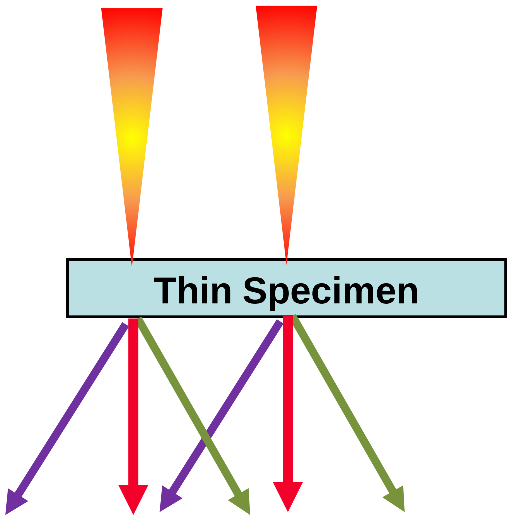
Introduction to Transmission Electron Microscopy (II)

Honghui Zhou, C. Q. Chen, Jade Wang

Materials Research Laboratory
MRL.Illinois.edu
University of Illinois at Urbana-Champaign

Scanning Transmission Electron Microscopy

Convergent / Focused Beam



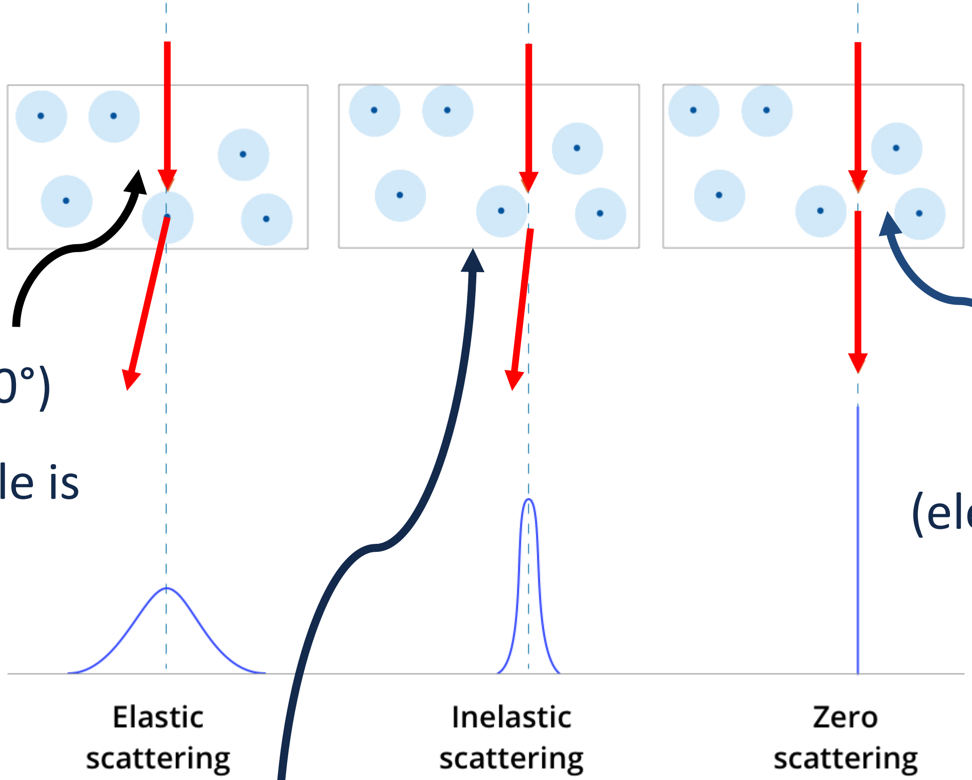
Scanning TEM (STEM)

- **Basic STEM imaging**
- **Aberration corrected STEM**
- **Analytical STEM**

Electron beam interaction with a thin specimen

Interact with the nucleus

- No energy/momentum transfer
- **Larger scattering angles** (up to 180°)
- Coherent when the scattering angle is relatively small (<10°)
- Less coherent as scattering angle becomes large (>10°)



https://myscope.training/

No interaction

(electrons pass between atoms)

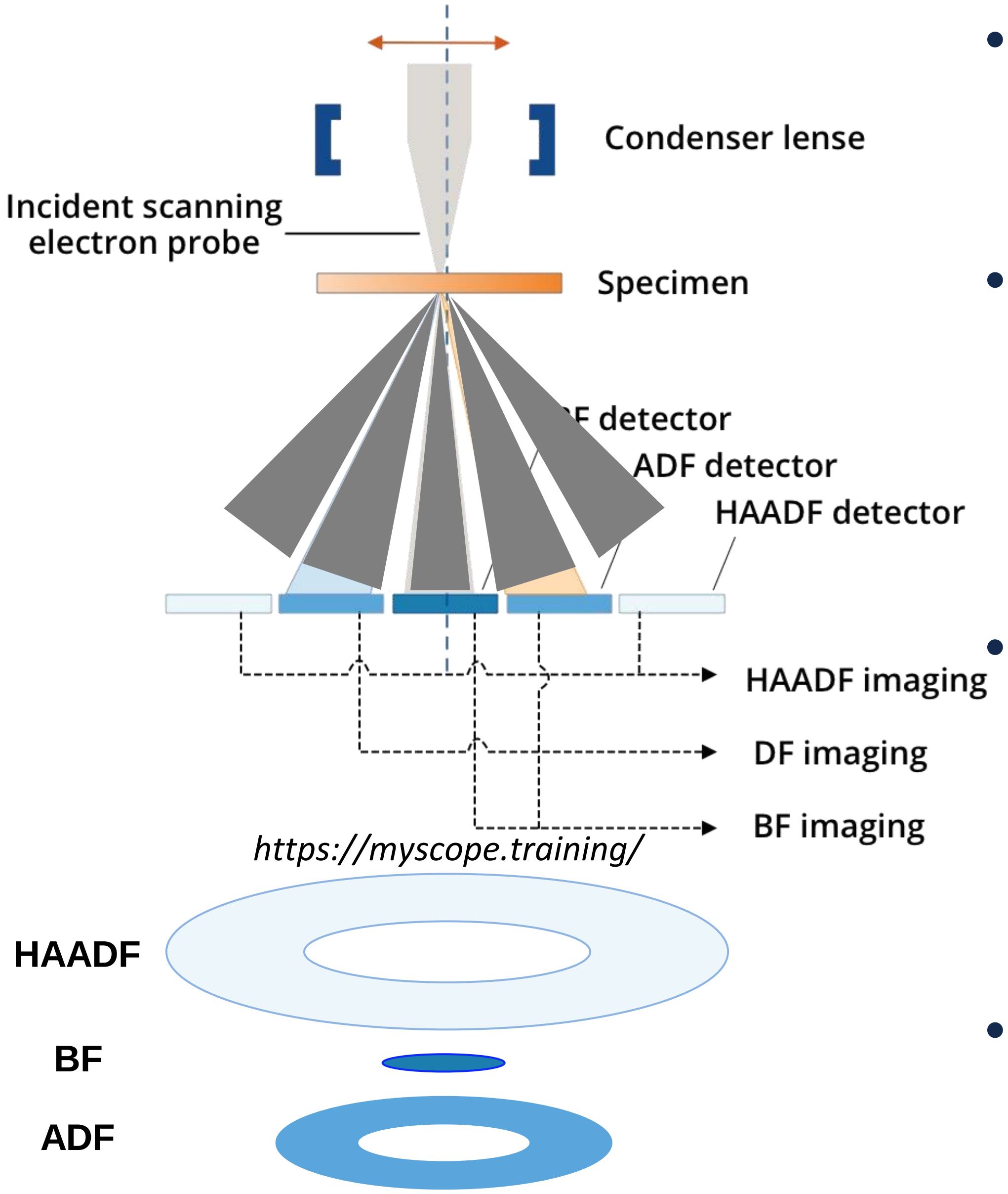
- No energy loss
- No change of direction

Interact with the electron cloud of an atom

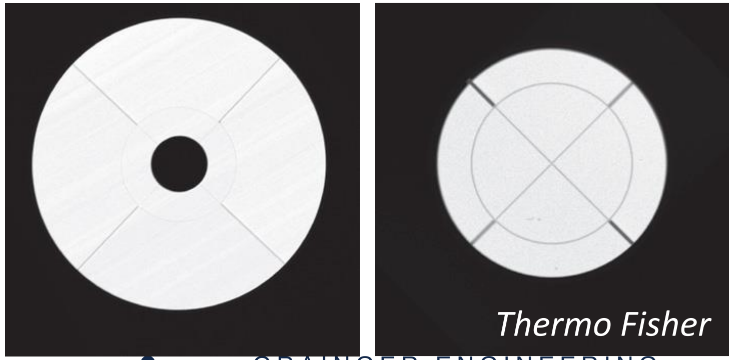
- **Energy Loss & very small scattering angle**
  - Incoherent (longer wavelength)

Scattered electrons are collected for imagining depending on the scattering angle with detectors of different shapes and sizes

STEM Imaging Detectors

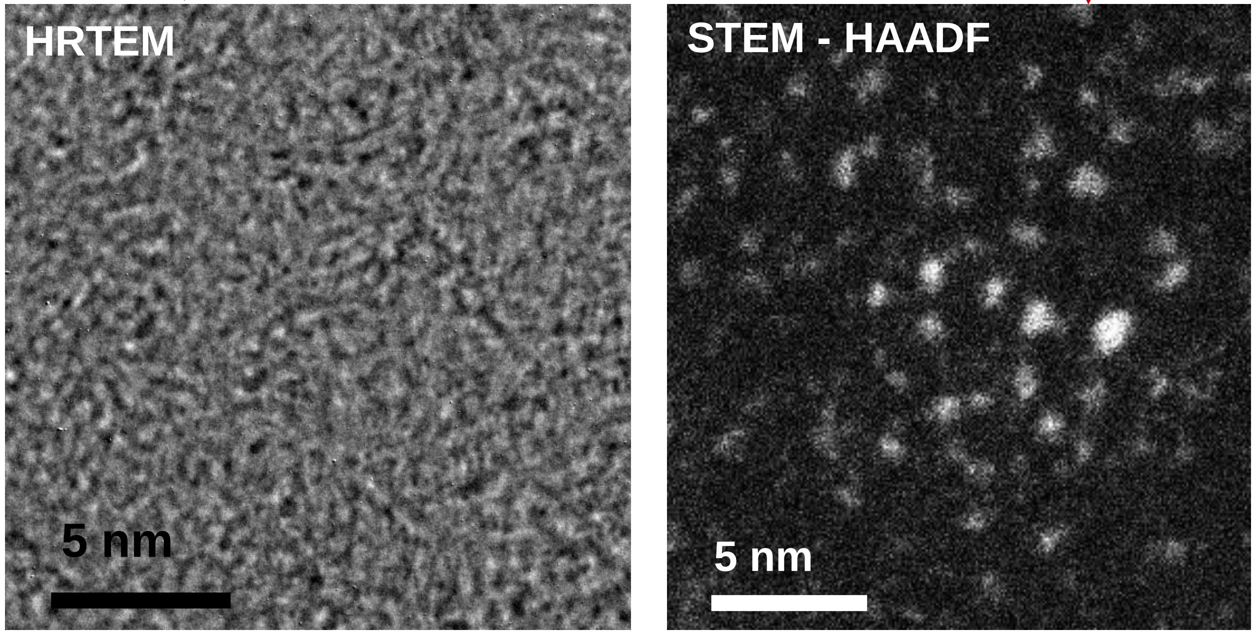


- **Bright-field (BF)**
  — a small disc-shaped detector
  — collects on-axis forward-scattered electrons (bright disk)
- **Annular dark-field (ADF)** (concentric with the BF)
  — a low-medium angle annular detector
  — collects coherent elastically scattered electrons
  — diffraction contrast dominant
- **High-angle annular dark-field (HAADF)**
  — a large angle annular detector
  — collects incoherent elastically scattered electrons
  — z contrast only (~ z^2)
- **Segmented detector**
  — Multimodal imaging
  BF, ADF, HAADF, etc.



STEM – (HA)ADF Imaging Compared to CTEM Imaging

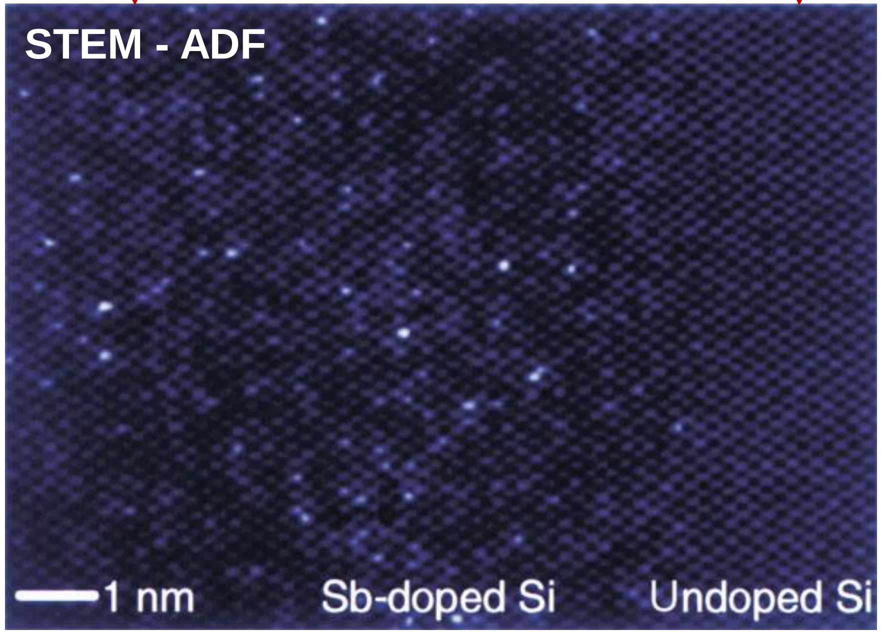
Iridium (Ir) nanoparticles
on an amorphous carbon film



Jianguo Wen, Chapter 5 from "Practical Materials Characterization"

The tiny heavy element particles seen clearly in the STEM image but not in the TEM image.

Cross section
of highly Sb-doped Si

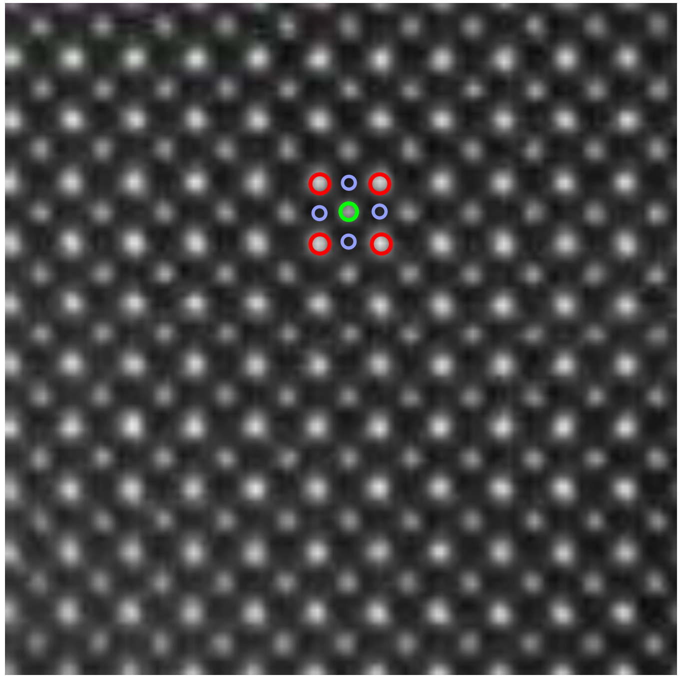


P M Voyles, et. al., Nature, 2002 Apr 25;416(6883):826-9

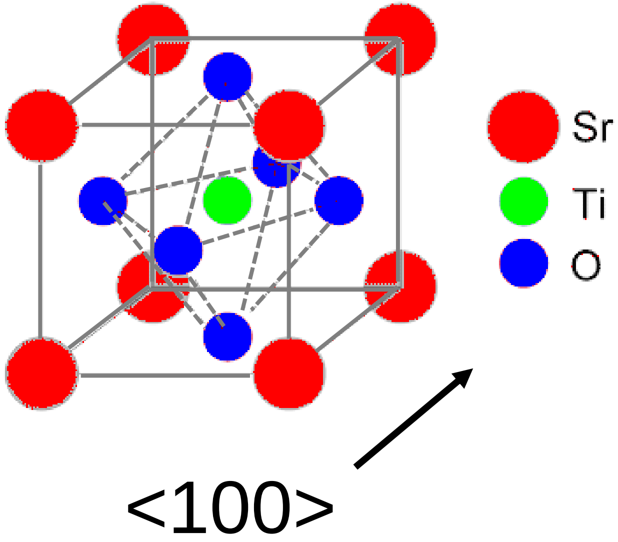
The brightest dots are atomic columns containing one or more Sb atoms.

- Chemical sensitive
- Intuitive contrast interpretation

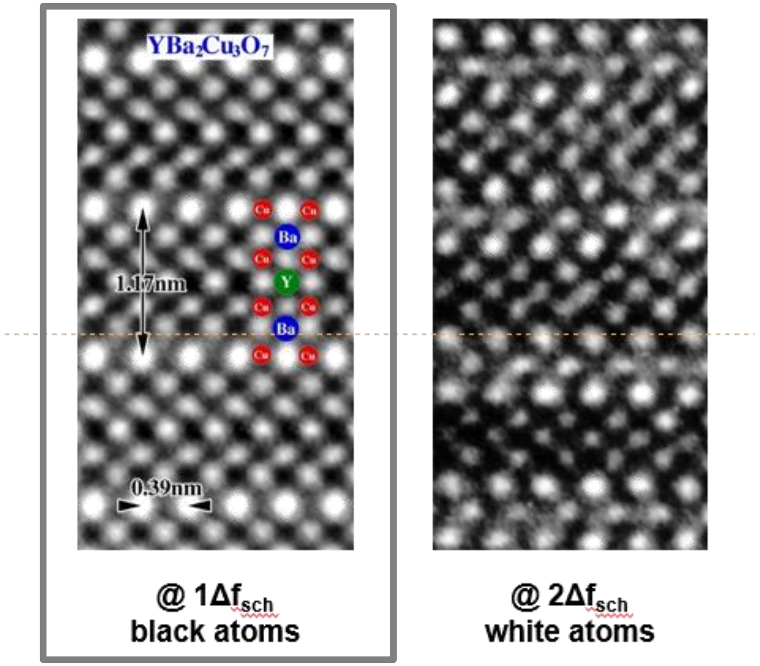
STEM Imaging Compared to CTEM Imaging — Intuitive interpretation at atomic scale



<100> Atomic resolution HAADF image of $SrTiO_3$



"See" atomic columns?



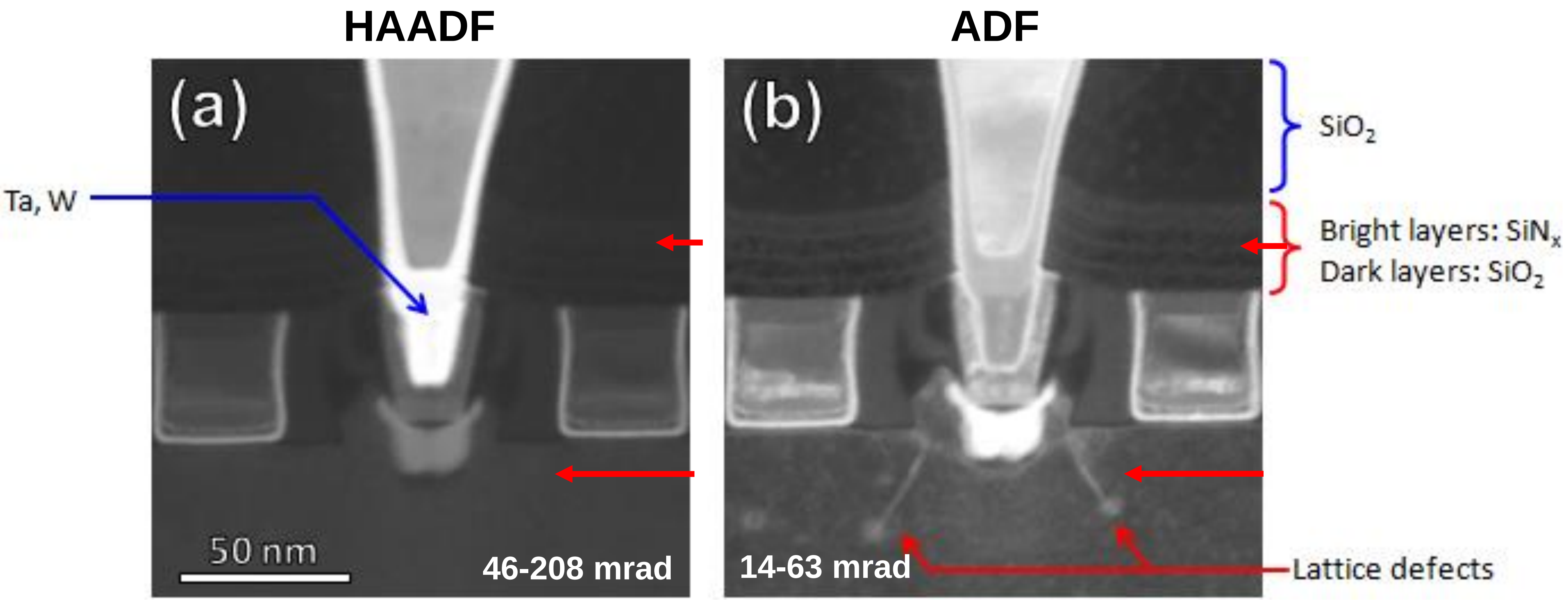
Jianguo Wen, Chapter 5 "Practical Materials Characterization"

- HAADF imaging always shows a positive contrast transfer
- The observed bright dots directly correspond to atomic columns
- Insensitive to light elements when imaged with heavy elements due to a lower scattering power of the light elements

CTEM-HR image interpretation is not straightforward

The images contrast is very sensitive to several factors, e.g., focus condition.

