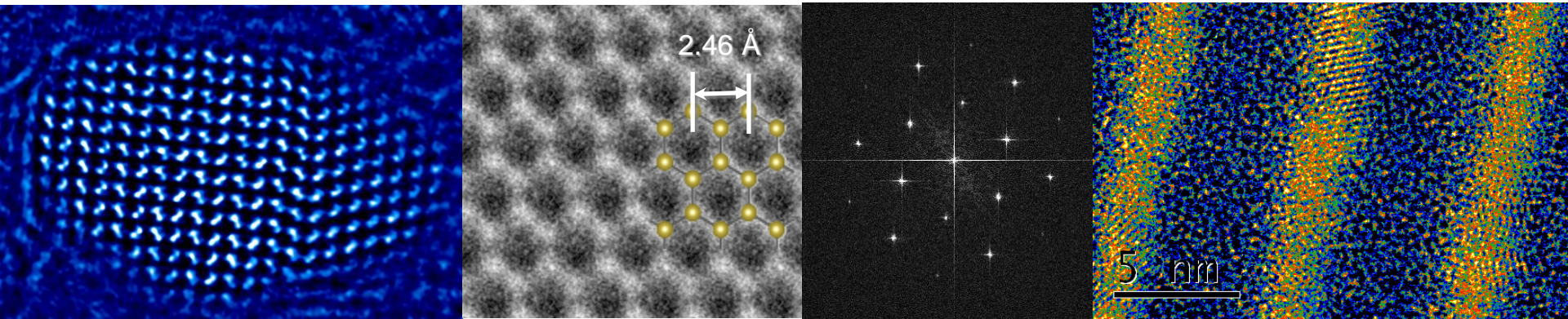


Electron energy loss spectroscopy (EELS) and Energy Filtering TEM (EFTEM)

