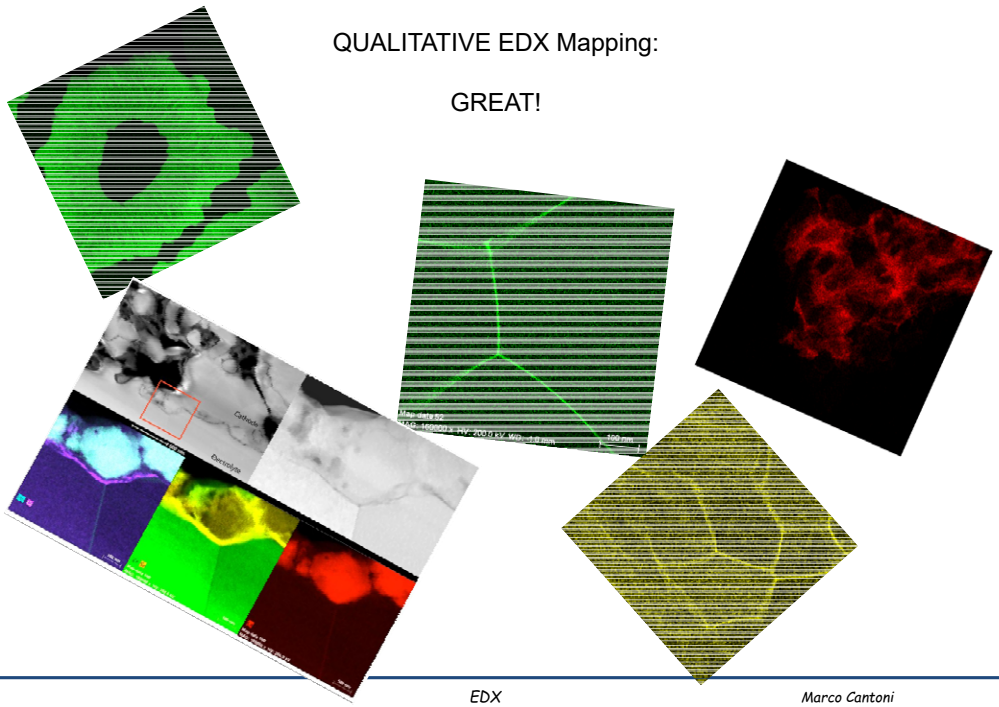


STEM DF Cu Sn

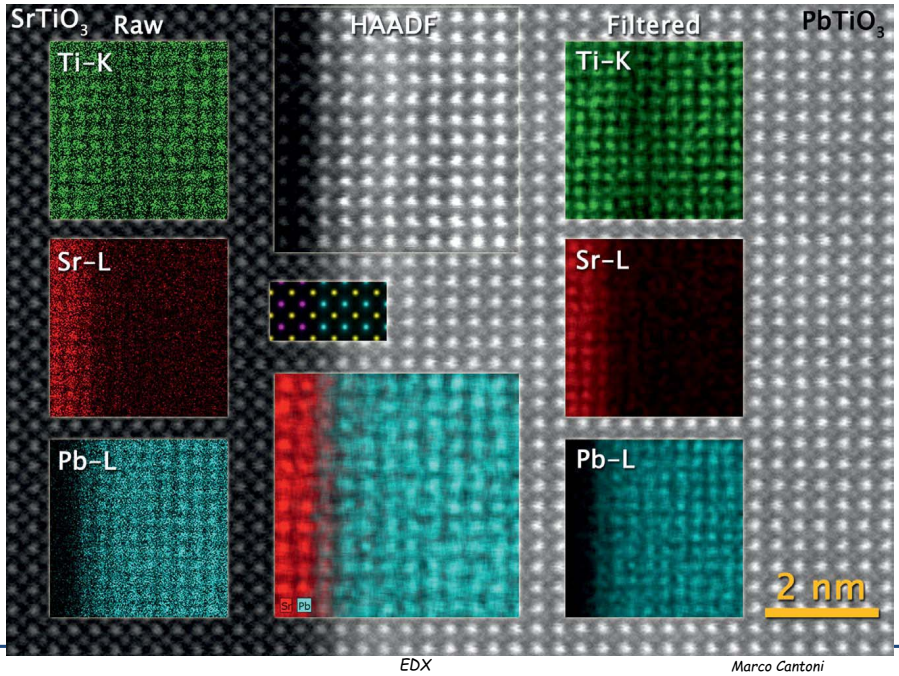
- 400x400 pixels (500nmx500nm)
- 160'000 spectra
- 4msec., (10min.), 2.5nA