(LA)ADF vs. HAADF



https://www.jeol.com/words/emterms/20121023.063558.php#gsc.tab=0

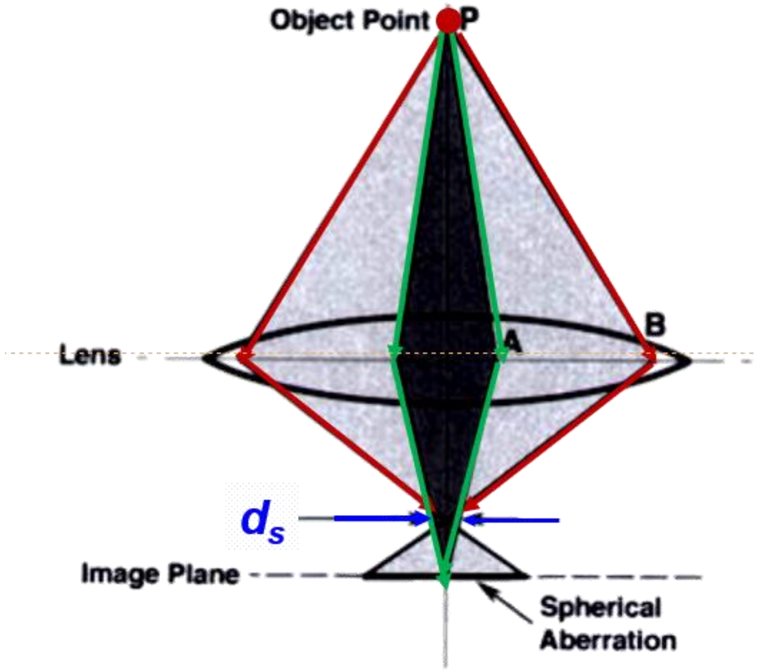
STEM images of the cross-sectional thin film of a semiconductor device

- ADF works better for light elements
- ADF has diffraction contrast/strain contrast

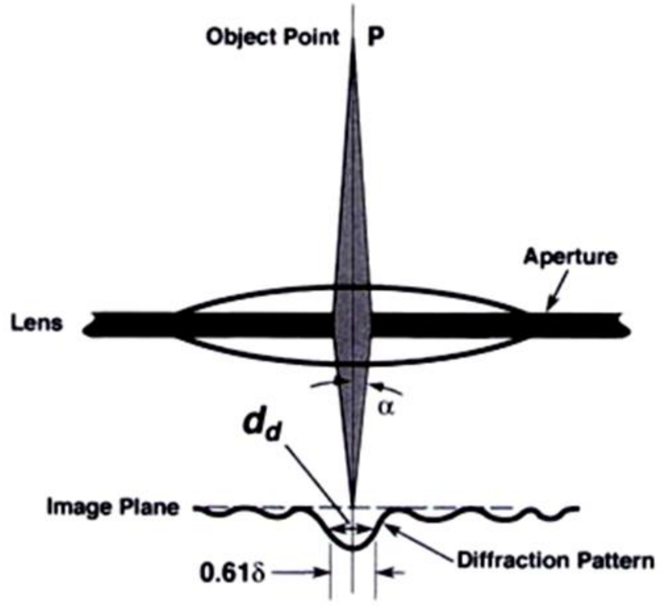
Outline

1. Basics of Scanning Transmission Electron Microscopy
2. **Aberration-corrected Scanning Transmission Electron Microscopy**
3. Analytical Scanning/Transmission Electron Microscopy

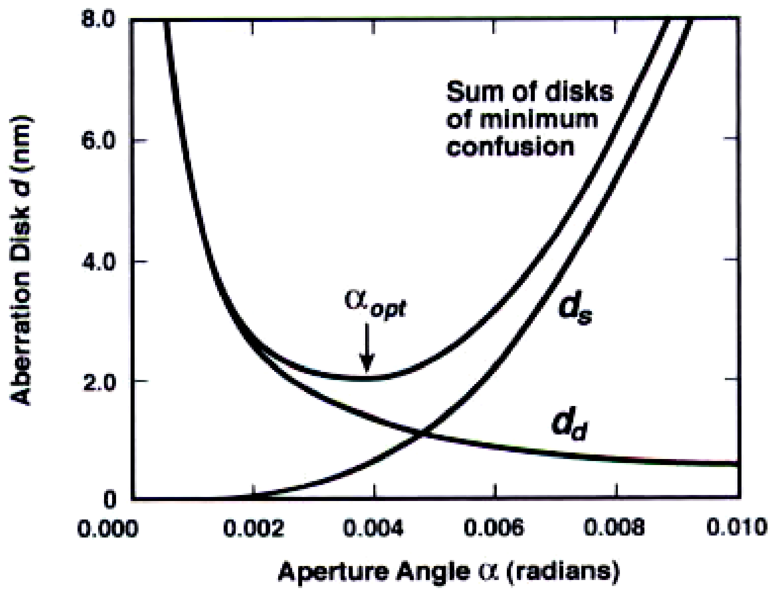
STEM Resolution is Limited by Lens Aberration



$$d_s = \frac{1}{2} C_s \alpha^3$$



$$d_d = \frac{0.61\,\lambda}{\alpha}$$



Adapted from *Scanning Electron Microscopy and X-Ray Microanalysis*, Joseph I. Goldstein et al. Plenum Press

- Spherical aberration and aperture diffraction pose a fundamental limit to the achievable probe size
- The disc of least confusion from spherical aberration is proportional to aberration coefficient Cs as well as the cube of the semi-convergence angle α
- To improve the spatial resolution, Cs needs to be addressed

Spherical Aberration Correction

The era of aberration correction : it all began in 1936…

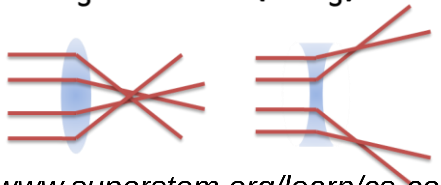
In 1936, Scherzer proved that any electron optical system will always suffer from ***spherical aberration*** (*Cs*) and ***chromatic aberration*** (*Cc*) if simultaneously:

- the optical system is rotationally symmetric
- the system produces a real image of the object
- the fields of the system do not vary with time
- there is no charge on the axis

Breaking the rotational symmetry
— achieved by using a highly complex computer-controlled sets of multiple lenses

The idea is to introduce a corrector that produces negative lens to give a total of zero spherical aberration, i.e., the rays are re-converged to a point rather than a disk

$$C_s \quad + \quad (-C_s) = 0$$

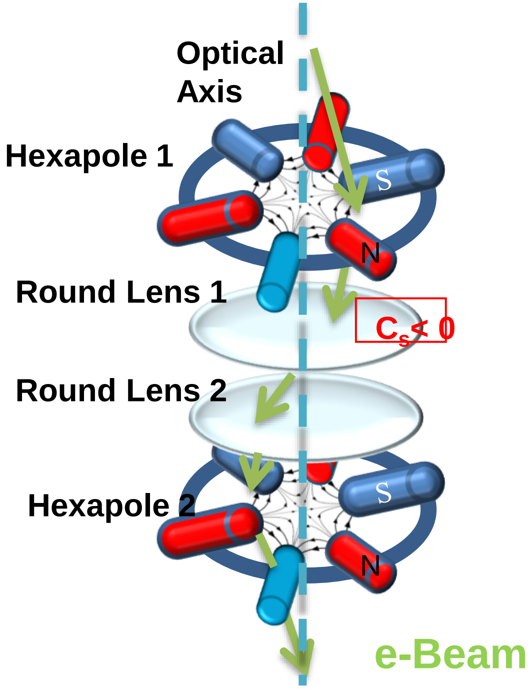


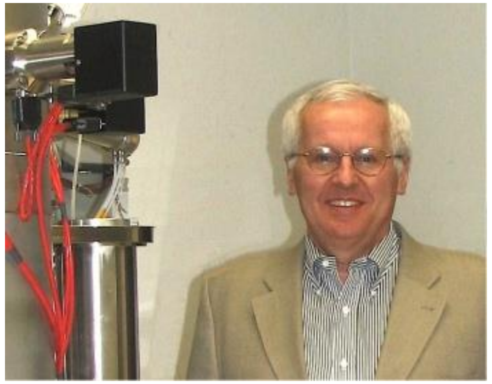
https://www.superstem.org/learn/cs-correction

Maximilian Haider, Harald Rose & Knut Urban

https://www.agenciasinc.es/Noticias/Haider-Rose-y-Urban-premio-Fronteras-del-Conocimiento-por-inventar-el-microscopio-de-precision-subatomica

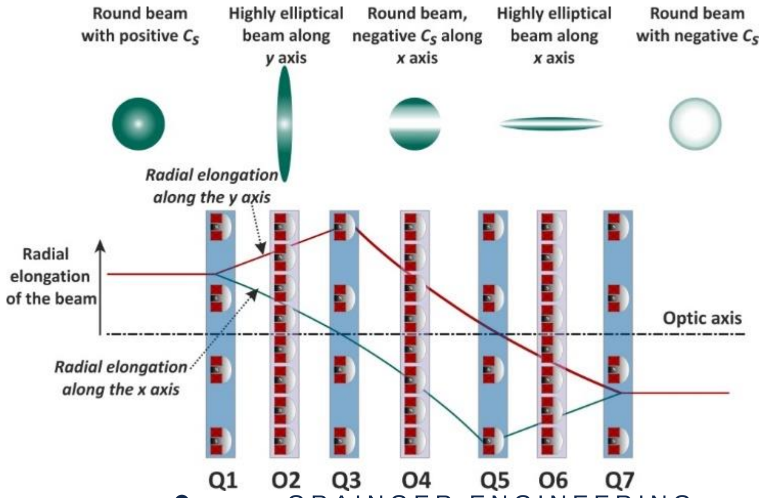
Hexapole C_s Corrector
CTEM & STEM



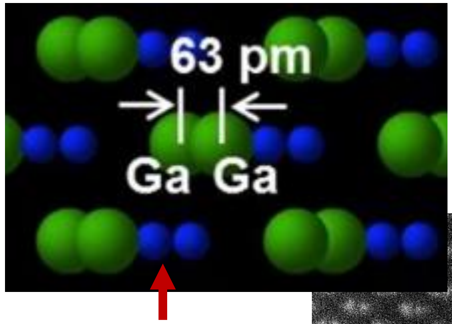


Ondrej Krivanek
Nion Company

Quadrupole-Octupole C_s corrector
STEM



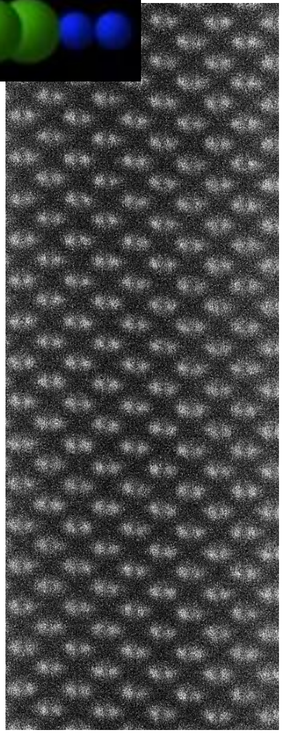
Spherical Aberration Correction

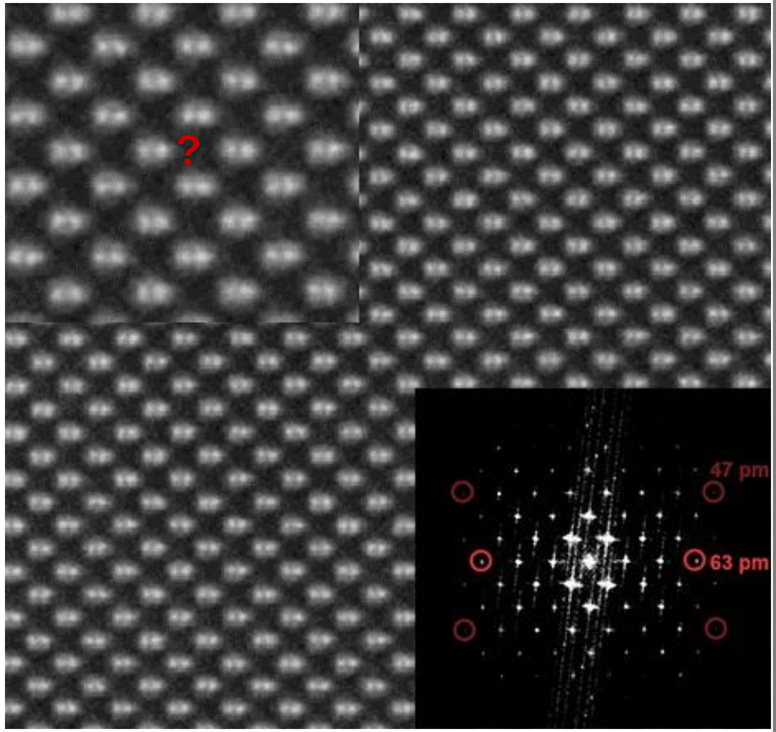


Ga

N

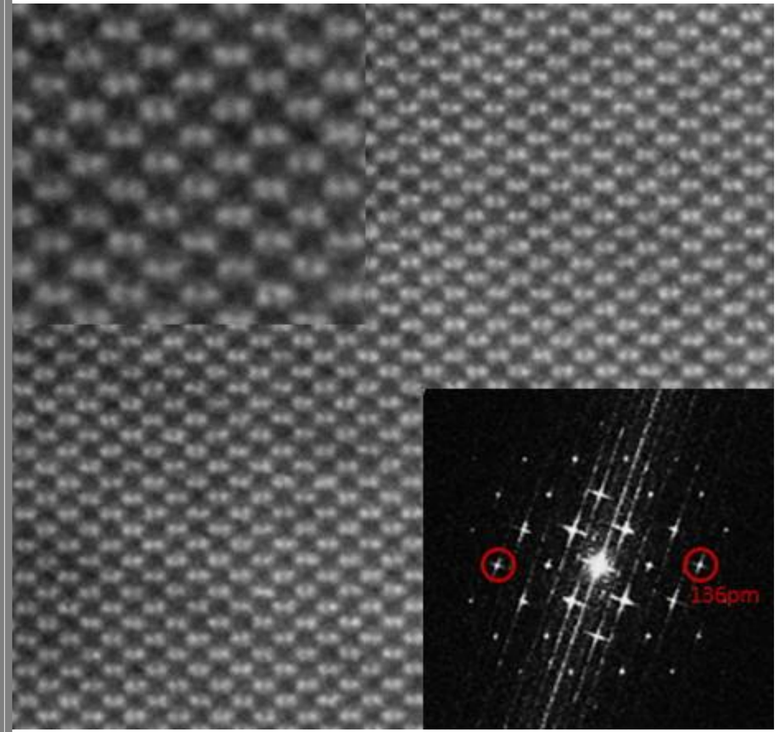
GaN [211] imaged at 300 kV
Ga dumbbell well resolved
< 63 pm resolution





C Chen, Themis

Si [110] imaged at 60 kV
Si dumbbell well resolved
< 136 pm resolution

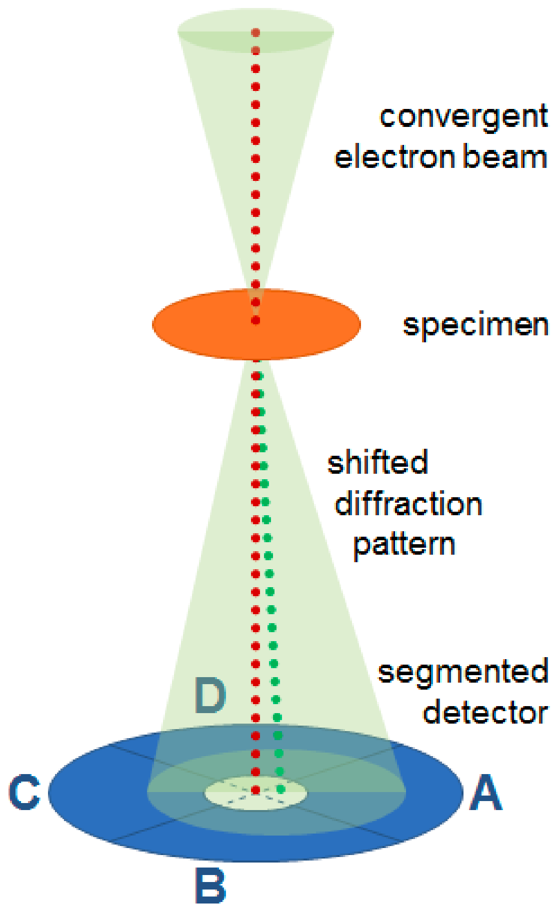


https://www.fei.com/products/ter /themis-z-for-materials-science/

With the 2nd generation probe corrector, high order aberrations are correctable, therefore better imager resolution, especially at lower kV, e.g., 60 kV

Integrated Differential Phase Contrast (iDPC)

- The electric field of the specimen atoms deflect the electron beam
- The intensity difference caused by the deflection is measured by a segmented detector
- The difference produces a vector image: DPC → relate to the sample's electric field
- The DPC is integrated into a scalar image: iDPC → electrostatic potential visualized
- The contrast of iDPC is proportional to the atomic number Z



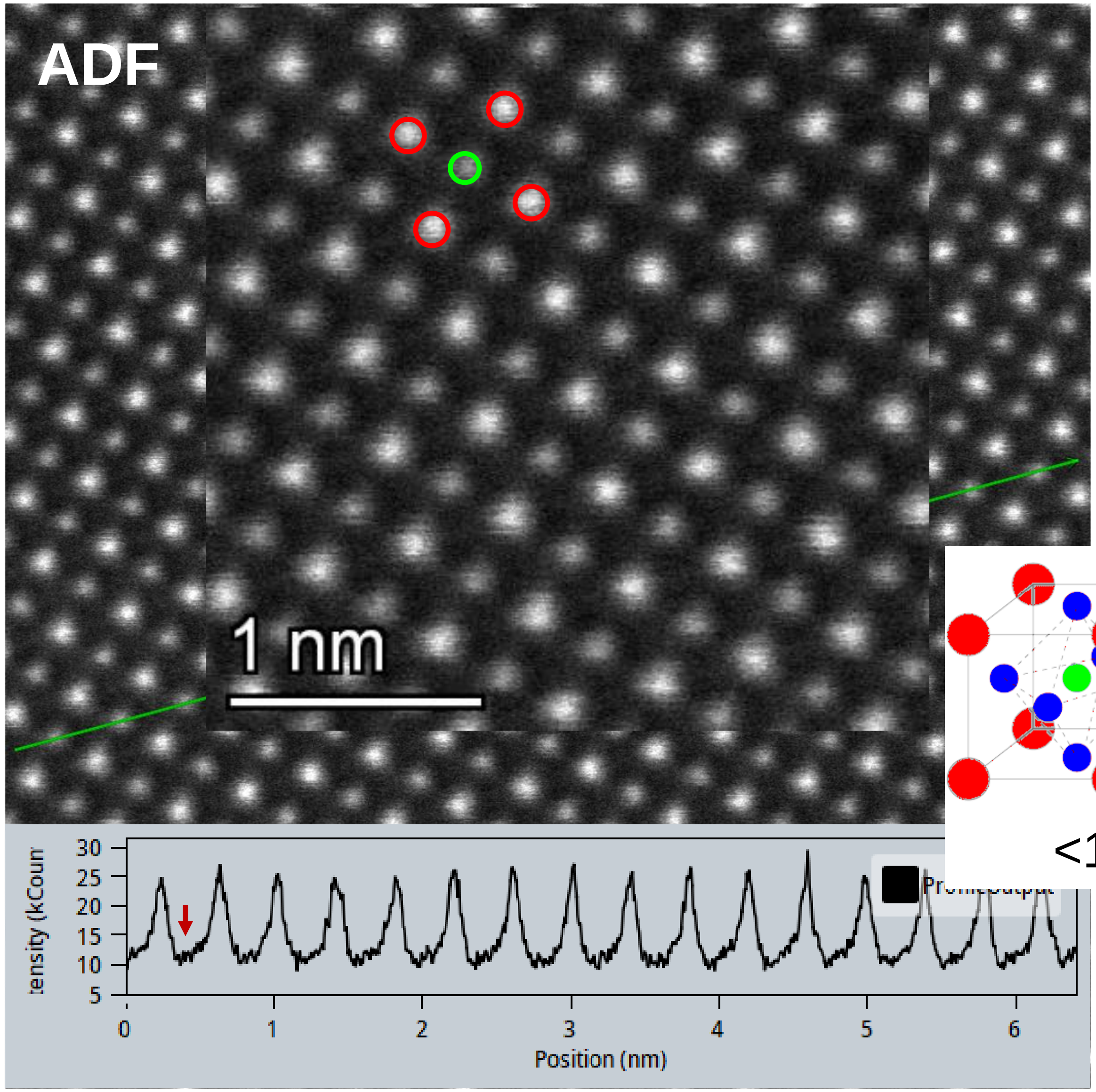
Why it works for light atoms better than HAADF?