Joachim Mayer

RWTH Aachen University and
Forschungszentrum Jülich



Outline

Basics of EELS

EELS/EFTEM-Instrumentation

STEM-EELS

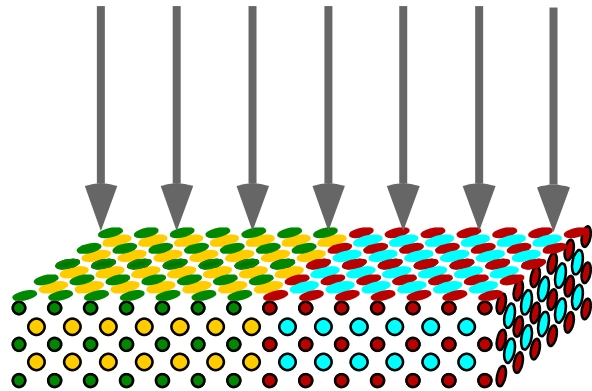
ELNES / Bonding Information

Elemental Mapping

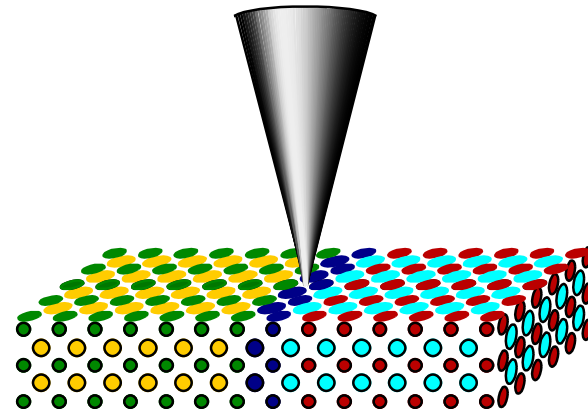
Cc-correction: PICO

EFTEM / EELS Analysis

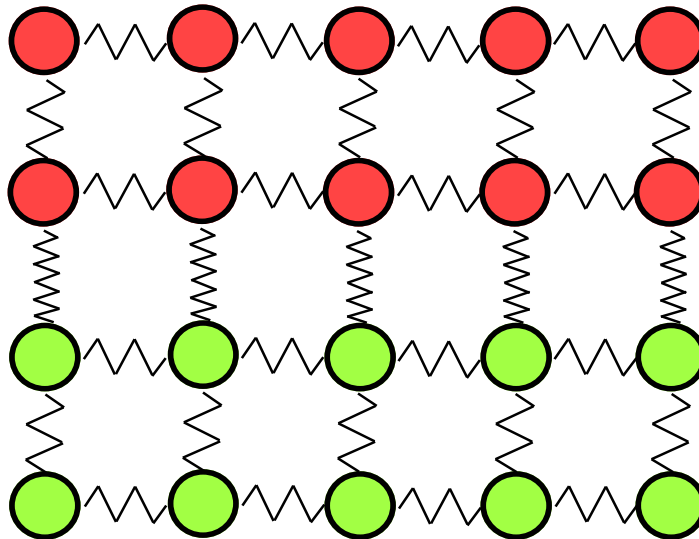
Structure



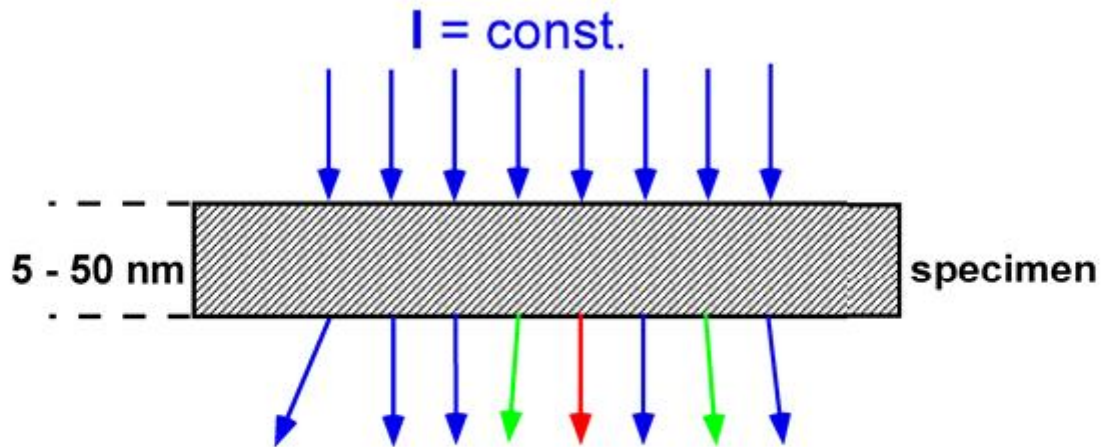
Chemistry



Bonding



Analytical TEM: Electron Intensity Distribution



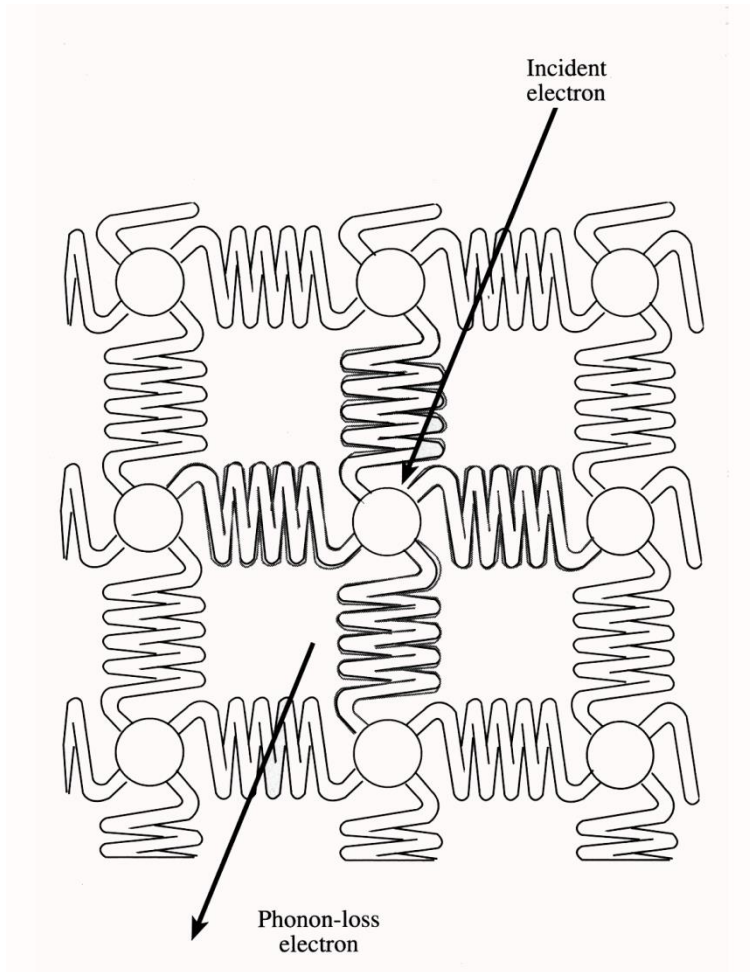
$$I = I(x, y, \theta_x, \theta_y, \Delta E)$$