QUALITATIVE EDX Mapping:

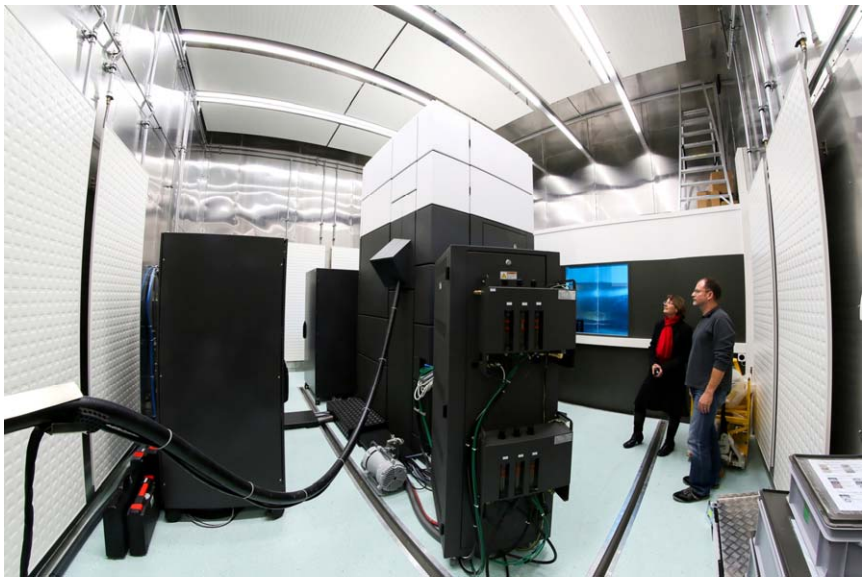
GREAT!