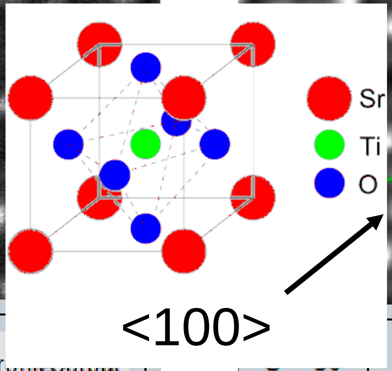
- The contrast of iDPC is proportional to the atomic number Z (compared to Z^2 in HAADF)
- HAADF collects high angle scattered electrons, but light atoms have lower probability of high angle scattering.
- iDPC collects electrons from the center transmitted disc, not high angle scattered electrons, therefore SNR is high, even for light atoms

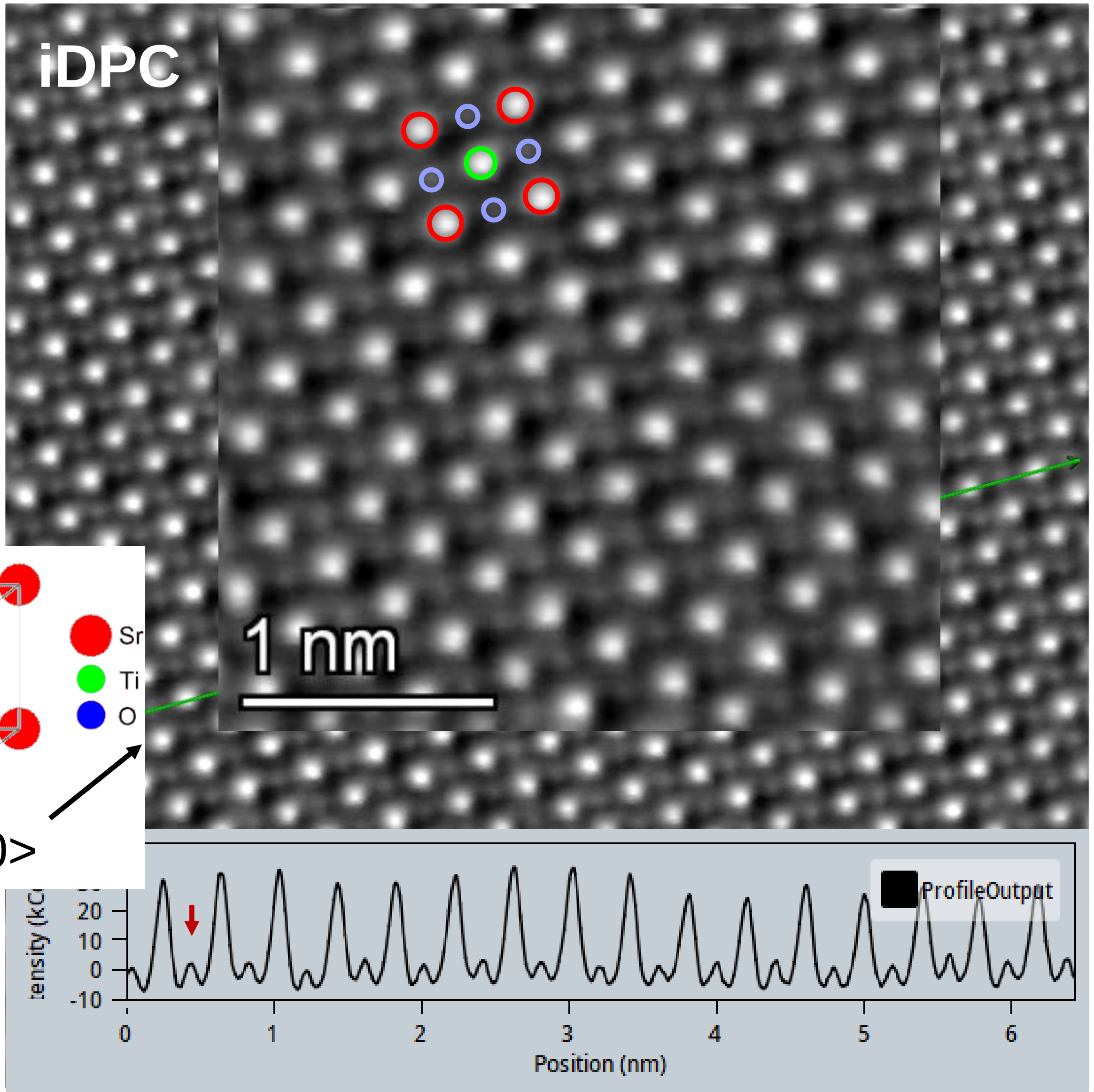
$$DPC_x = A - C$$

$$DPC_y = B - D$$

Simultaneous Imaging Light Elements & Heavy elements by iDPC-STEM







$SrTiO_3$ <100> @ 300 kV

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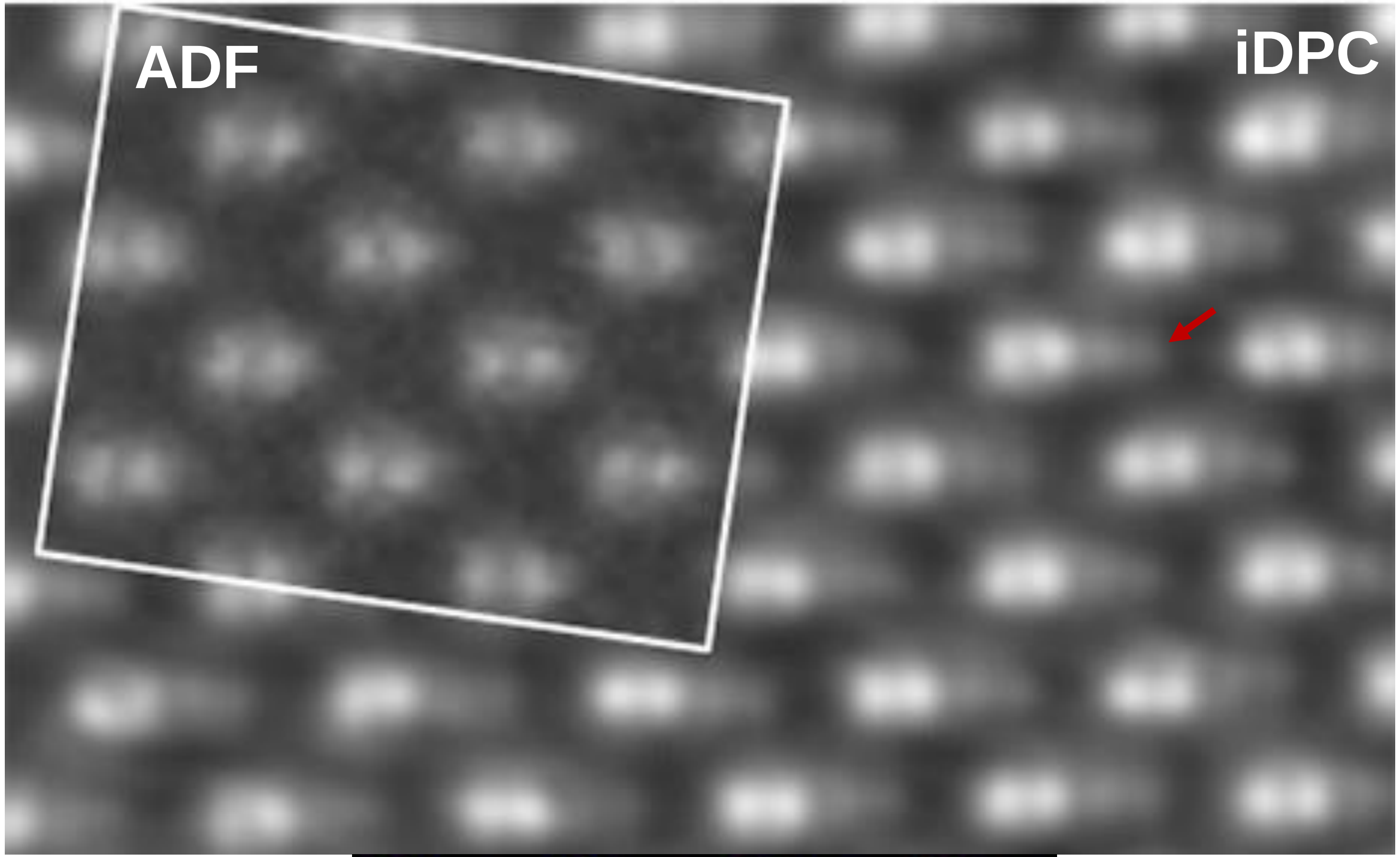
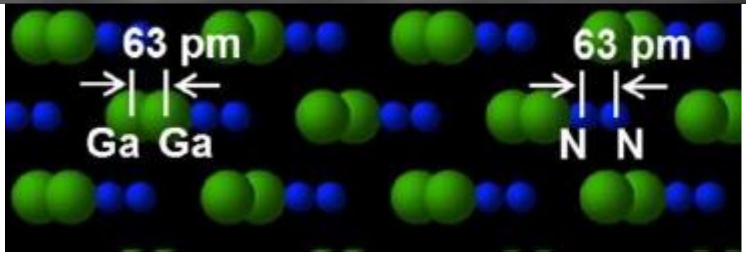
GaN <211> @ 300 kV





ThermoFisher SCIENTIFIC

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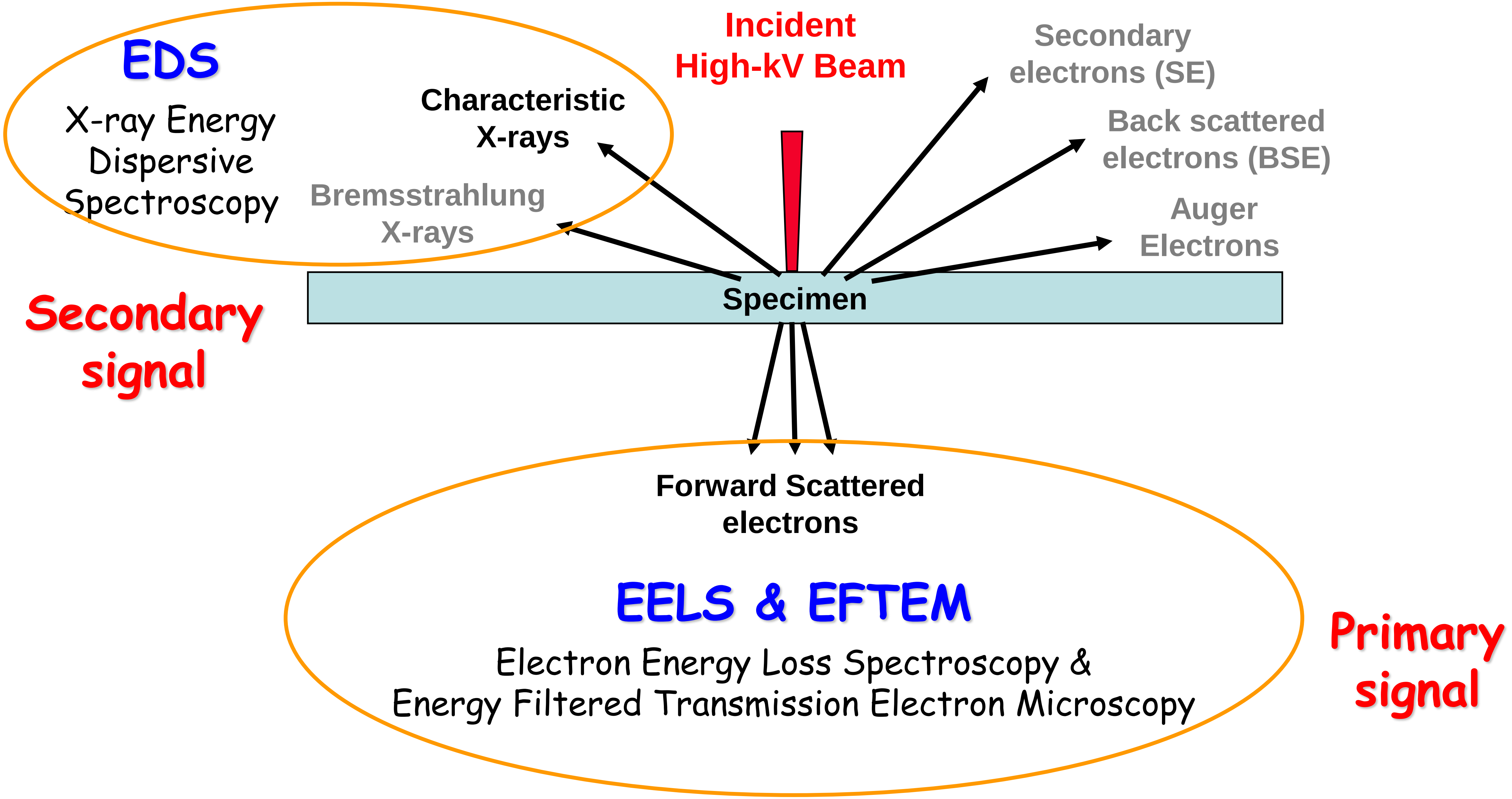
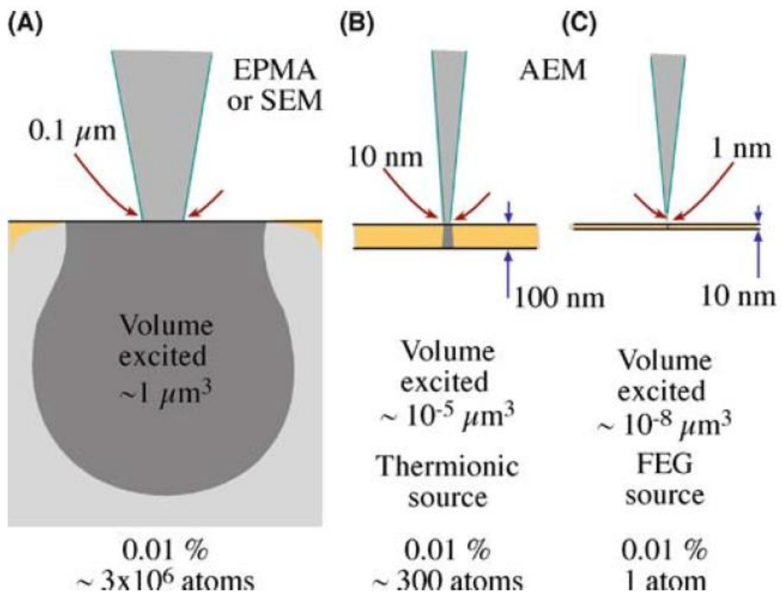
Analytical Transmission Electron Microscopy



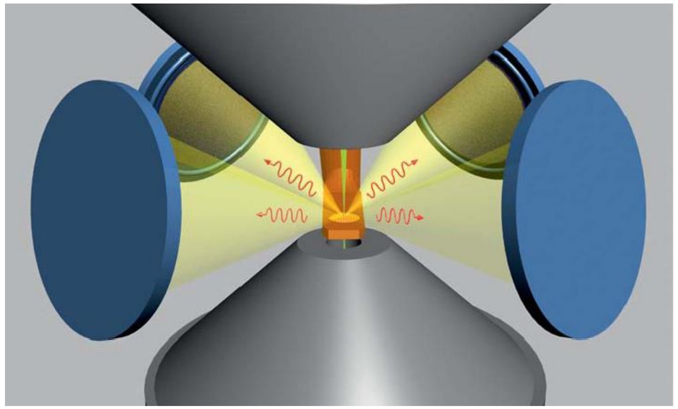
STEM-EDS Compared with SEM-EDS

SEM **STEM**



Williams and Carter (2nd edition)

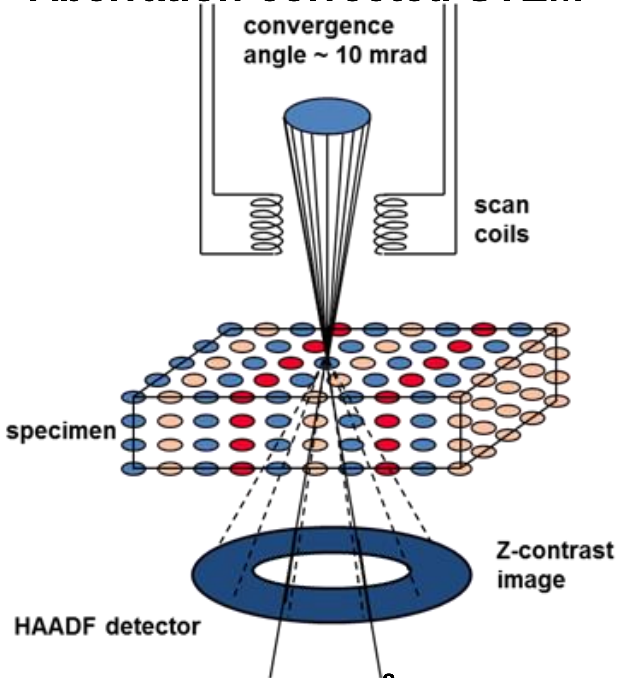
Super-X SDD EDS detectors



4-crystals detection system

0.7 steradians

Aberration-corrected STEM



100 pA in a 1 Å probe

- **Higher spatial resolution**

  (~ nm compared with ~ μm in SEM)

  — smaller incident probe

  — minimum beam broadening

- **Detection sensitivity?**

- **Advanced instrumentation**

  – better EDS detector design

  – larger EDS collection solid angle

  – higher collection efficiency

Advanced instrumentation

— brighter electron source

— aberration correction

— smaller probe carrying higher current

Atomic resolution achievable!

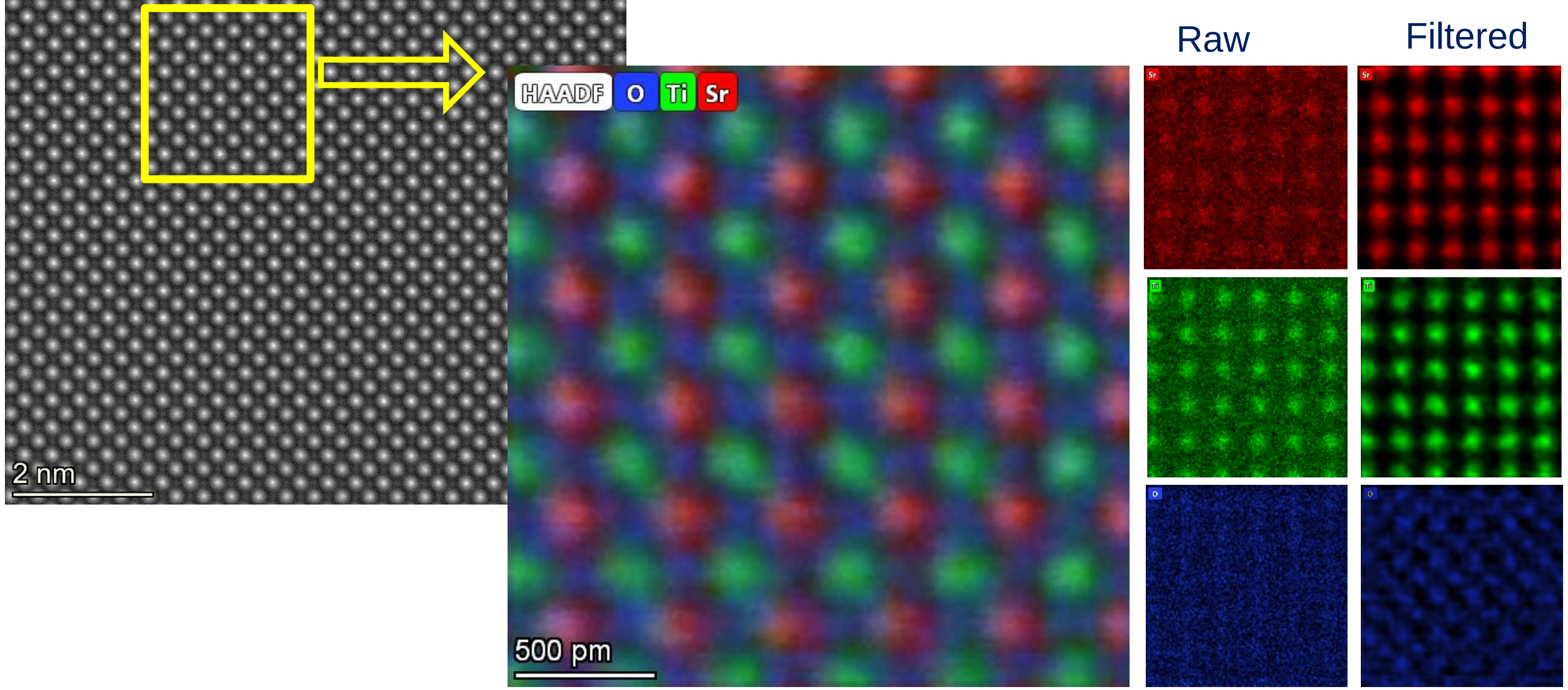
Atomic Resolution EDS Mapping with an Aberration Corrected STEM