conventional TEM EELS

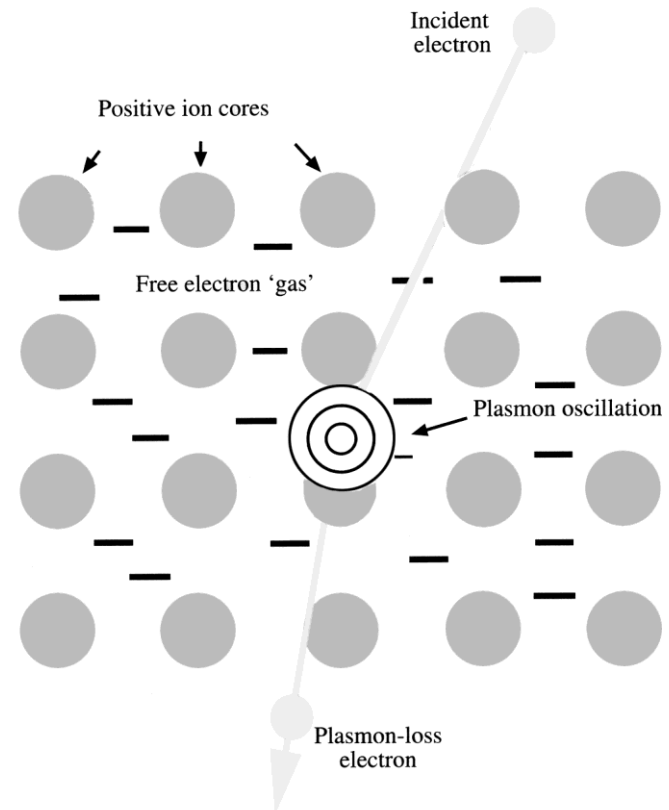
Electron Spectroscopic Imaging (ESI)
Diffraction (ESD)