Chemical analysis on atom columns

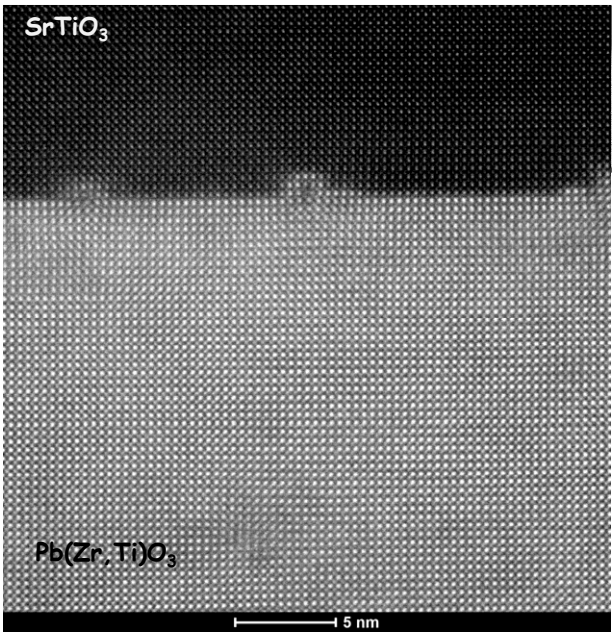


October 2014: Titan THEMIS @CIME



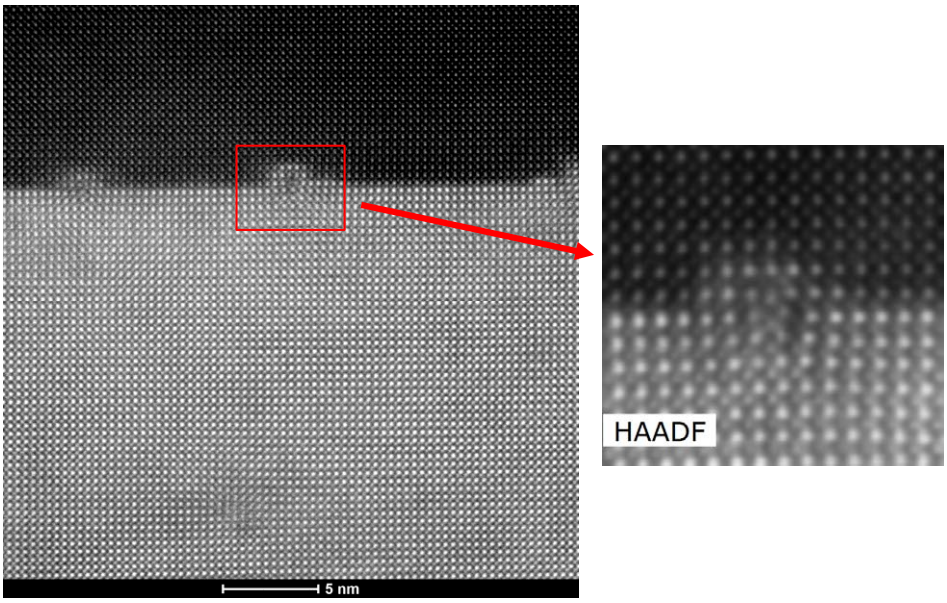
EPFL Titan THEMIS

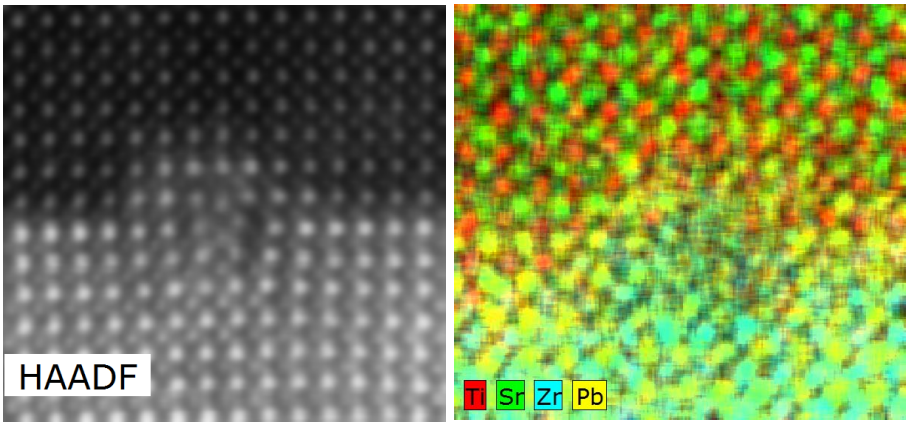
STEM HAADF atomic resolution



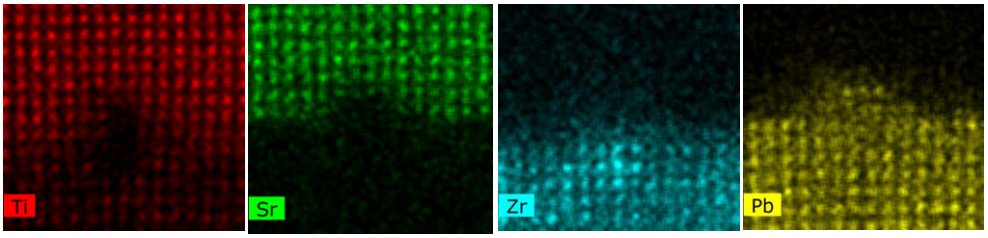
EPFL Titan THEMIS

STEM HAADF (z-contrast): atomic resolution



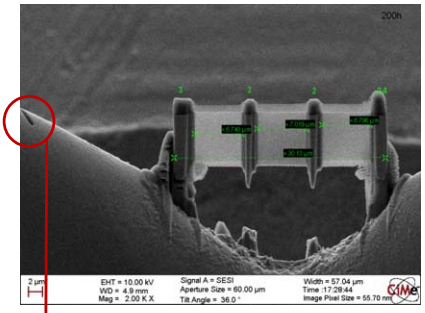


Atomic elemental mapping ..!



STEM EDX analysis of Cr diffusion into the Cu stabilizer of Nb_3Sn strand annealed for 200h

B. Bartova, G. Arnau Izquierdo, B. Bordini, P. Alknes, M. Cantoni

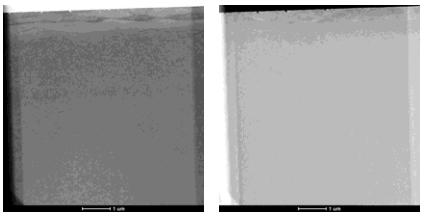


Marker made by FIB to recognize the Cr side of the lamella.

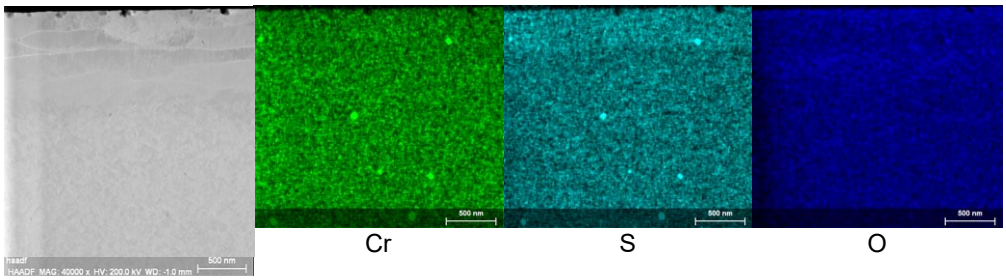
TEM lamella was prepared by FIB. 30 microns wide area was lifted out next to the chromium plating. Three windows of 7 microns were thinned down to the electron transparency. 2-3 microns thick areas were kept in order to ensure the stability of the sample.