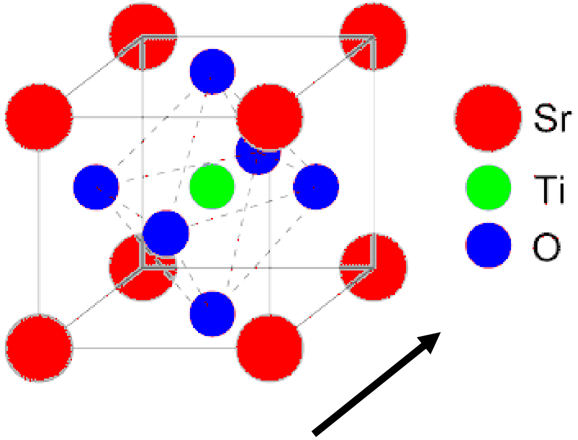
Strontium Titanium Oxide ($SrTiO_3$):

elemental mapping of **individual columns** of atoms

Atomic mapping of light element oxygen

DCFI HAADF





12 minutes acquisition time, 100pA, 300kV

<100>

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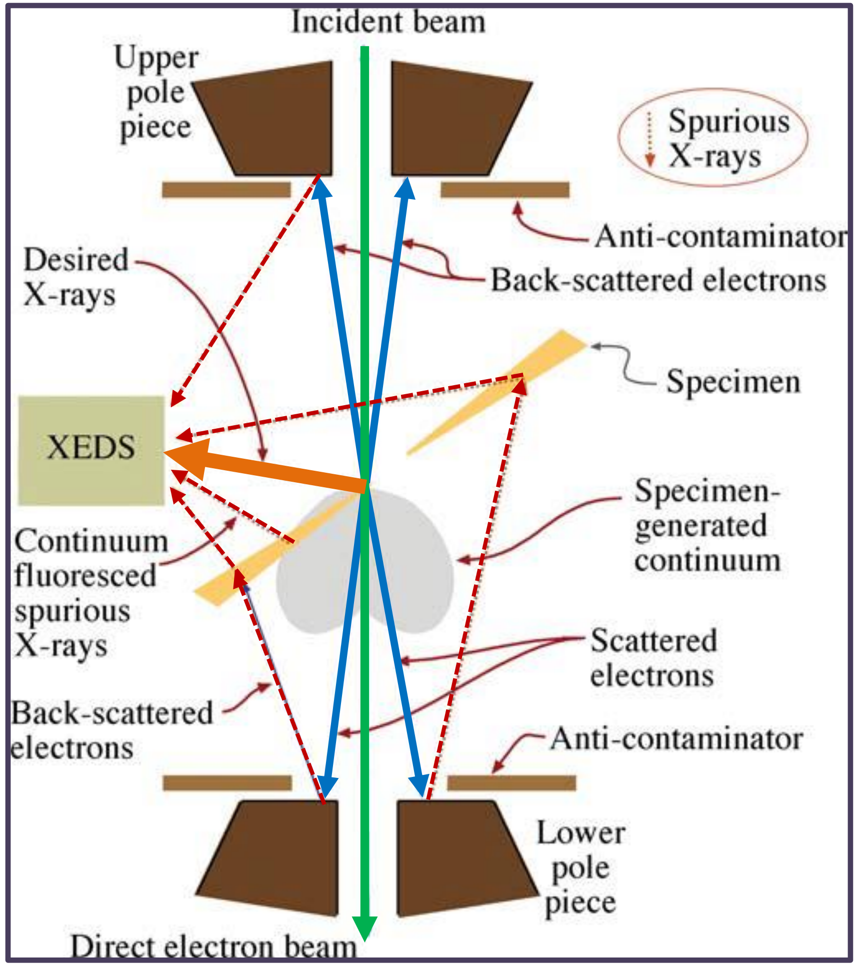
Some Limitations of TEM-EDS

- ✓❑ Unwanted system and spurious X-rays
  - Forward and backward scattered electrons excite system X-rays in stage & pole-pieces
  - Spurious X-rays elsewhere in the specimen by Bremsstrahlung (gray-shaded) and system X-rays
  - X-rays from support grid or TEM holder
- ✓❑ Collection efficiency is relatively low
- ✓❑ Challenging for light elements
- ✓❑ Relatively poor energy resolution



Modified from Williams and Carter 2009

Strength of Electron Energy Loss Spectroscopy (EELS)

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EELS vs. EDS

	EELS	EDS
Collection Efficiency	High (close to 100 %)	Low (1-10 %)
Spatial Resolution	0.1 - 1 nm Atomic (with aberration correction)	0.1 nm – 10 nm Atomic (with aberration correction)
	EELS > EDS	
Energy Resolution	**~ 1 eV (better with Monochromator)**	**~ 130 eV (Mn Kα)**
Information Available	**Atomic, chemical, electronic, optical and more …**	**Atomic only**
Elements Light/Heavy	**Excellent for light elements** **Signal weak in high loss region**	**Excellent for medium to heavy elements** **Low yield for light elements**
Quantification	**Absolute & Relative**	**Relative only**
Easy to Use?	Getting easier with advanced software	Easy to use and interpret for basic applications

Electron Energy Loss Spectroscopy (EELS)

<u>Interact with the nucleus</u>

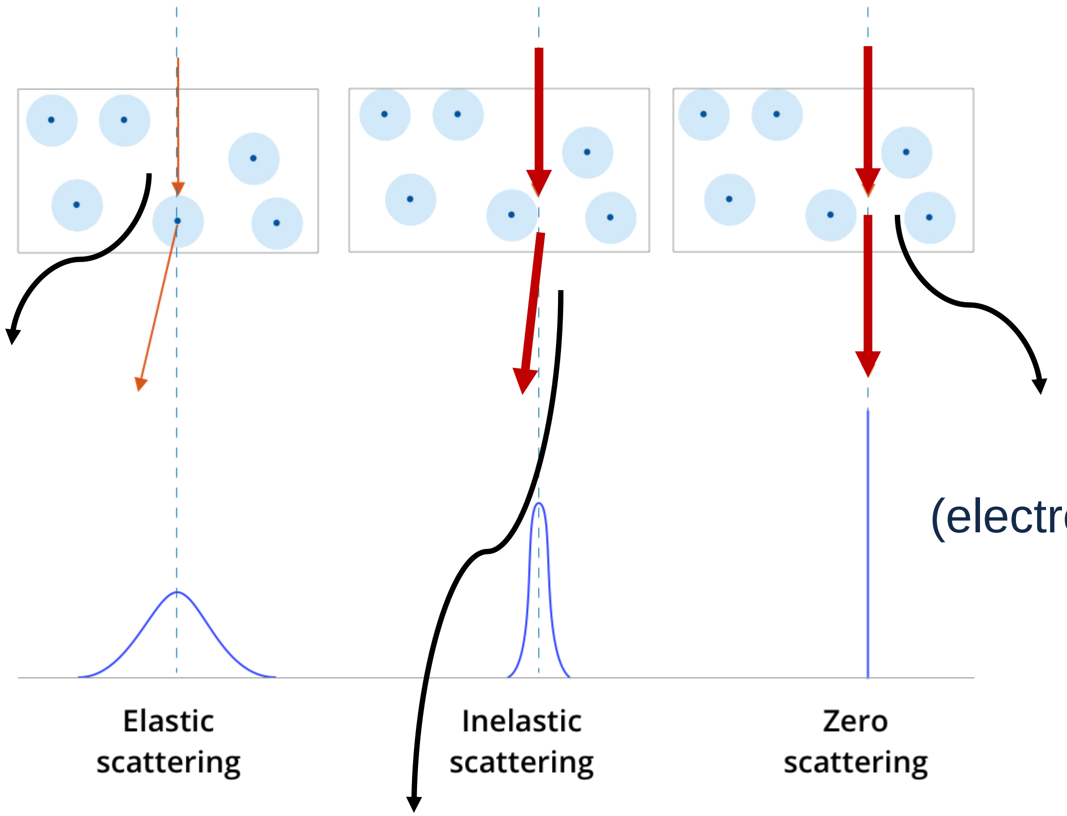
No energy transfer

(the large difference in mass!)

Larger scattering angles

Signal for Imaging

(HAADF and ADF)



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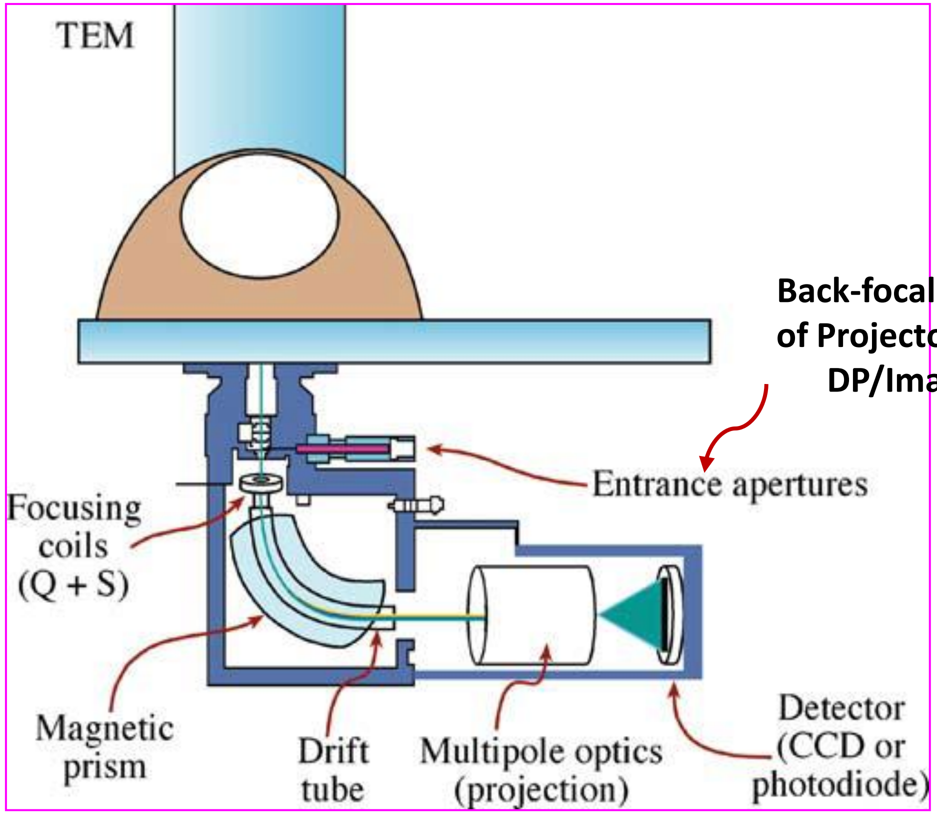
No interaction

(electrons pass between atoms)

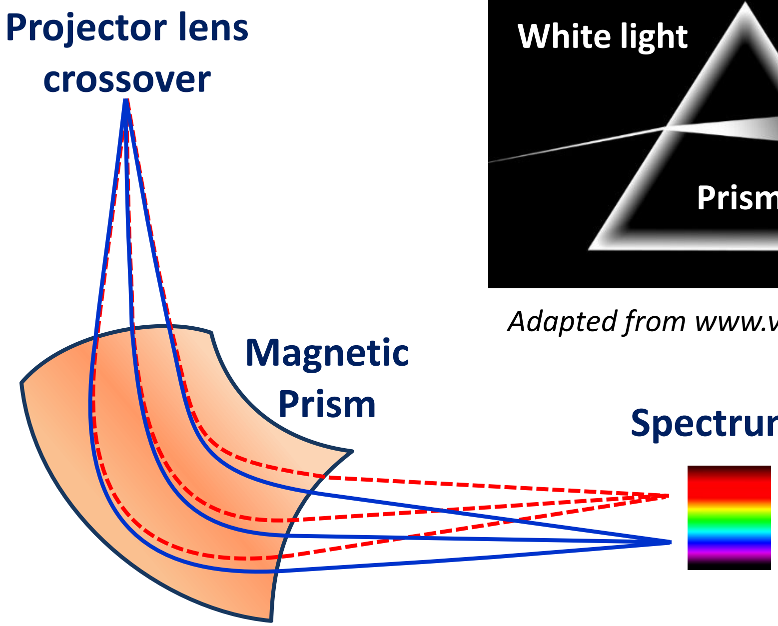
Interact with the electron cloud of an atom

Energy Loss & Small scattering angle

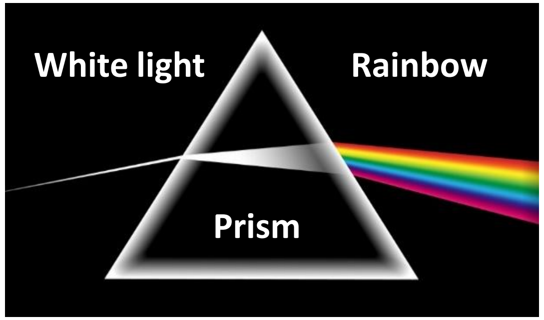
EELS Electron Optical System -how are electron energies measured in EELS?



Williams and Carter 2013



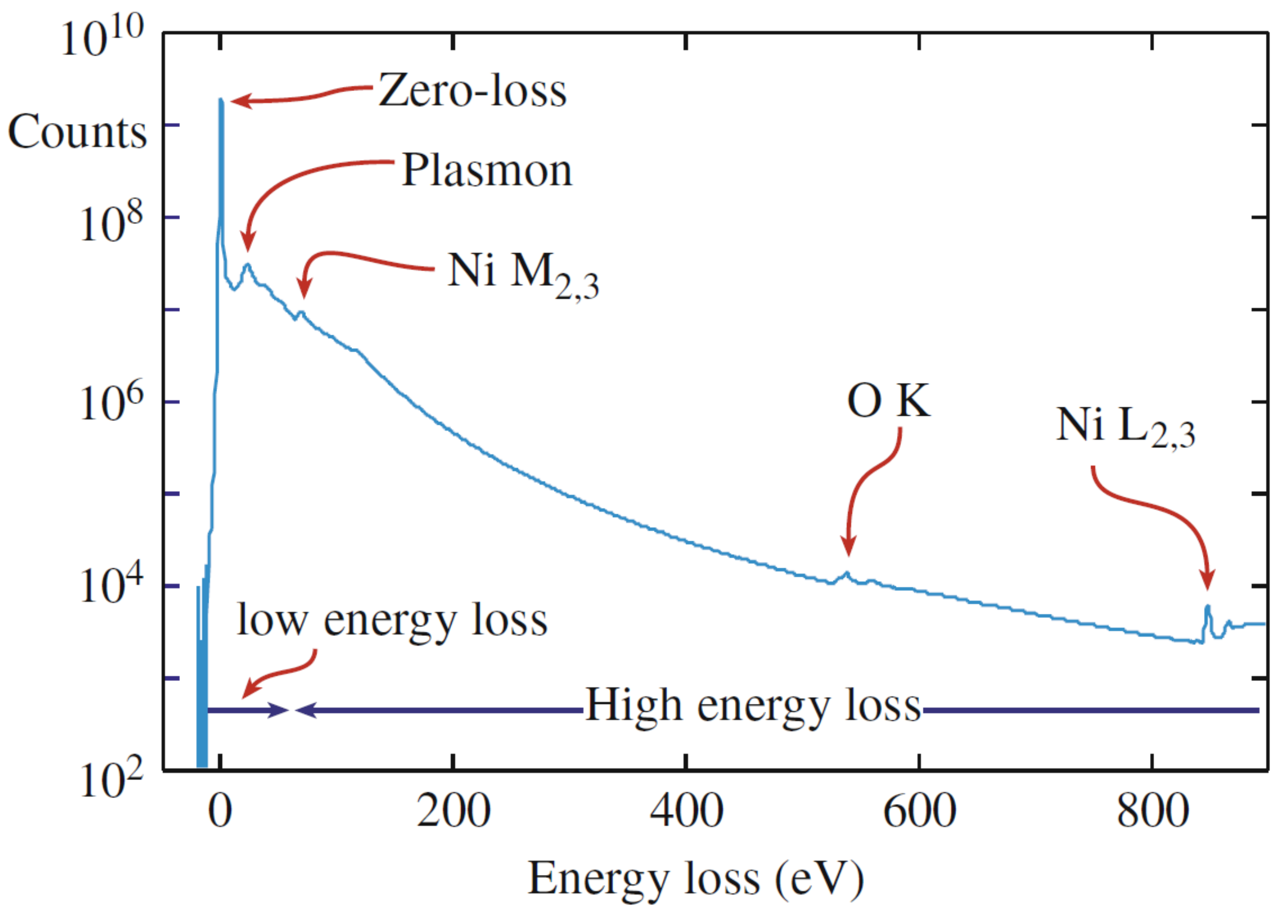
Adapted from R. F. Egerton, 3rd Ed, 2011



Adapted from www.vectorstock.com

- EELS analyzes the energy distribution of electrons that have passed through the specimen
- Electrons with different energy (loss) passing through the magnetic prism bent to different angles and form a spectrum (like white light can be broken into lights of different colors by an optic prism)

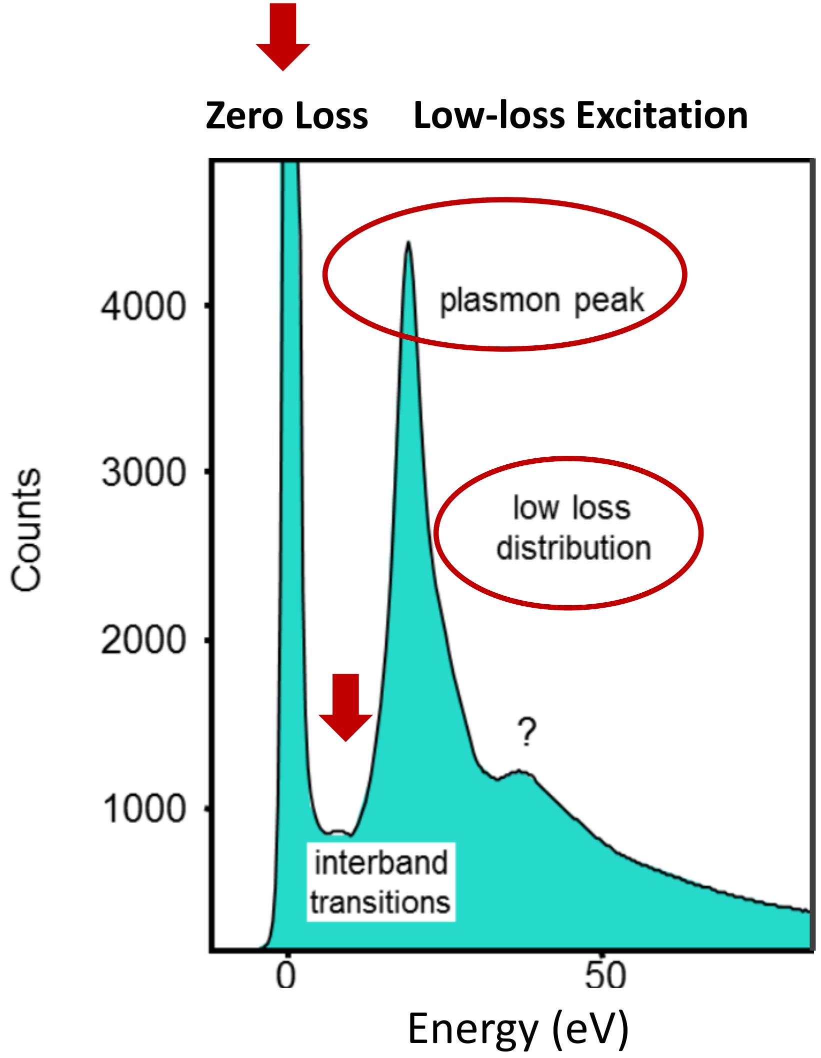
What an EELS spectrum looks like?



Williams and Carter (2nd edition)

- An extremely high intensity zero-loss peak
- The rest of the peaks appear as small bumps (edges) sitting on a high background
- The background falls rapidly with energy loss increases
- Intensity of the entire spectrum goes across many orders of magnitude
  - — Full view is only possible in log scale
- Energy resolution is much higher than that of EDS (~ 1 eV vs. ~130 eV)

EELS Spectrum Structure & Information Available (Zero-loss and Low-loss)



https://eels.info/

- **Zero-loss (ZLP)**

  From e- source energy spread, spectrometer resolution

  – specimen thickness, energy & intensity reference

- **Low-loss spectrum (< ~ 50 eV)**

  From interactions with weakly bound outer-shell electrons (valence/conduction) of the specimen atoms

  - **Plasmon excitation peak**

    Valence electron cloud deforms collectively in response to incident electron beam

    – valence/conduction electron density

  - **Near zero-loss feature**

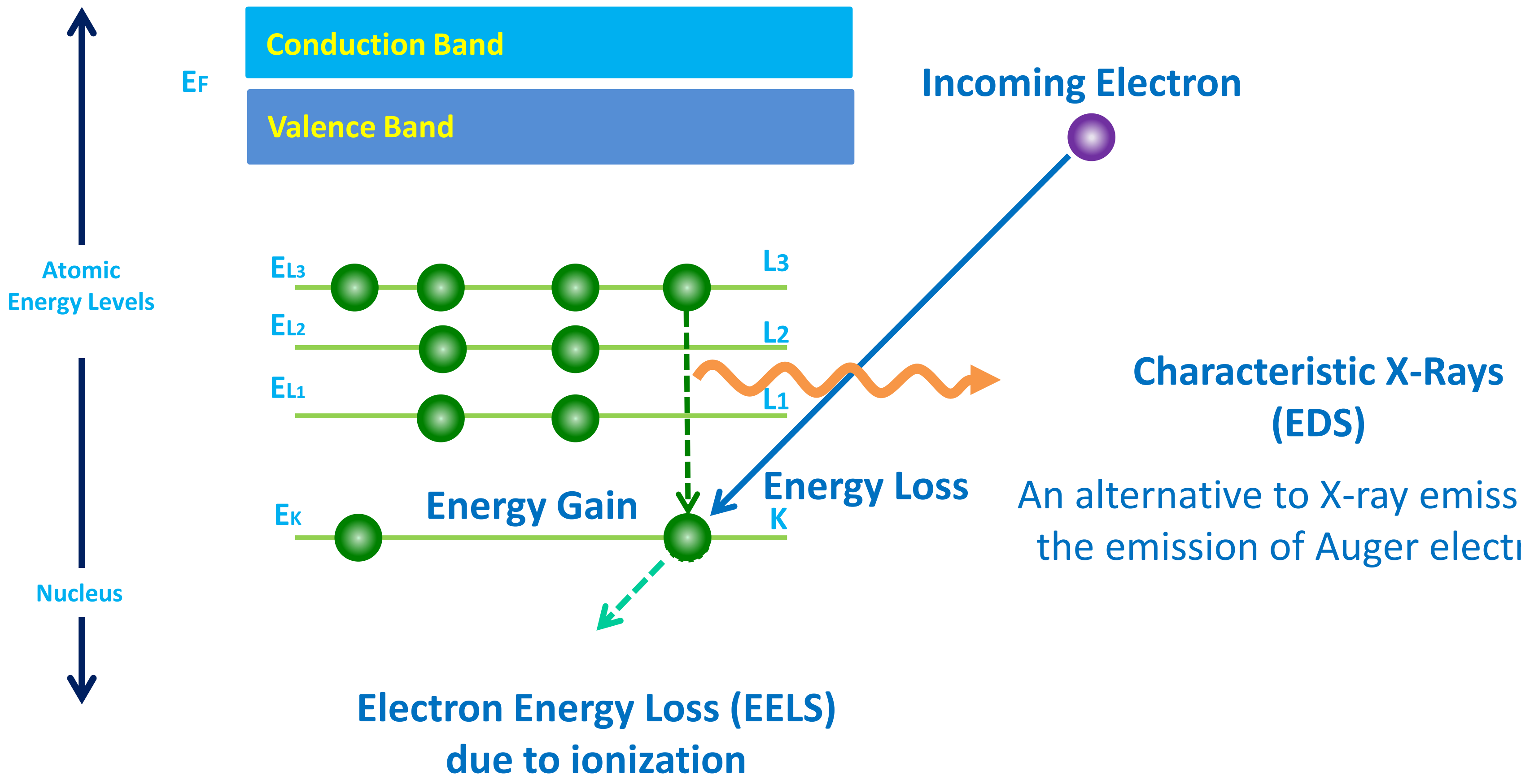
    – Inter-band transitions (e.g., band gap)