Energy Filtering TEM

Inelastic Scattering, low energy losses: phonon and plasmon excitation

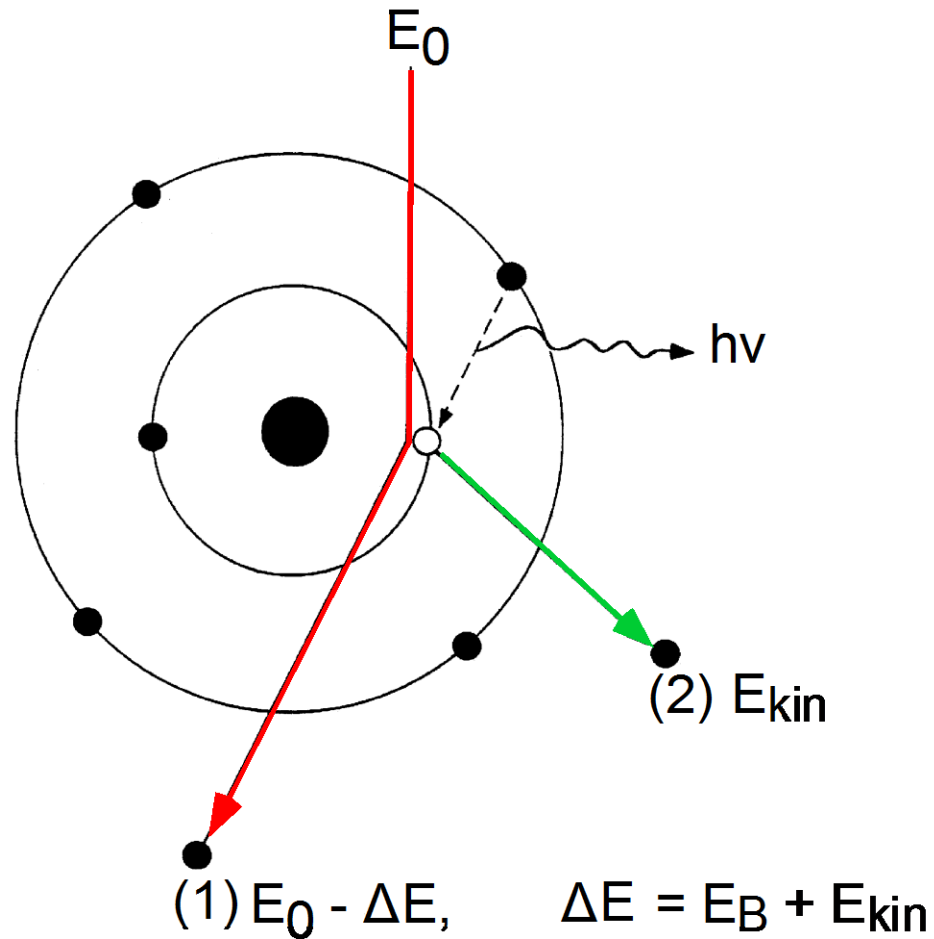


$$\Delta E = 1 \dots 50 \text{ meV}$$