In following slides STEM EDX analysis from each of the thinned windows is presented.

1st window in TEM lamella – 3 microns from Cr plating



BF and DF HAADF images of window 1



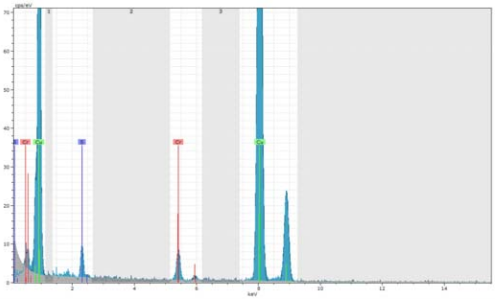
Cr S O

STEM EDS mapping revealed the presence of Cr-S rich precipitates that might contain also oxygen. However, oxygen was not taken into account since its proper quantification at very low quantities is difficult.

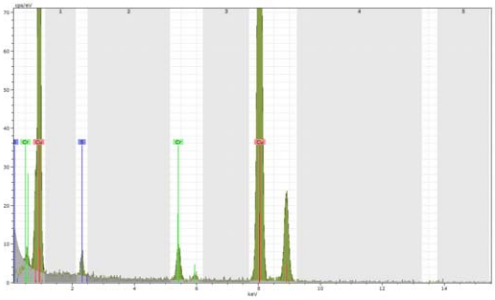
1st window in TEM lamella – 3 microns from Cr plating

3 spectra were analyzed in window 1
at higher magnification.
2 precipitates and the matrix.

1st window in TEM lamella – 3 microns from Cr plating



Precipitate 1- window 1



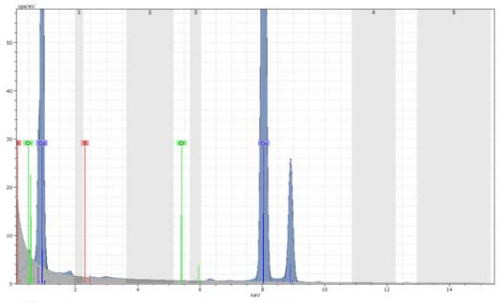
Precipitate 2 – window 1

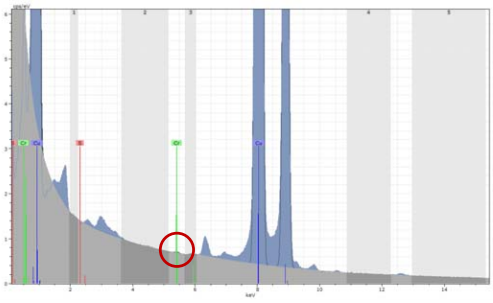
Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in wt.%
Chromium	K-series	2.85	2.85	3.41	0.15
Copper	K-series	95.50	95.50	93.39	2.08
Sulfur	K-series	1.65	1.65	3.21	0.11
	Sum:	100	100	100	

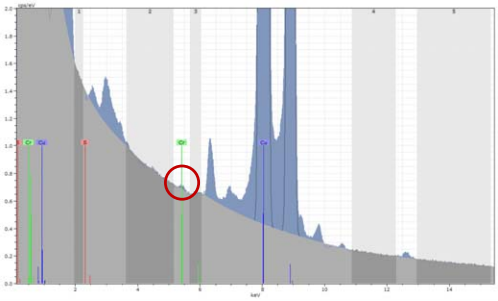
Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in wt.%
Chromium	K-series	3.40	3.40	4.08	0.18
Copper	K-series	95.39	95.39	93.58	2.13
Sulfur	K-series	1.21	1.21	2.34	0.11
	Sum:	100	100	100	

The precipitates contain chromium and sulfur and their ratio is close to 1:1. The peaks at Kα (5.411) and Kβ (5.947) lines for chromium and Kα (2.307) for sulfur are evident.

1st window in TEM lamella – 3 microns from Cr plating







Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in wt.%
Chromium	K-series	0.0100	0.0100	0.0123	0.0003
Copper	K-series	99.9900	99.9900	99.9877	2.0249
Sulfur	K-series	0	0	0	0
	Sum:	100	100	100	

The quantification of the spectra from matrix is showing 0.01 at.% of chromium. In order to verify chromium presence, original spectra needs to be magnified. For certain spectra the automatic background deconvolution was slightly ajusted.