  - **Low loss distribution (< ~ 50 eV)**

    – complex dielectric function

Plural scattering removal/correction

EELS Spectrum Structure — Core-Loss



An alternative to X-ray emission is the emission of Auger electrons

EELS Ionization Edges

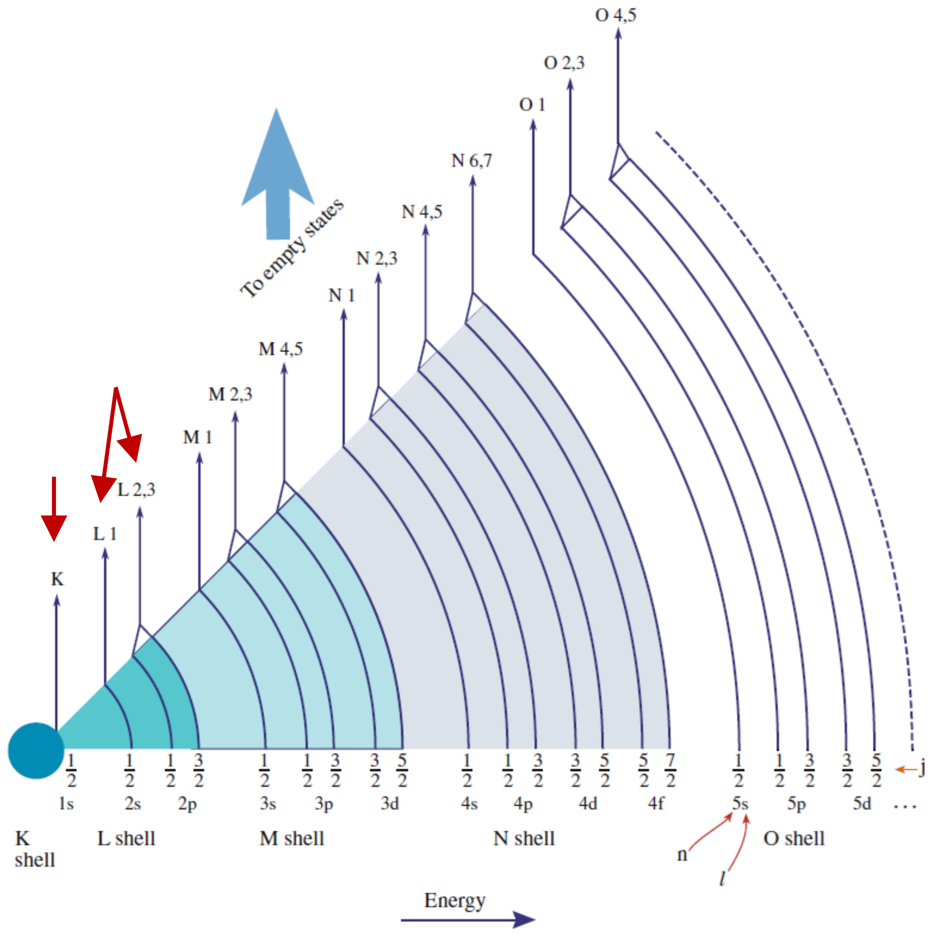
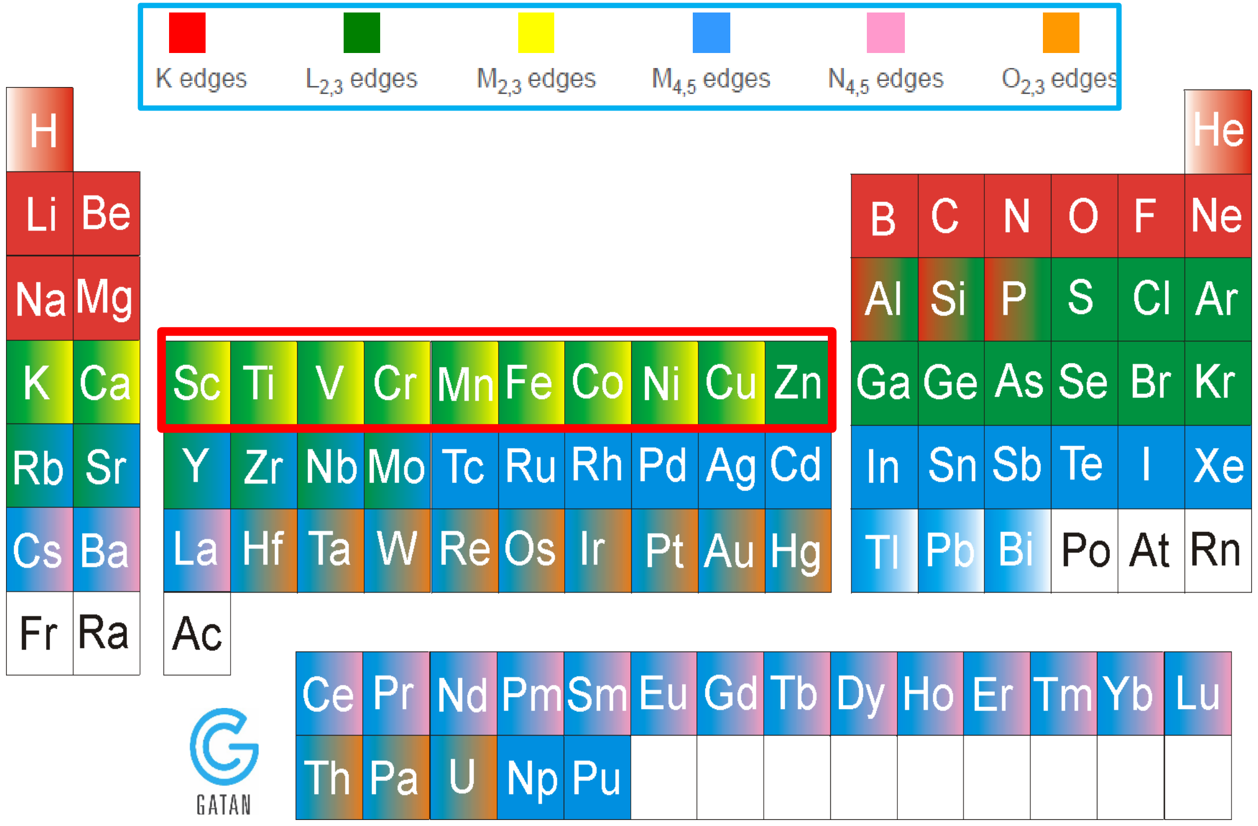


FIGURE 39.1. The full range of possible edges in the energy-loss spectrum due to core-shell ionization and the associated nomenclature.

Williams and Carter (2nd edition)

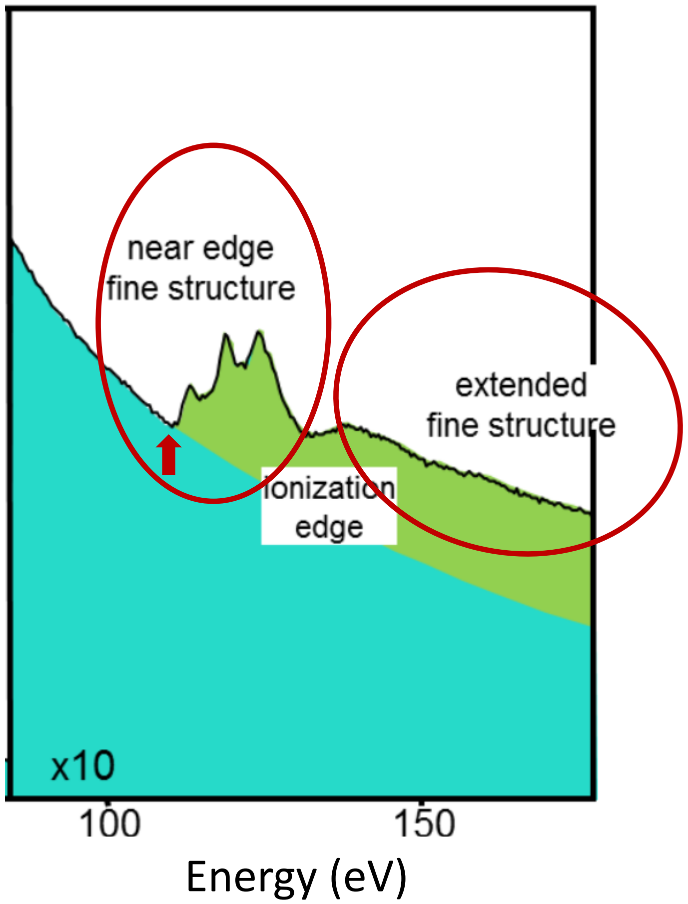
- EELS edges are classified according to the initial state of the excited electron (K, L, M, …)



- The edges suitable for EELS analysis for all the elements
- EELS works extremely well with light elements
- Highly complementary to EDS

EELS Spectrum Structure & Information Available (Core-loss)

Core level ionization

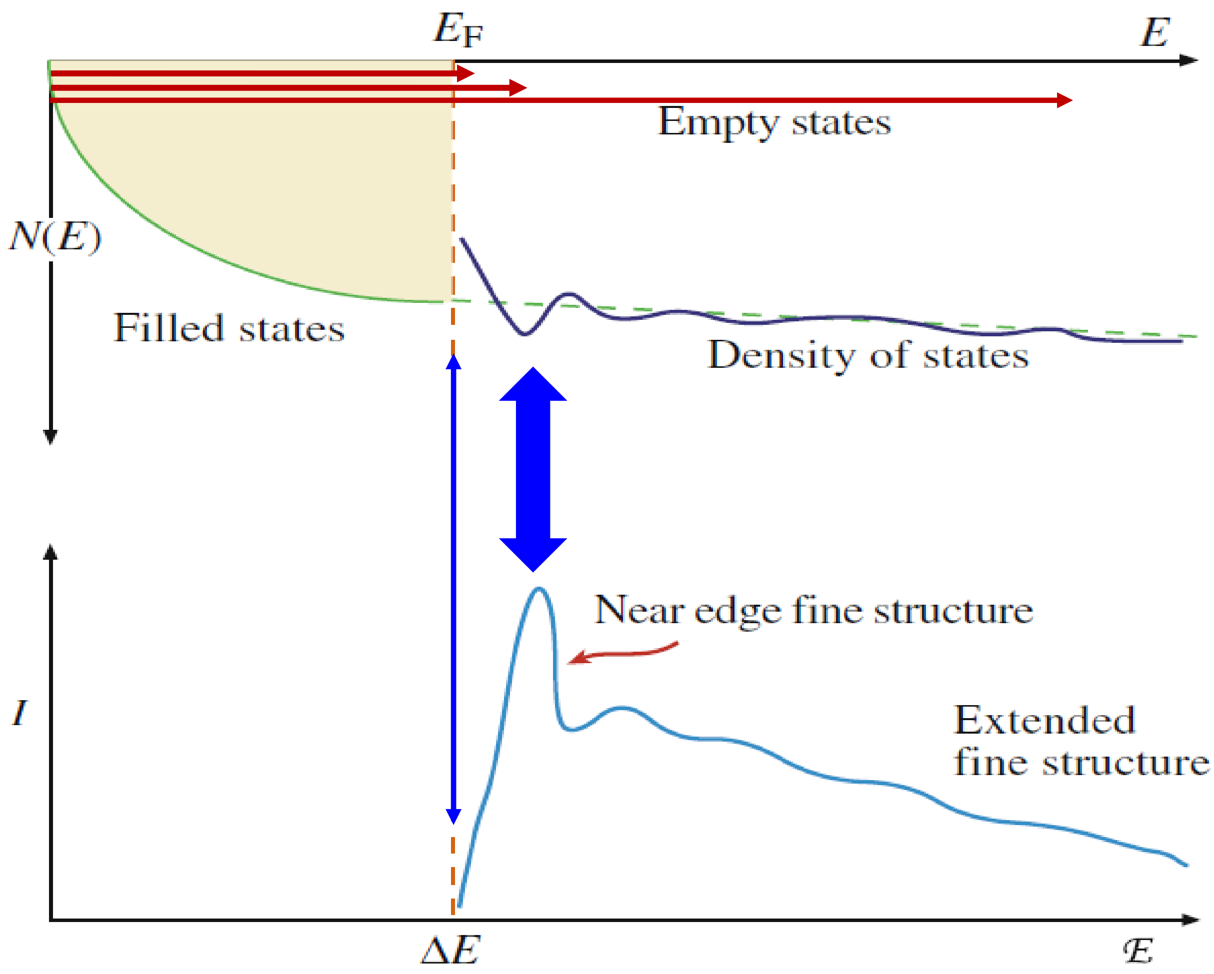


https://eels.info/

➢ Core-loss spectrum (> ~ 50 eV)

From interactions with tightly bound inner-shell electrons (core-shell) of the specimen atoms (ionization)

- **Core-Loss edge**
  — elemental identification/composition
- **Near edge fine structure (ELNES)**:
  — information about electronic structure (bonding, density of states)
- **Extended fine structures (EXELFS)**
  — atom-specific radical distribution of near neighbors (RDF — Radial-Distribution Function)



ELNES intensity corresponds to empty DOS (density of states)

Williams and Carter (2nd edition)

- The edge onset is characteristic of elements
  – element identification
- Core shell electrons can only be excited to:

  1. the unoccupied states above the Fermi level (ELNES)
  – the possible energy transfer values are controlled by the energy distribution of these available states
  – exploring unoccupied density of states/bonding

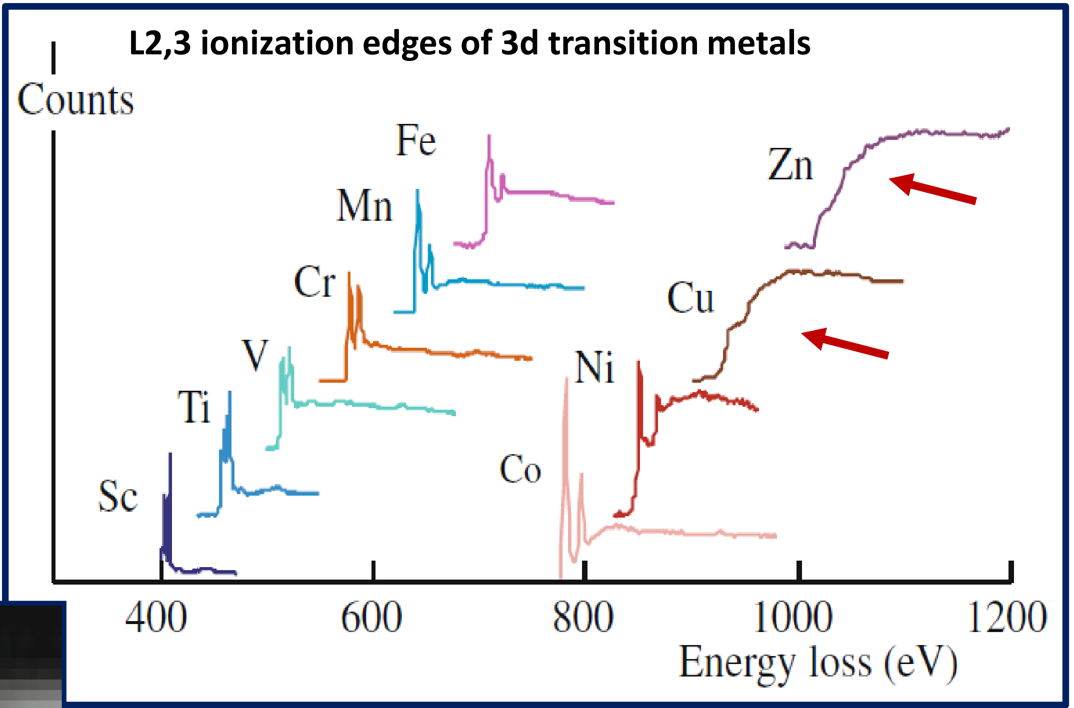
  2. “free” electron states if it receives sufficient energy (EXELFS)
  – exploring distribution of neighboring atoms
- Probability of ionization occurring decreases with energy increasing above E_F

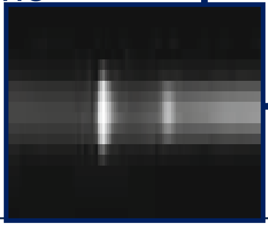
Example of ELNES – White Lines in Transition Metals

Atomic nr	21	22	23	24	25	26	27	28	29	30
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electron configuration	$3d^{1}4s^{2}$	$3d^{2}4s^{2}$	$3d^{3}4s^{2}$	$3d^{5}4s^{1}$	$3d^{5}4s^{2}$	$3d^{6}4s^{2}$	$3d^{7}4s^{2}$	$3d^{8}4s^{2}$	$3d^{10}4s^{1}$	$3d^{10}4s^{2}$

en.wikipedia.org/wiki/Transition metal

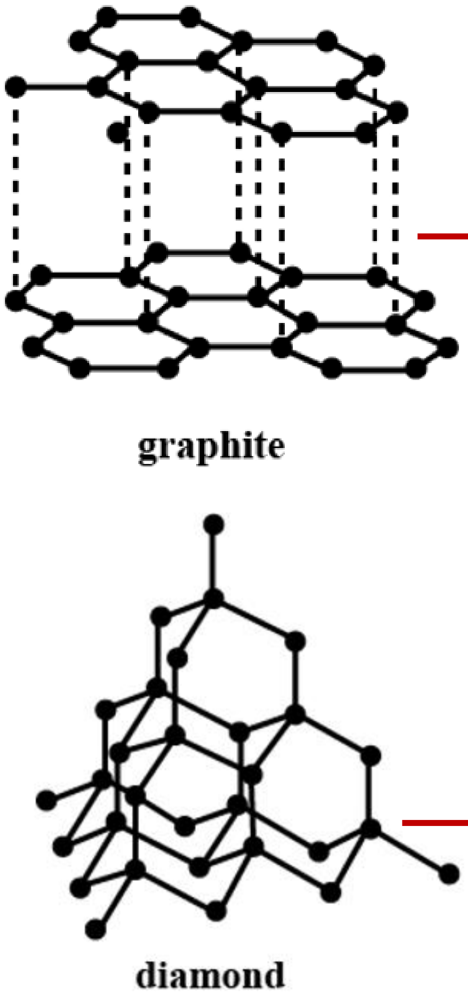
- For 3d transition metal, the white lines are corresponding to the transitions of 2p electrons to the partially unoccupied 3d-states.
- The d bands are energetically narrow, leading to sharp peaks
- There is a systematic variation in the intensity as a function of the number of d electrons. Therefore, the intensity can be related to the d bands occupancy (oxidation state)
- In Cu and Zn, 3d bands are fully occupied, so there are no white lines in the spectrum.
- Same happens to 4d transition metals