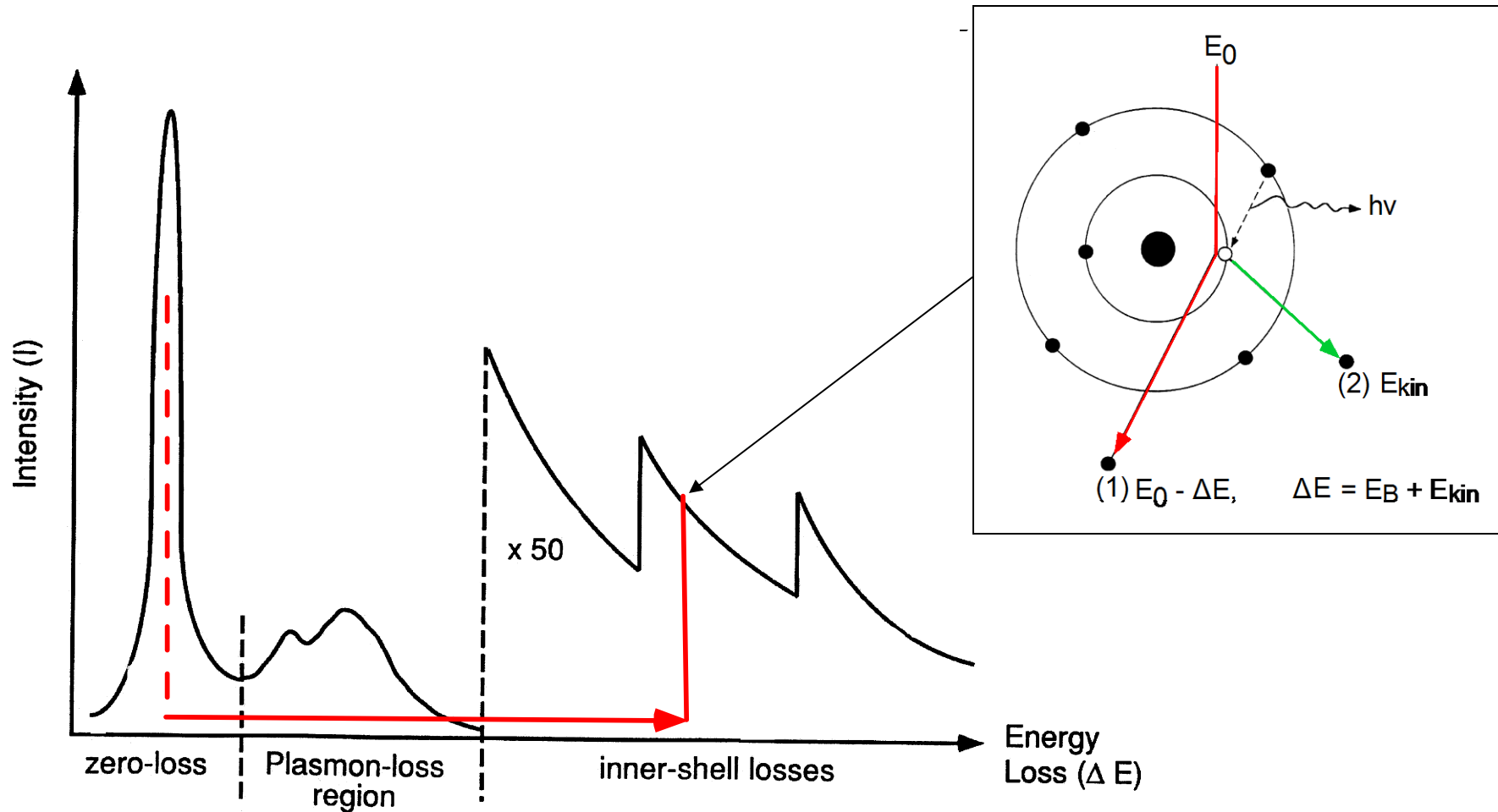


$$\Delta E = 1 \dots 50 \text{ eV}$$

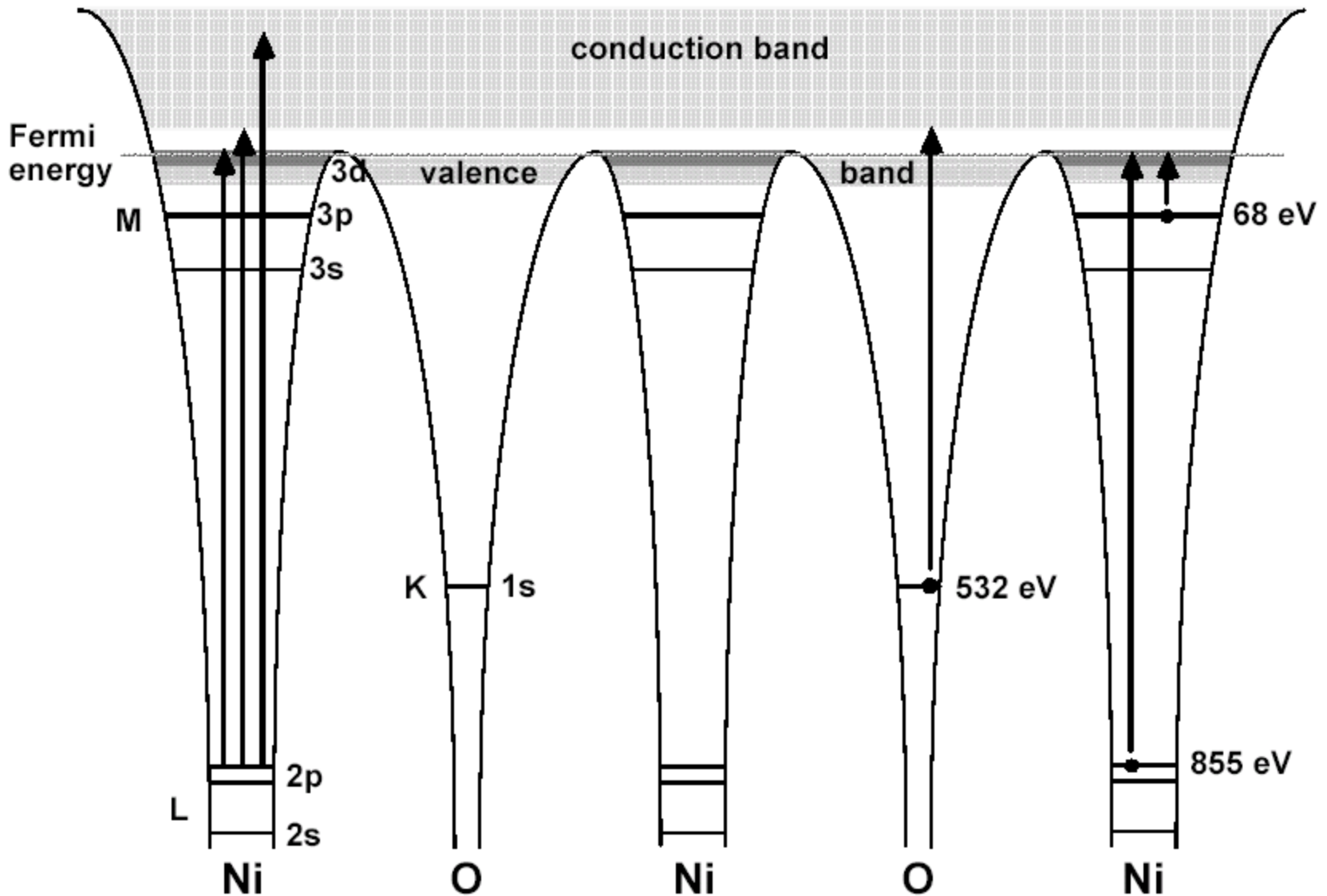
Inelastic Scattering: Inner Shell Excitation