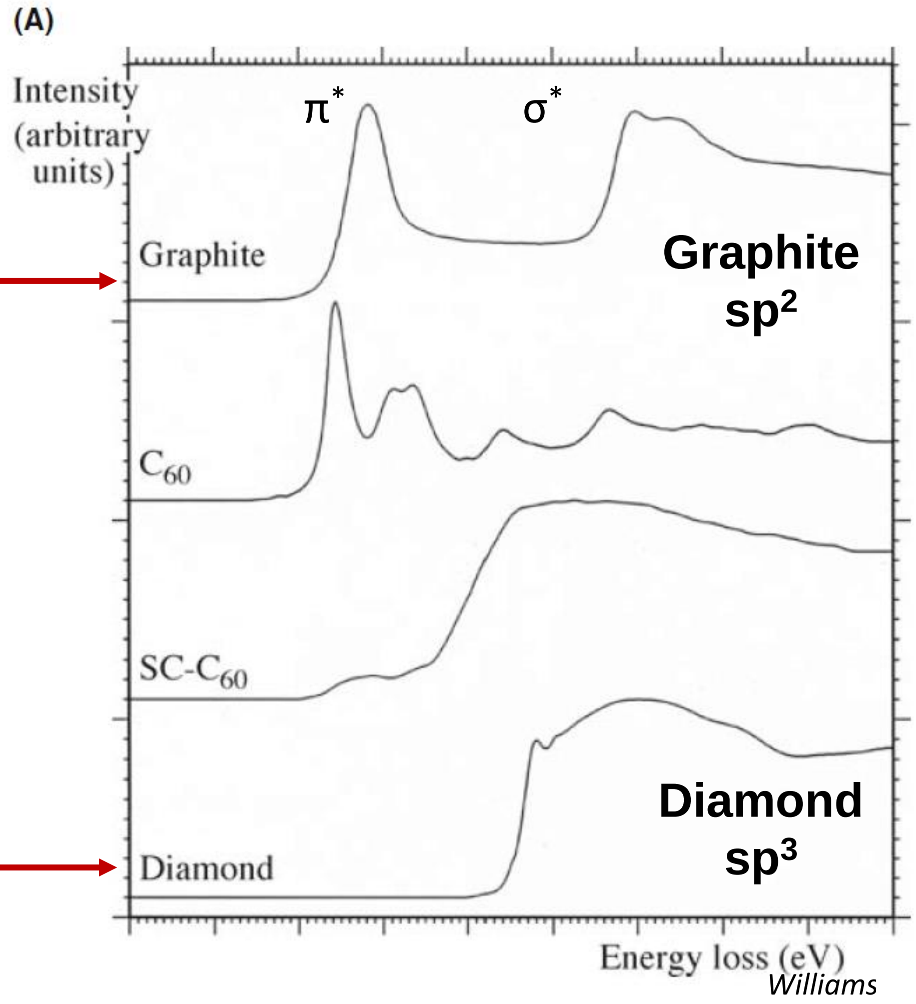


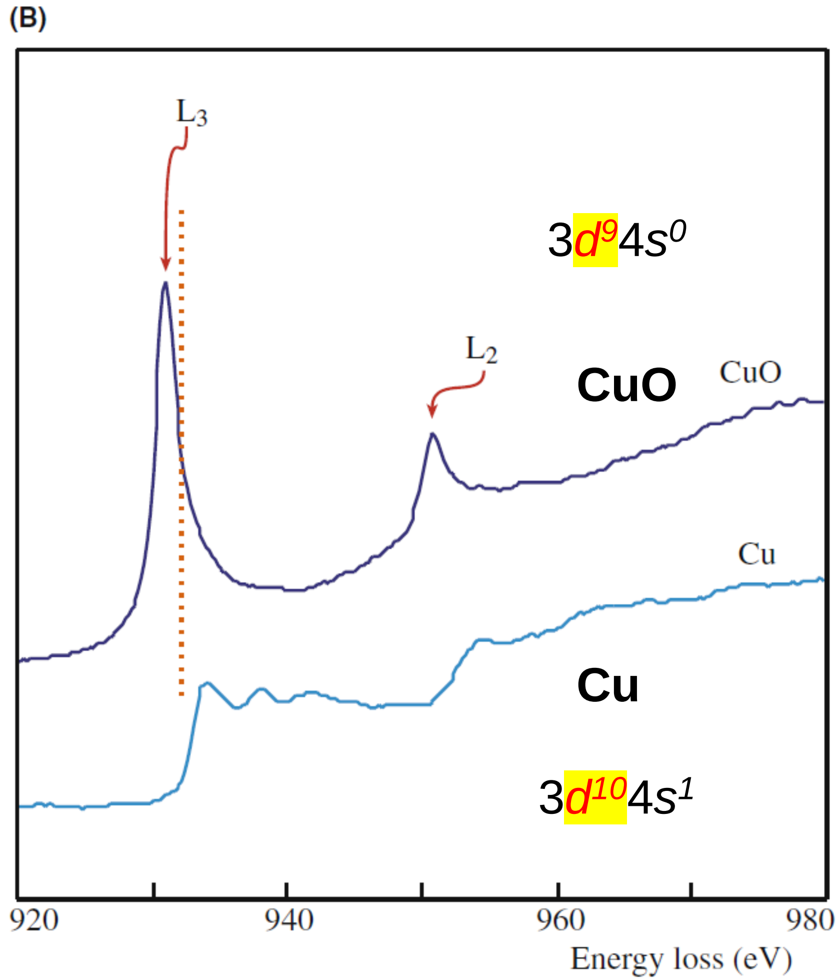


Williams and Carter (2nd edition)

EELS Near Edge Structure (ELNES) — Chemical Bonding



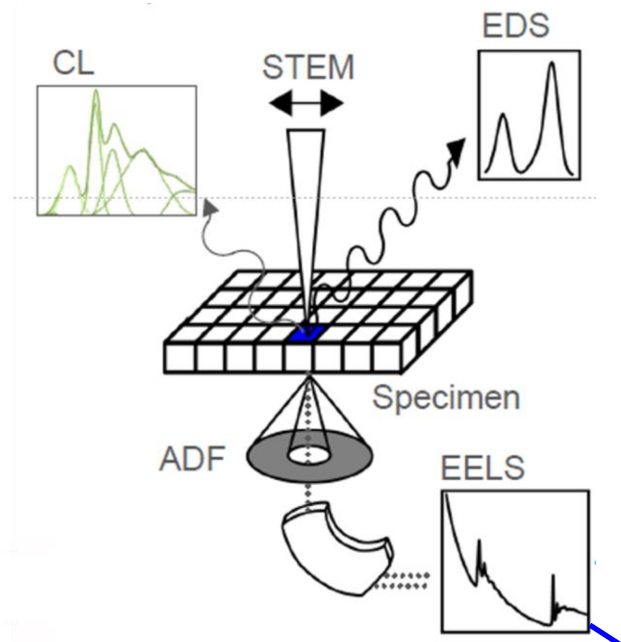


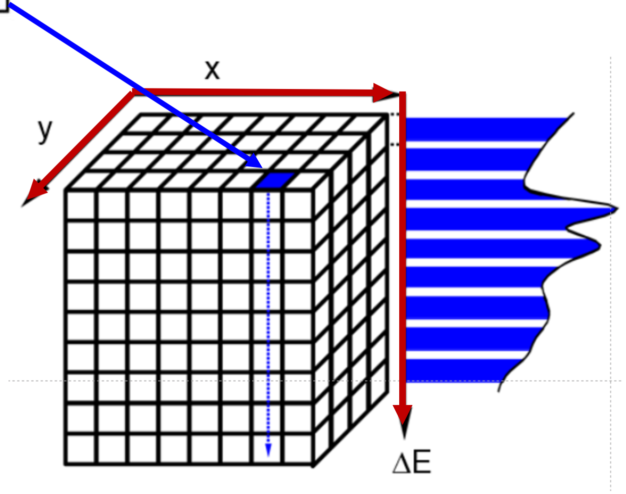


Graphite – sp^2 bonding at the basal plane – $\pi^* + \sigma$
Diamond – sp^3 bonding – σ

When oxidized, Cu 3d states lose electrons, 3d are not filled anymore – white line appears

Spectrum Imaging: Building a 3D Dataset





Gatan Spectrum imaging fundamentals

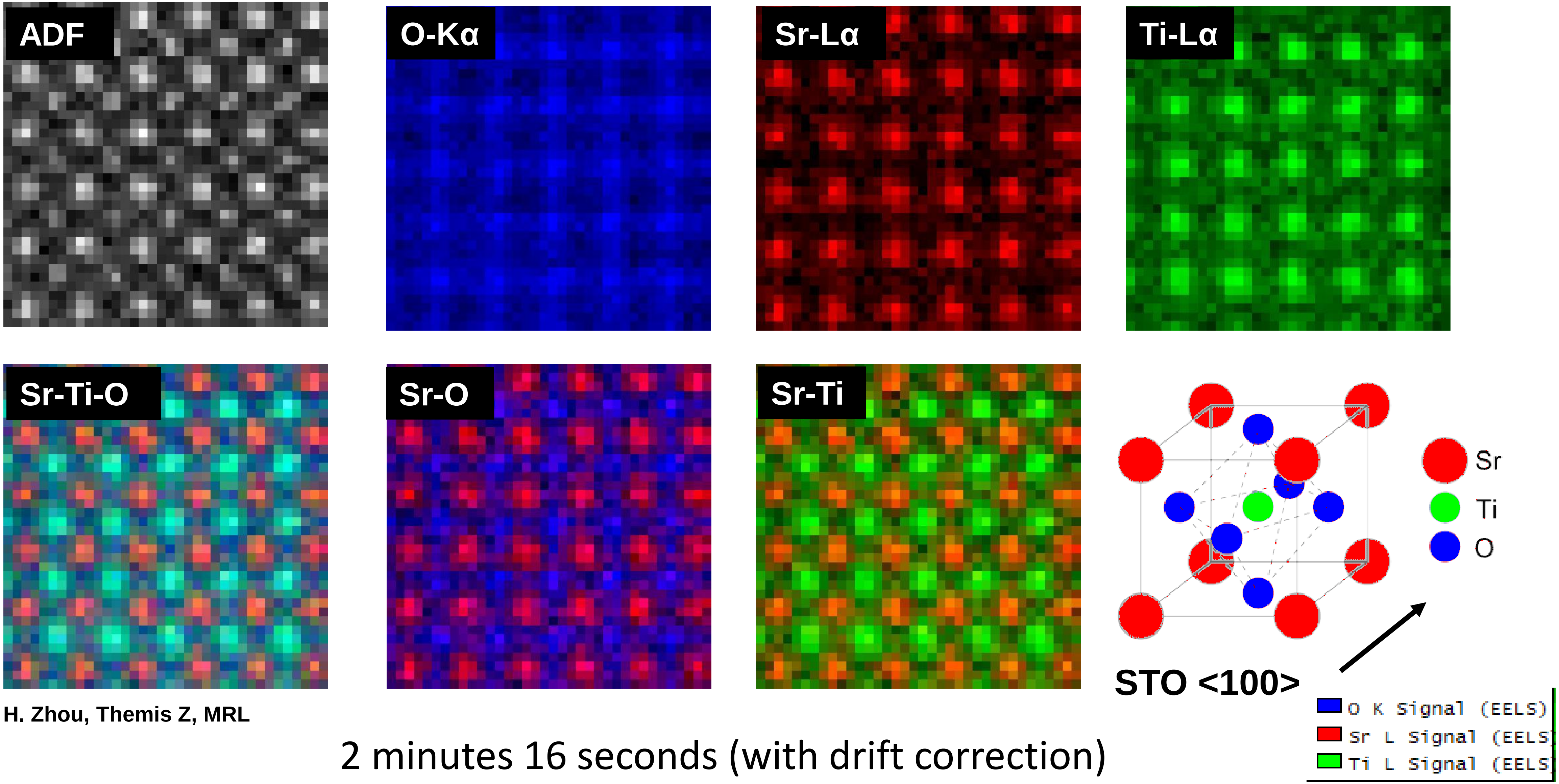
<u>STEM Spectrum Imaging</u>

- Acquired by stepping a focused electron beam
- At each step, a spectrum is recorded along with ADF signal to fill the data cube
- Each image pixel carries a spectrum

Collect and store detailed spatial & spectroscopy info together in a data cube

Allows processing decisions after acquisition!

Atomic Resolution EELS Mapping

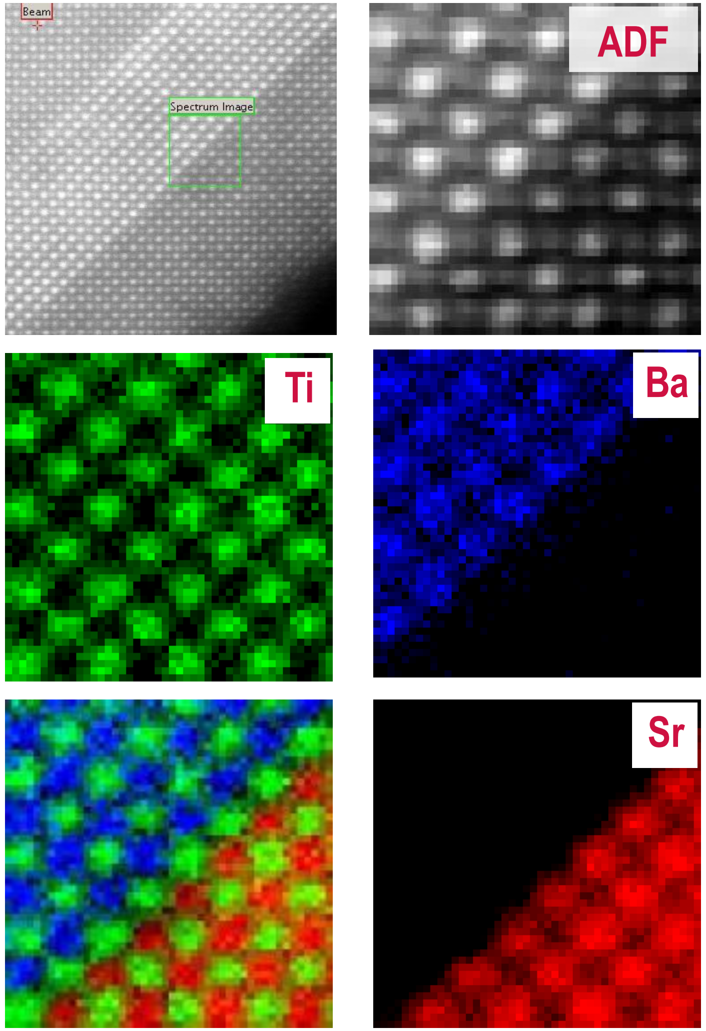


H. Zhou, Themis Z, MRL

2 minutes 16 seconds (with drift correction)

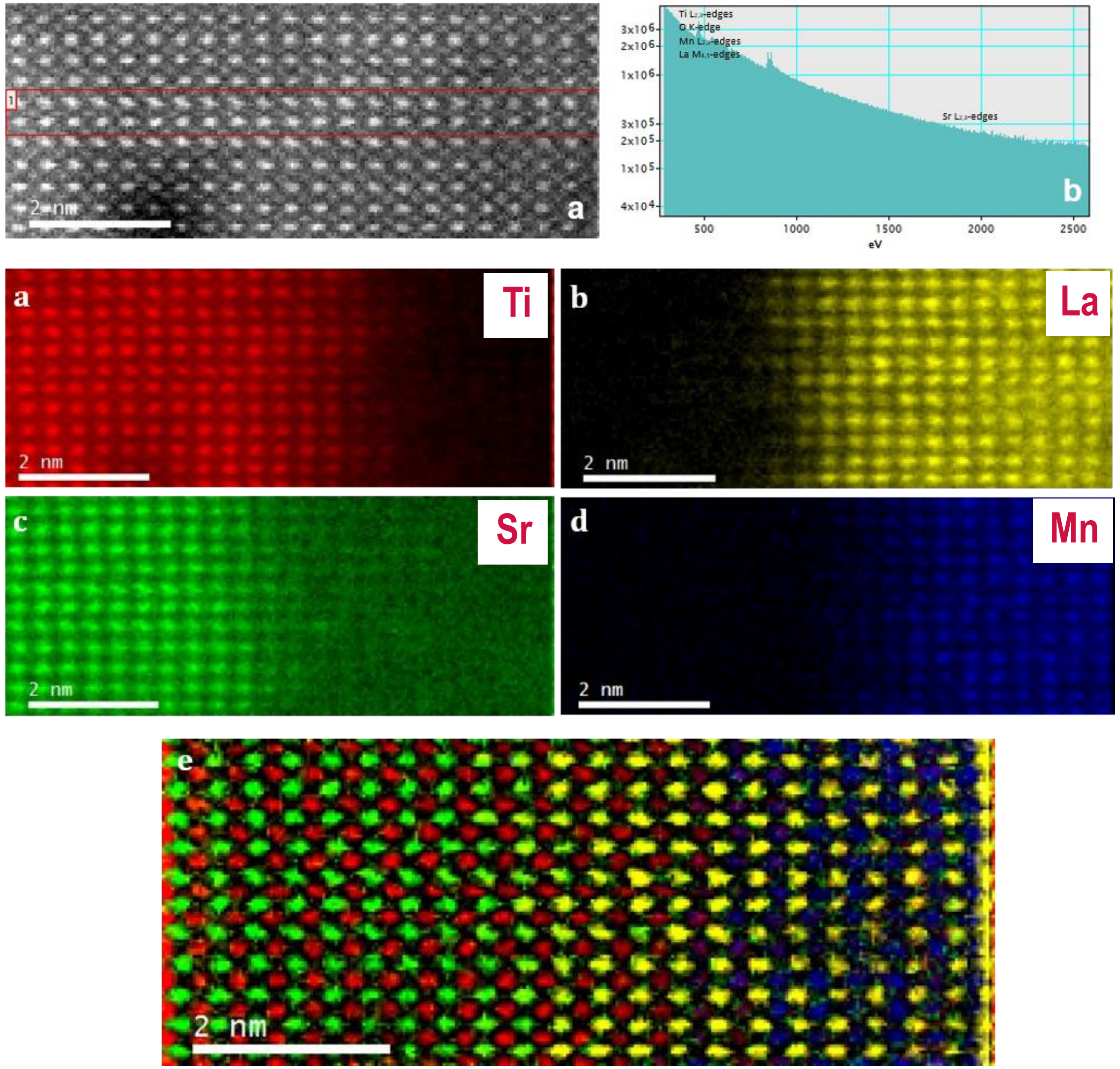
Much faster than EDS mapping owing to a close to 100 % collection efficiency

Atomic Resolution EELS Mapping



$BaTiO_3/SrTiO_3$ Interface
Atomically sharp

Botton, et al, Ultramicroscopy 110 (2010) 926–934



$SrTiO_3/LaMnO_3$ Interface
Intermixing between Mn & Ti and Sr & La

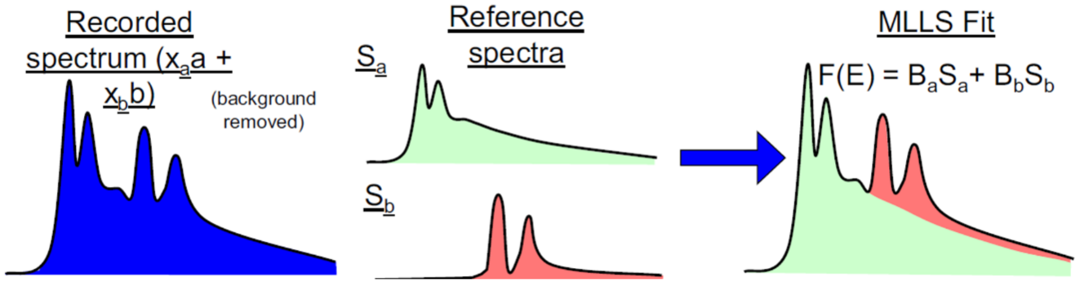
https://www.gatan.com/atomic-level-eels-mapping-using-high-energy-edges-dualeels-mode

Chemical Phase Mapping

Multiple linear least squares (MLLS) method can be used to map overlapping features

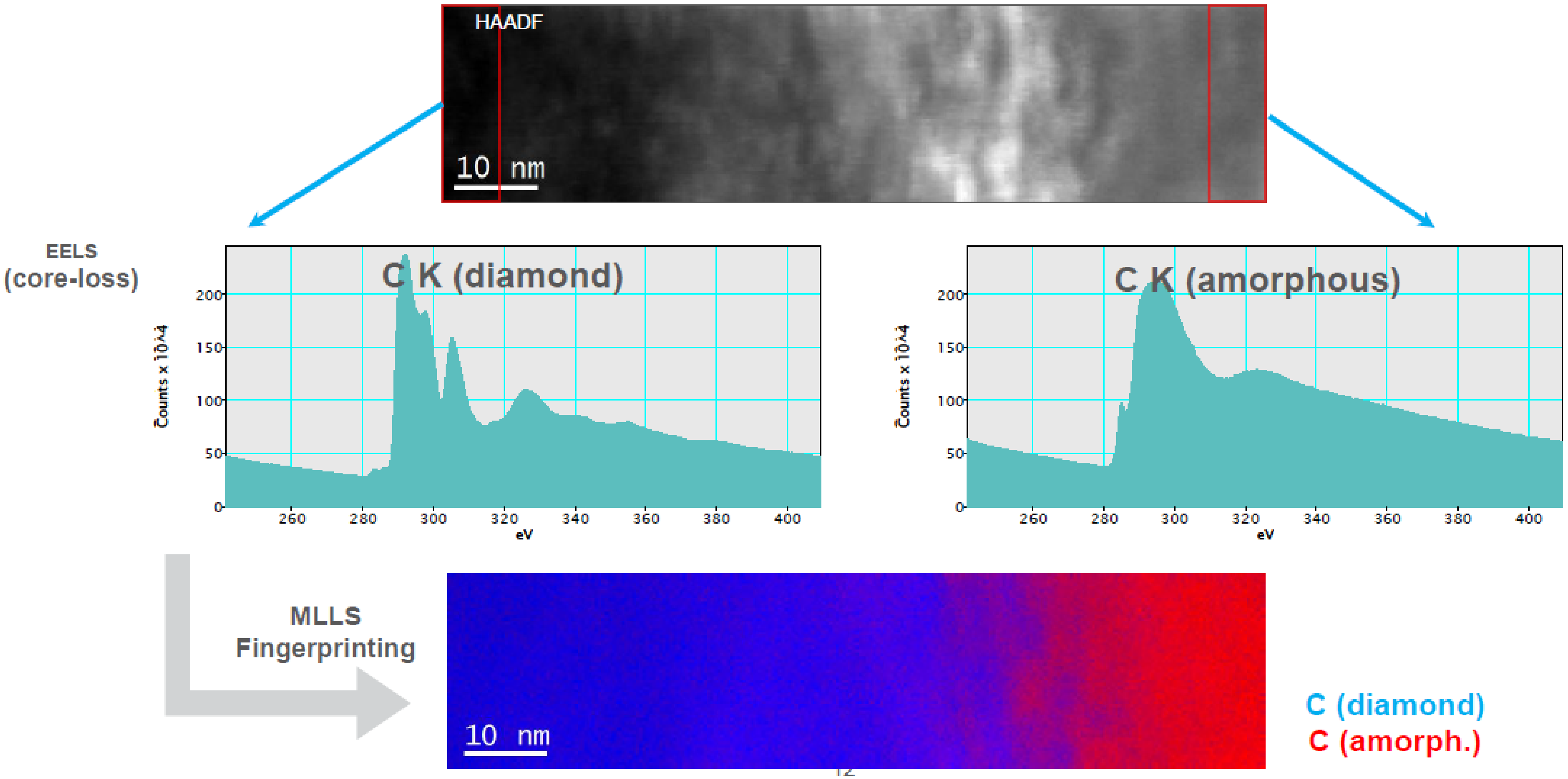
$$F(E) = AE^{-r} + B_a S_a(E) + B_b S_b(E) + \dots$$

$S_a(E)$, $S_b(E)$ … – reference models
B_a, B_b … – Scaling coefficients



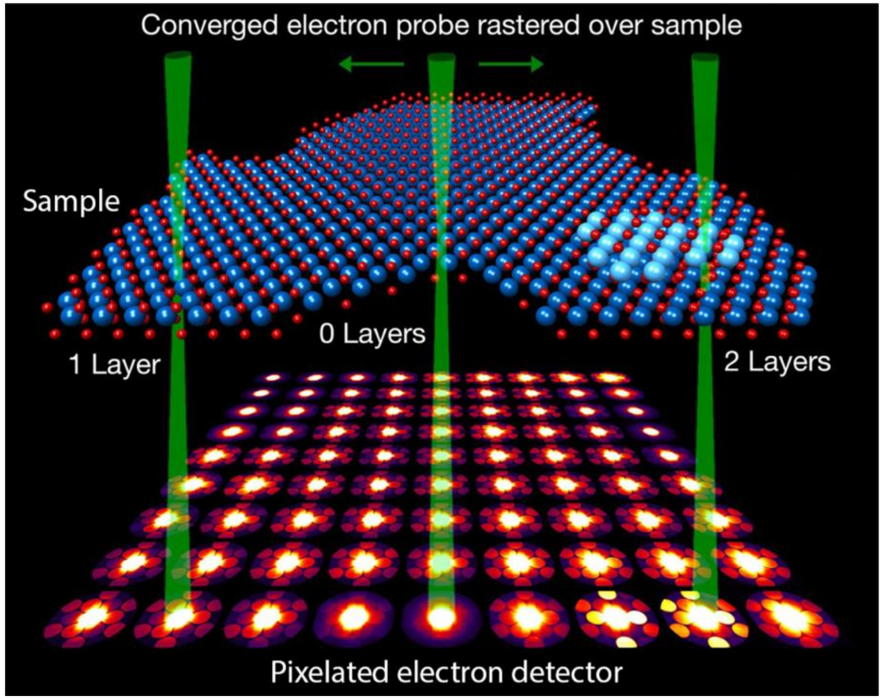
https://eels.info/

Interface in diamond after C ion implantation

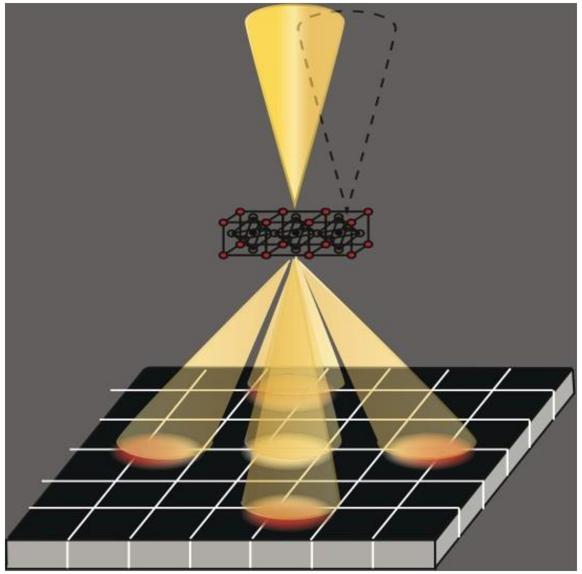


GATAN AMETEK

Four-dimensional Scanning Transmission Electron Microscopy (4D-STEM)



Colin Ophus, Microanal, Volume 25, Issue 3, 1 June 2019, Pages 563–582



Thermo Fisher Scientific

Electron **M**icroscope **P**ixel **A**rray **D**etector

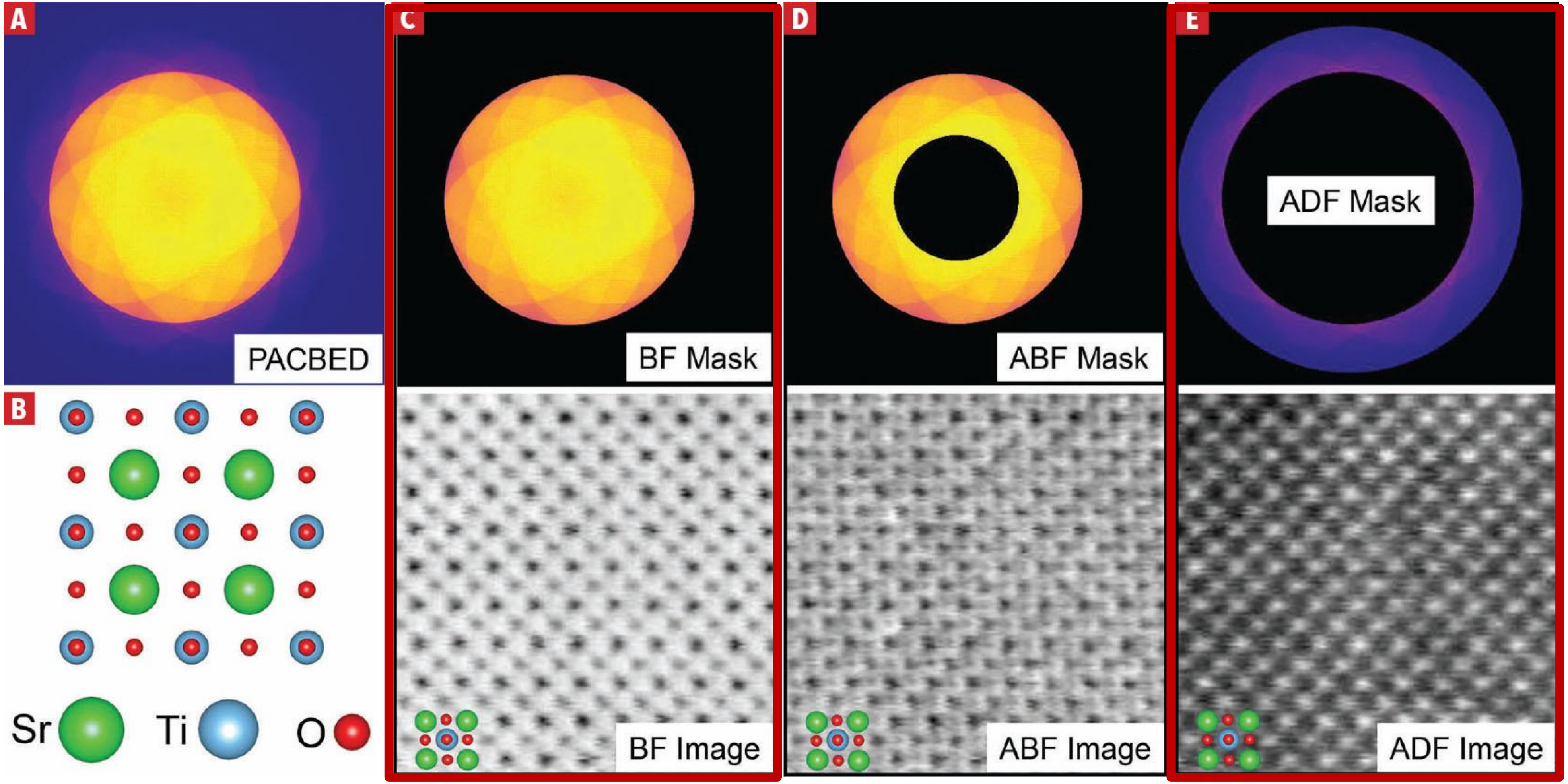
- Record diffraction pattern for each STEM pixel
- Extract structural info from the dataset
- Requires high sensitivity, speed & dynamic range detectors
- Powerful computers (more memory, high data transfer speed)
- Data analysis algorithms

Applications:

- Virtual imaging
- Orientation mapping
- Strain mapping
- Differential phase contrast imaging
- Electron ptychography

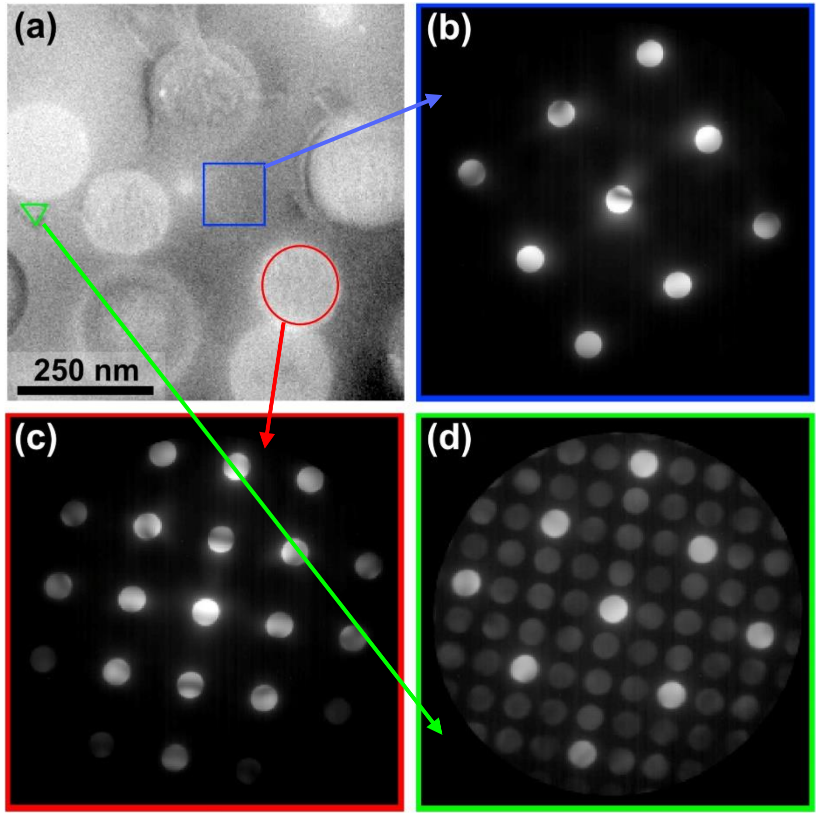
and more ...

Example of 4D-STEM Applications – Virtual Imaging



Barnaby D.A. Levin, et. al., "4D STEM with a direct electron detector"
https://analyticalscience.wiley.com/content/article-do/4d-stem-direct-electron-detector#was.auth.LevinB

Applying virtual detectors to reconstruct STEM images
$SrTiO_3$ along <110>

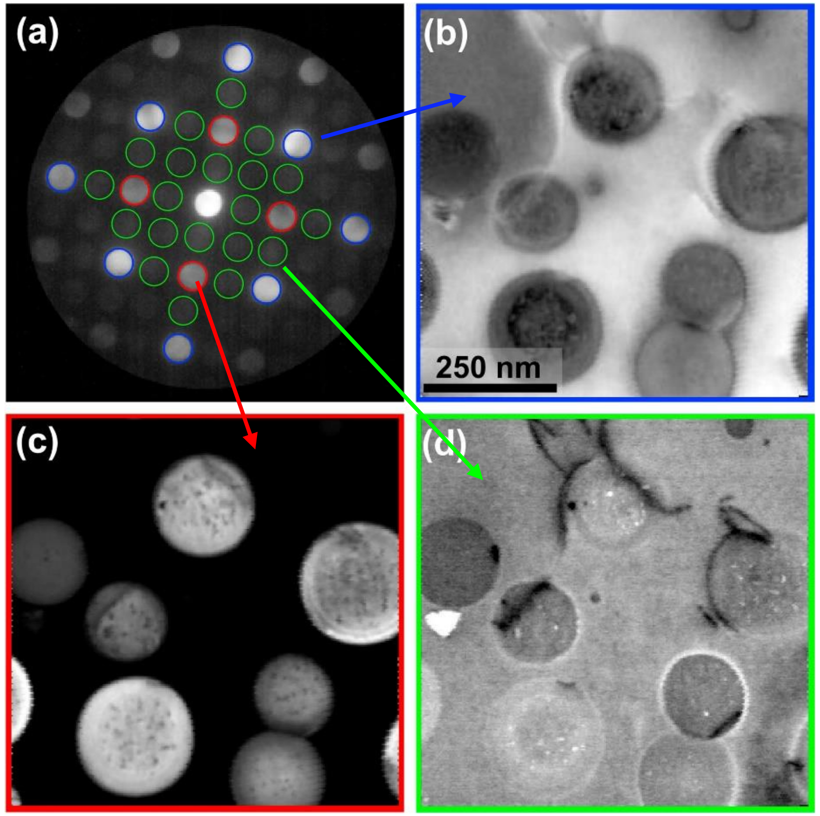


Virtual
SAD Aperture

Virtual
Objective Aperture

Fe–Al–Ni–Cr alloy

Gammer C, et al,
Ultramicroscopy 155 (2015) 1-10



Virtual selected area diffraction

Generated from ROIs in real space

Using virtual selected area apertures

Sum the diffraction patterns from multiple real space probe positions (pixels) in the 4D dataset

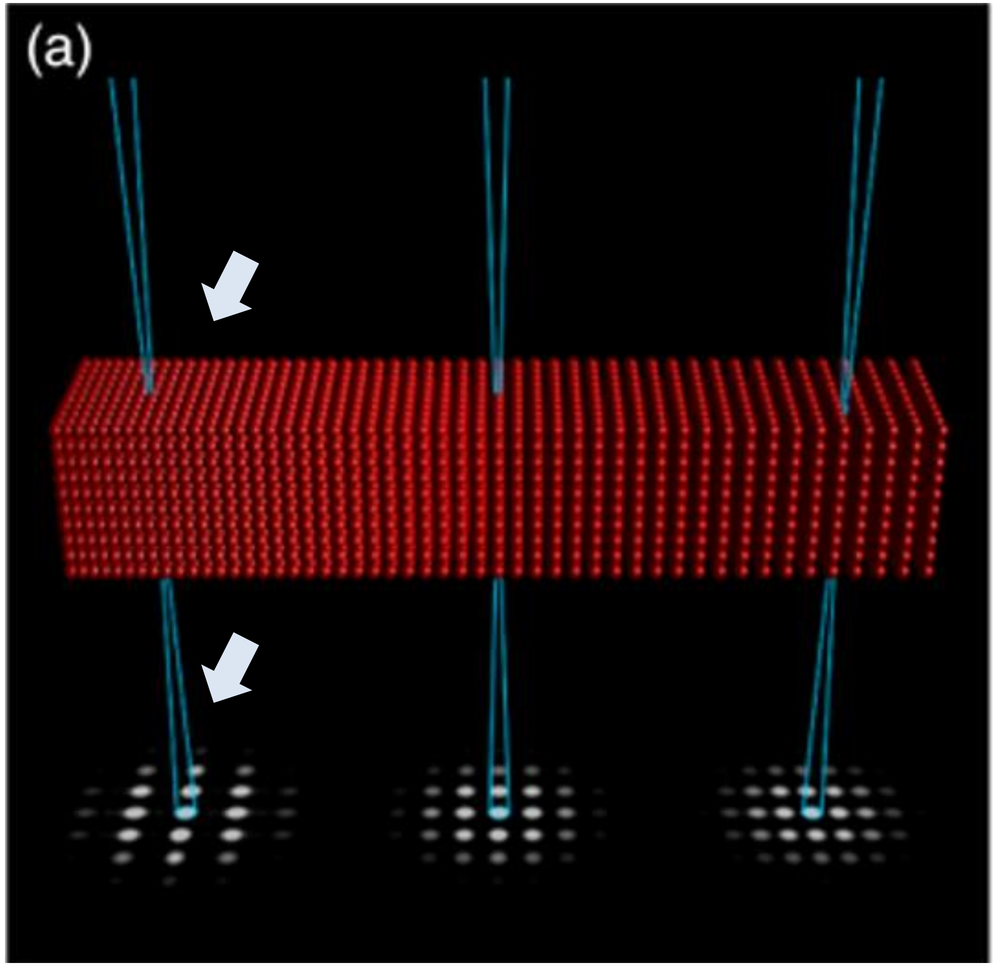
Virtual bright/dark field image

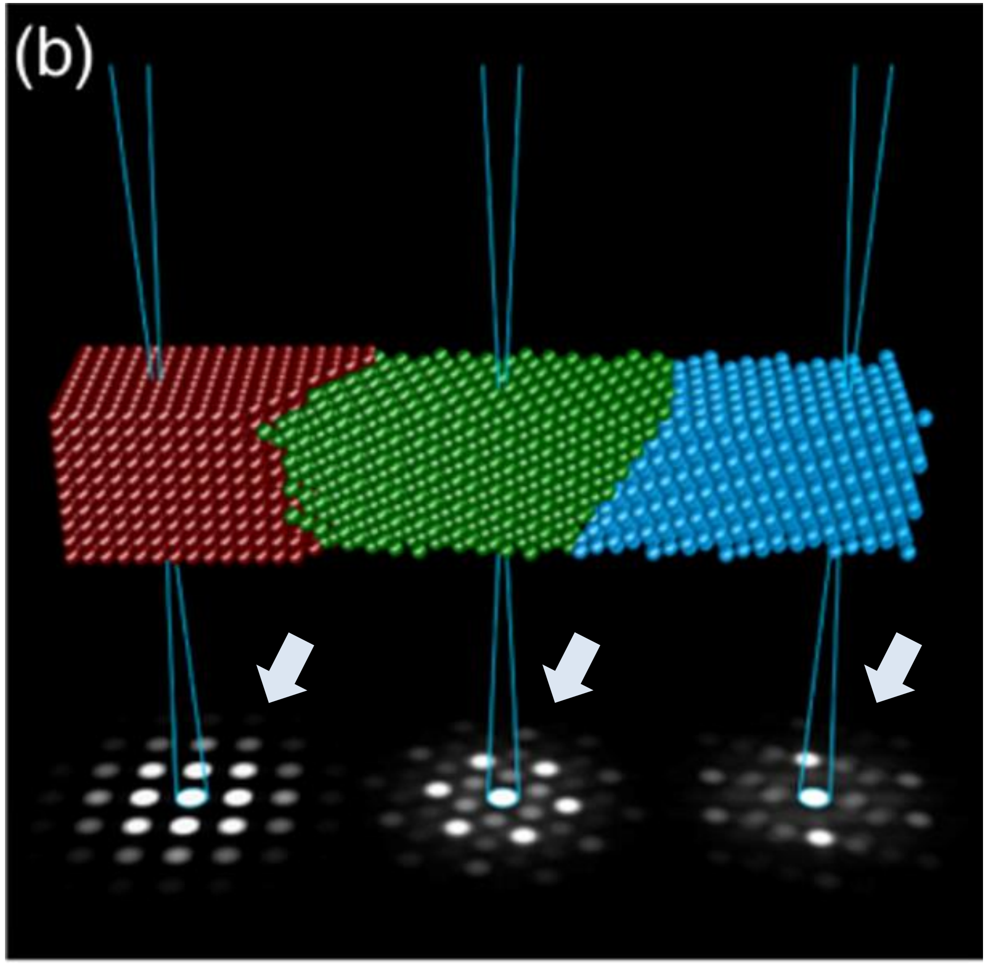
Generated from ROIs in diffraction space

Using virtual objective apertures

Sum the intensities of a subset of pixels in the diffraction space, assign it to corresponding pixels in the virtual image

Example of 4D-STEM Applications – Strain Mapping & Orientation Mapping



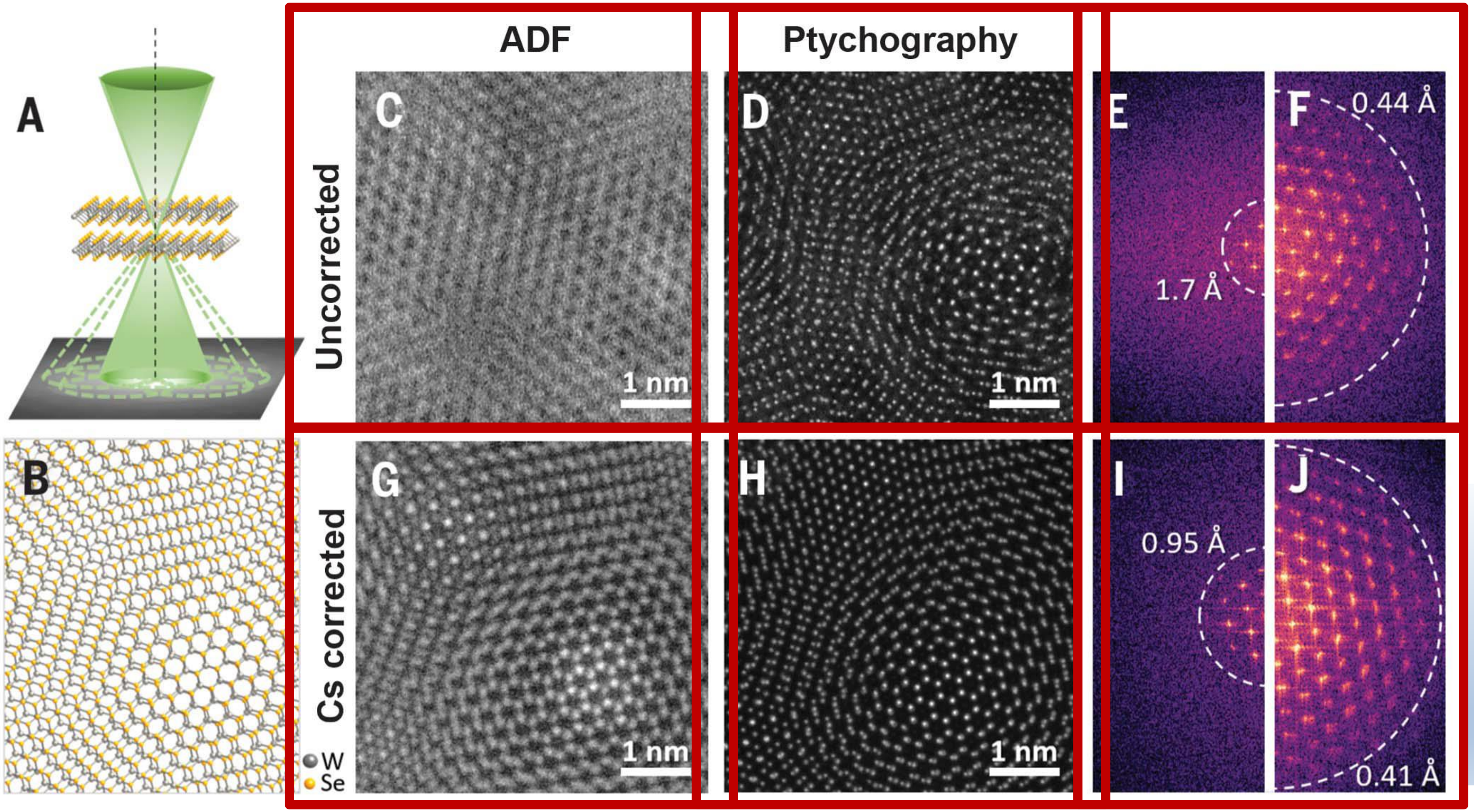


*Colin Ophus, *Microanal*, Volume 25, Issue 3, 1 June 2019, Pages 563–582, https://doi.org/10.1017/S1431927619000497