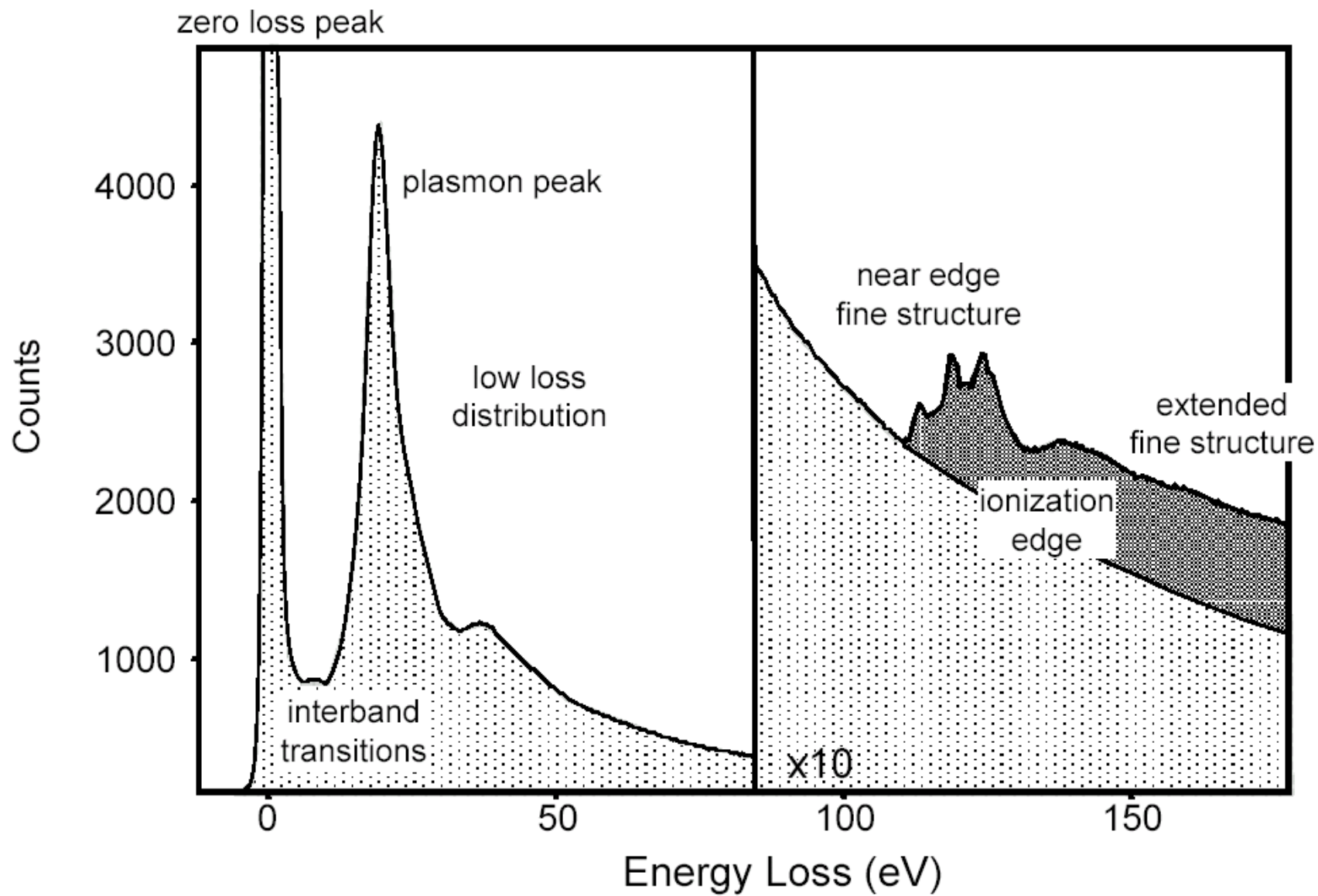


Schematical Energy Loss Spectrum