Strain Mapping

Orientation Mapping

Example of 4D-STEM Applications — Ptychography



ADF-STEM and ptychography of twisted bilayer WSe_2

Nguyen et al., Science 383, 865–870 (2024), Huang Group, UIUC

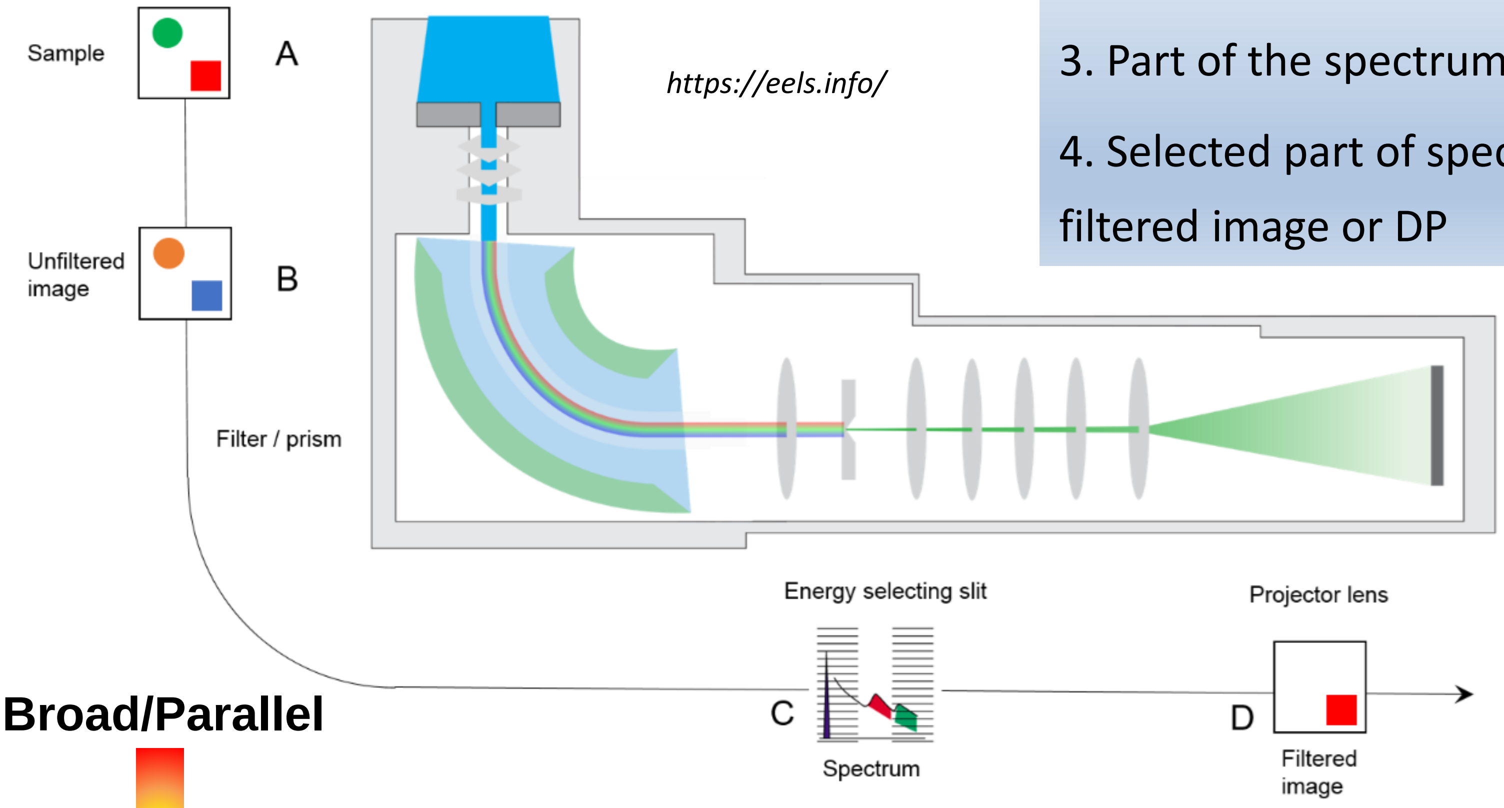
Sub-0.5-angstrom resolution

in an uncorrected Microscope

- Reconstruct phase info/crystal structure (image) with computational methods
- Spatial resolution improved greatly, beyond traditional STEM imaging techniques

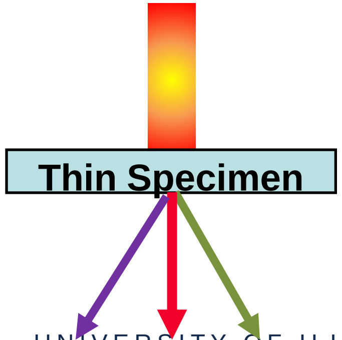
Energy Filtered Transmission Electron Microscopy (EFTEM)

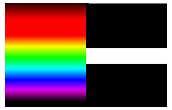
1. Unfiltered image or diffraction pattern (DP) is formed
2. Image or DP is transformed into the spectrum
3. Part of the spectrum is selected by energy-selecting slit
4. Selected part of spectrum is transformed back into an energy-filtered image or DP



- **Contrast & resolution enhancement**
  - zero-loss imaging
  - pre-carbon imaging
  - most probable loss imaging
- **Element/chemical mapping**
  - plasmon peak imaging
  - core-loss edge imaging
  - ELNES mapping

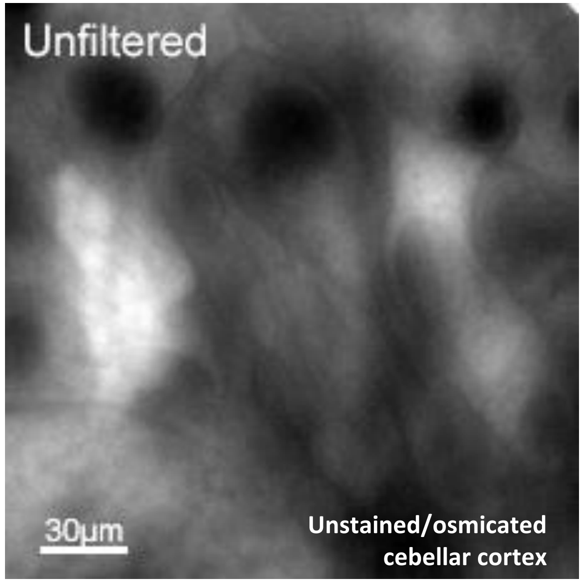
Broad/Parallel

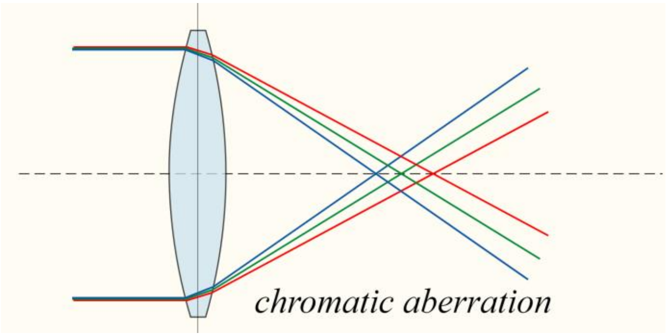




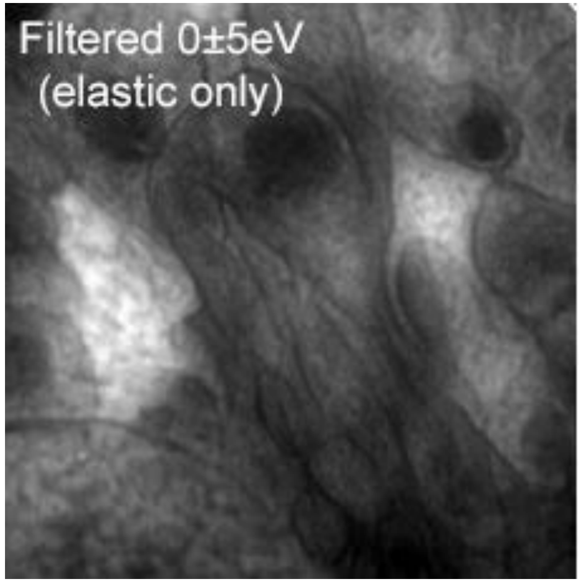
Energy Selecting Slit

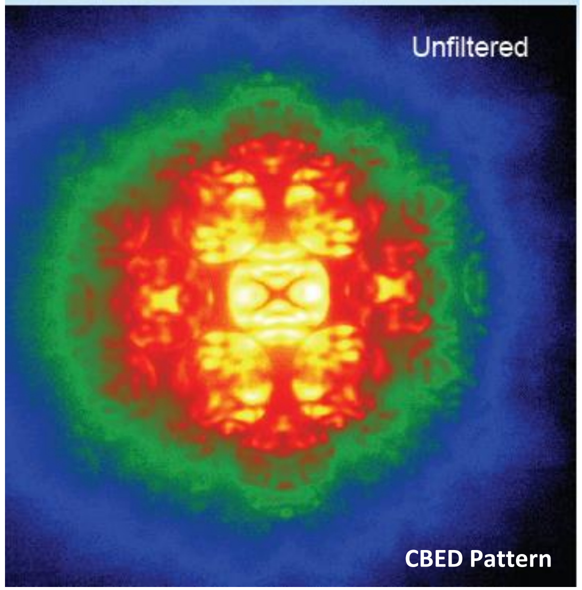
EFTEM – Zero-loss Peak imaging



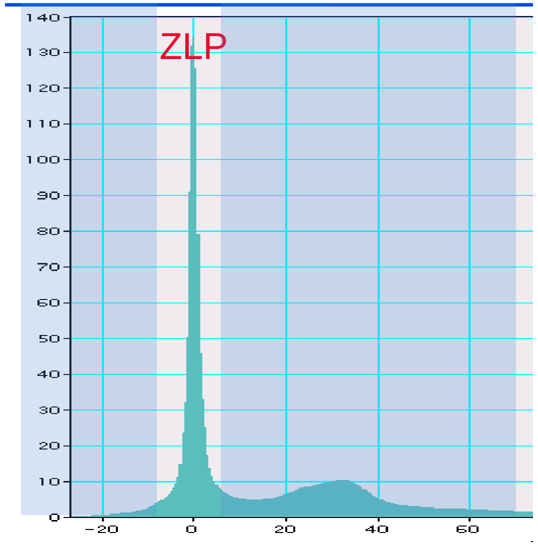


https://en.wikipedia.org/wiki/Chromatic_aberration

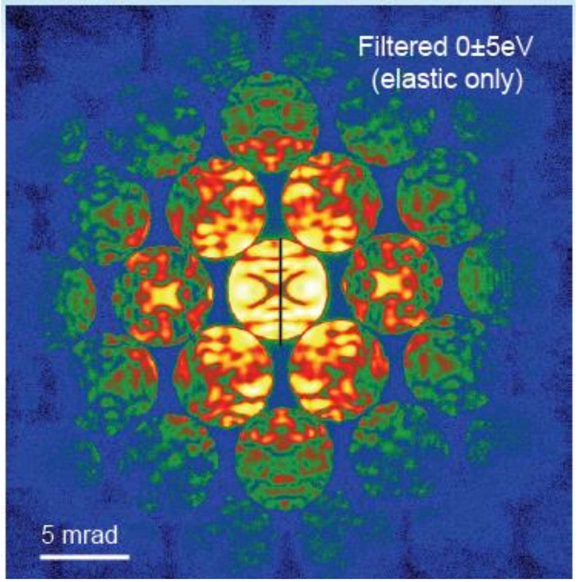




Elastic & inelastic electrons



Blocking inelastically scattered electrons

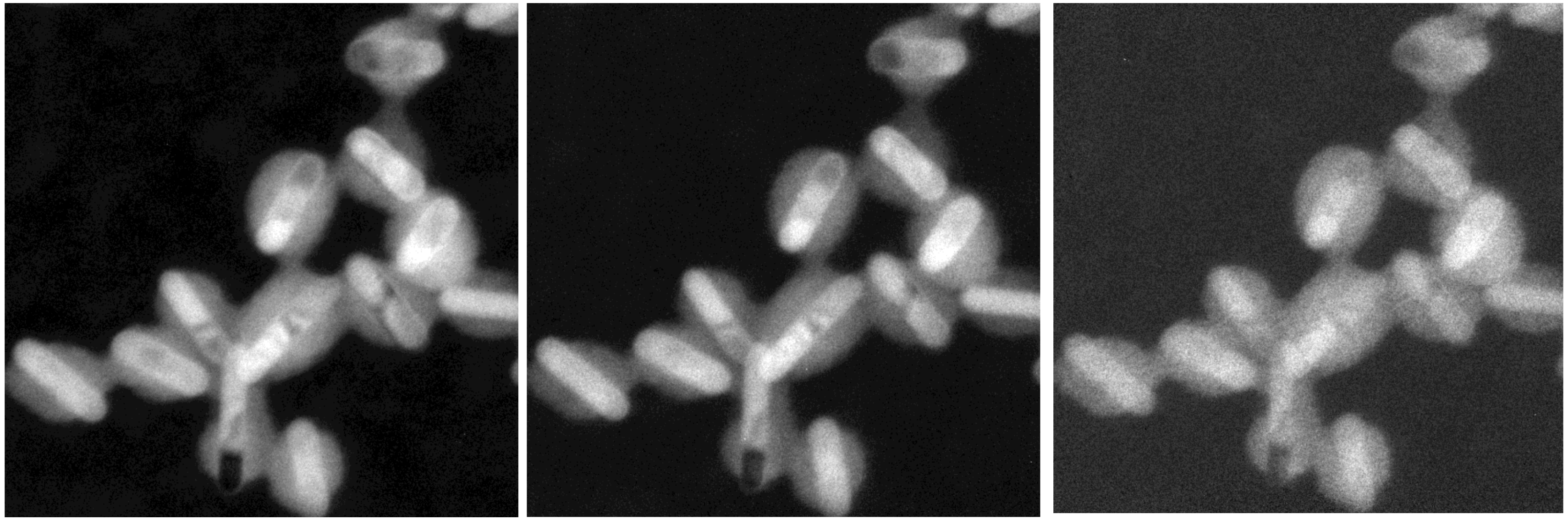


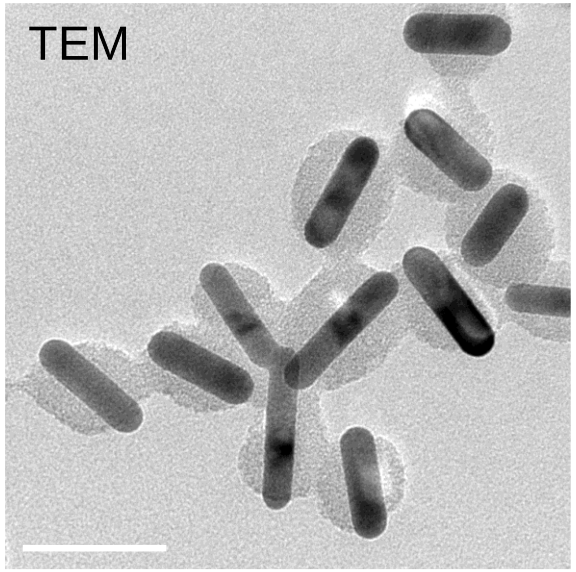
inelastic fog removed

Image courtesy Gatan

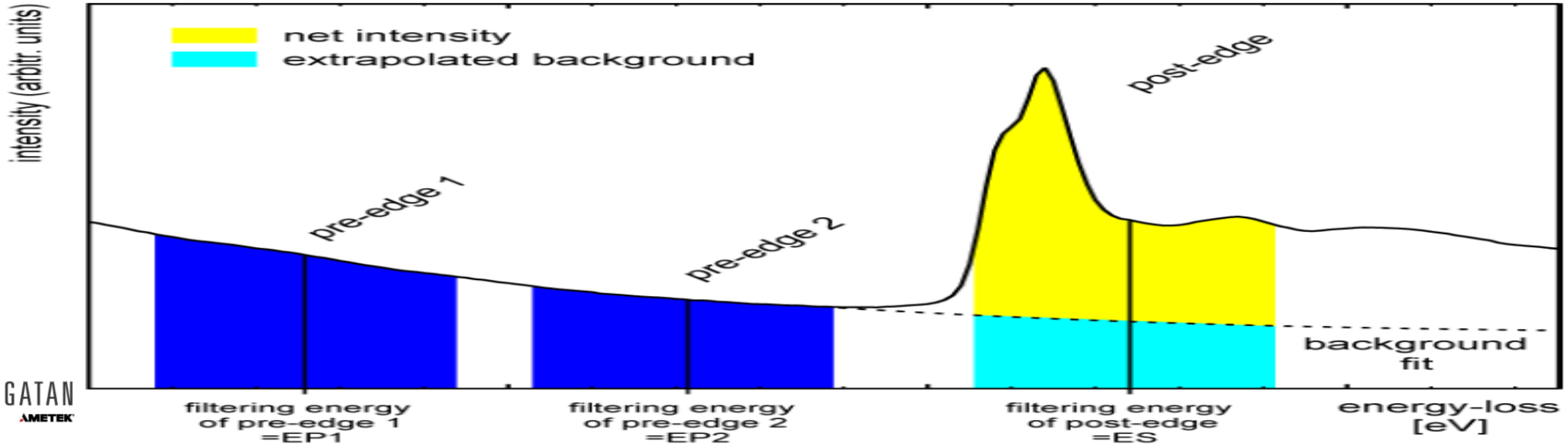
EFTEM – Core Loss Edge Imaging

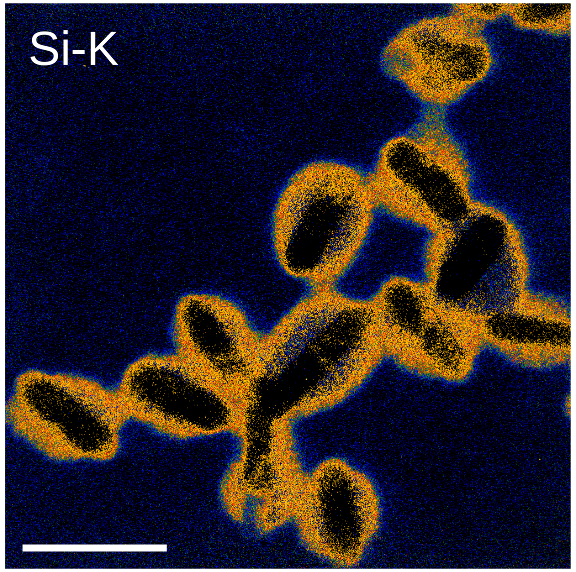
Pre-edge 1 **Pre-edge 2** **Post-edge**





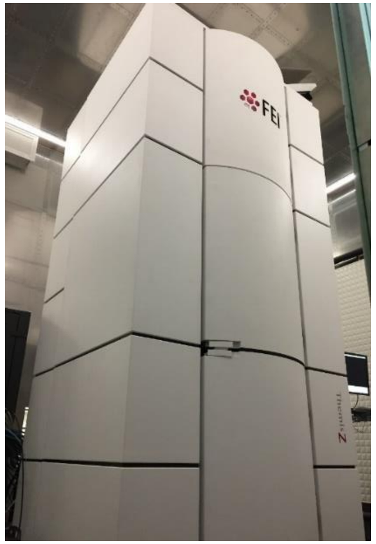
Si K-edge mapping using the three-window method reveals Si at the shell





C. Chen, MRL

TEMs Equipped with STEM or Analytical Capabilities at MRL



Themis Z STEM/TEM

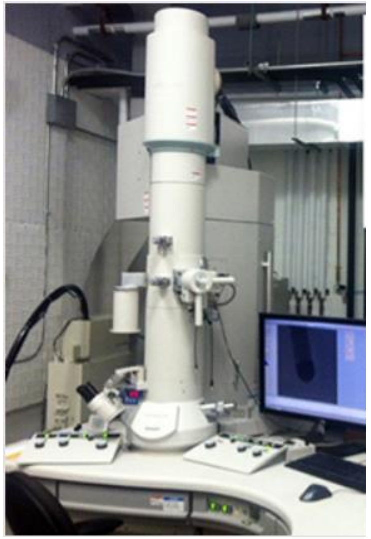
- 60-300 kV & Energy monochromator
- X-FEG high brightness electron source
- D-Corr spherical aberration probe corrector
- Super-X 4-quandrant SDD EDS detectors
- Gatan GIF Quantum ER image filter and Ultrafast DualEELS
- STEM/TEM Tomography acquisition
- iDPC: Integrated differential phase contrast imaging
- The EMPAD pixelated STEM detector

Aberration Correction, STEM-EELS, STEM-EDS EFTEM, iDPC & 4D-STEM

Talos F200X G2 STEM/TEM

- 80-200 kV
- Lorentz Lens for Magnetic samples
- The EMPAD pixelated STEM detector
- The 4D STEM software package
- Super-X SDD EDS detection system
- Segmented Panther STEM detector
- TEM, STEM Tomography, EDS Tomography
- iDPC: Integrated differential phase contrast imaging

STEM-EDS, iDPC & 4D-STEM



H-9500 Dynamic Environmental TEM

- 100-300 kV accelerating voltage
- Electron source: LaB6 (DC heating) Filament
- ETEM: gas injection system
- D-TEM: Gatan K2-IS direct electron camera
- Gatan GIF Quantum ER Filter on K2 Camera
- Hitachi in-situ gas injection heating holder
- Hummingbird liquid cell electrochemistry holder
- MEMS Heating Holder (Hitachi Blaze)

EFTEM

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