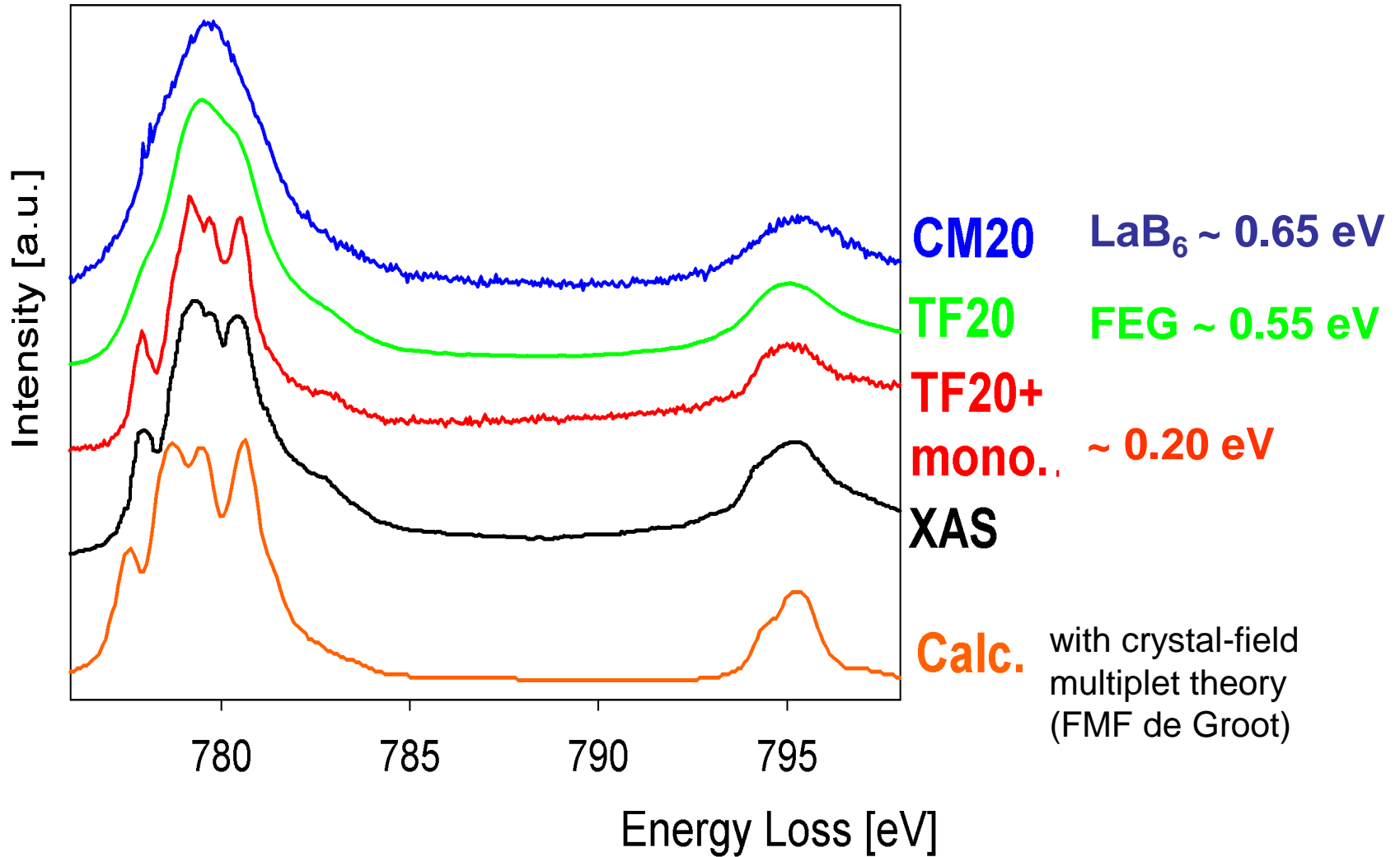


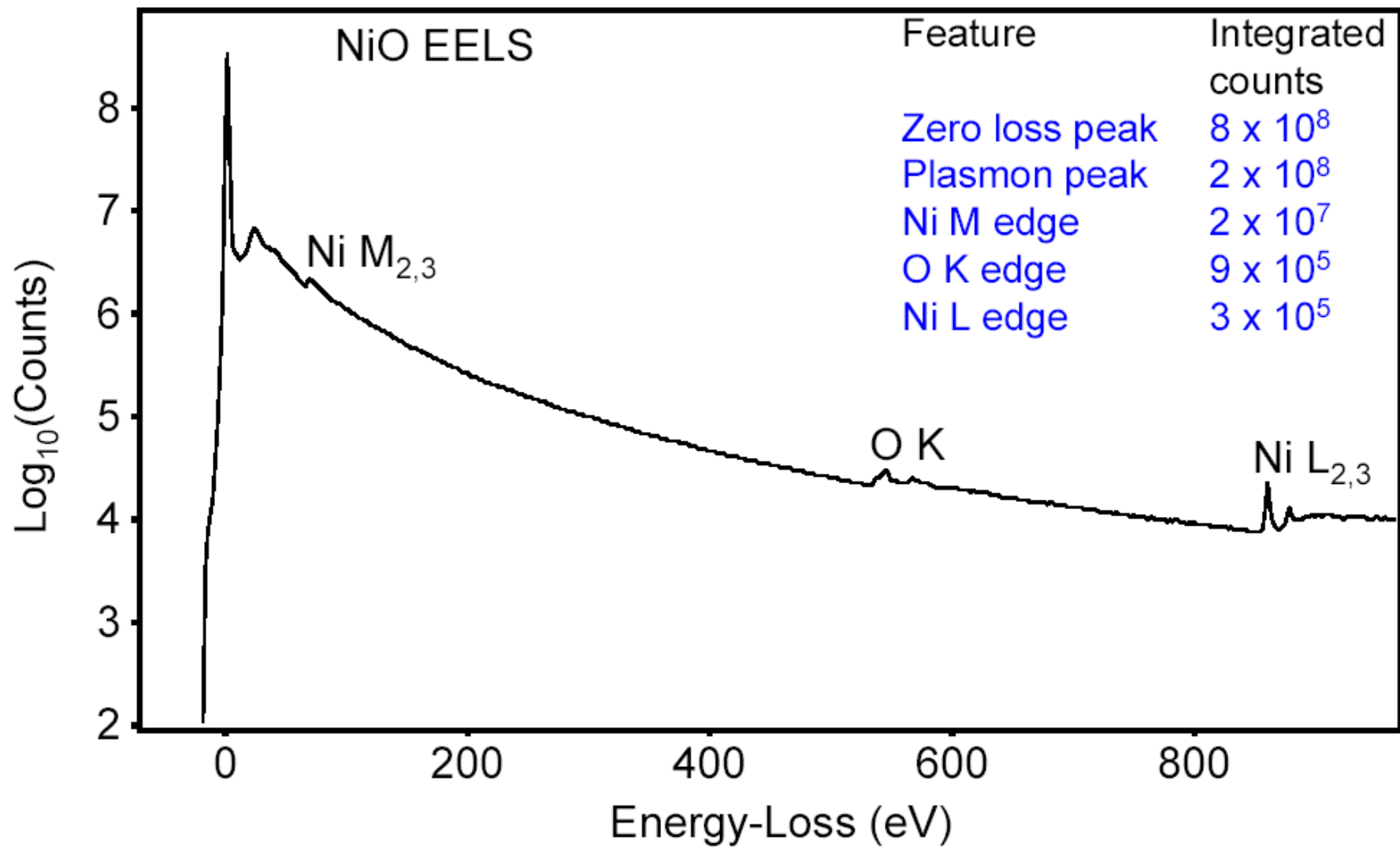
Inelastic Scattering: Solid State Model





HR-EELS of Co L_{2,3} of CoO



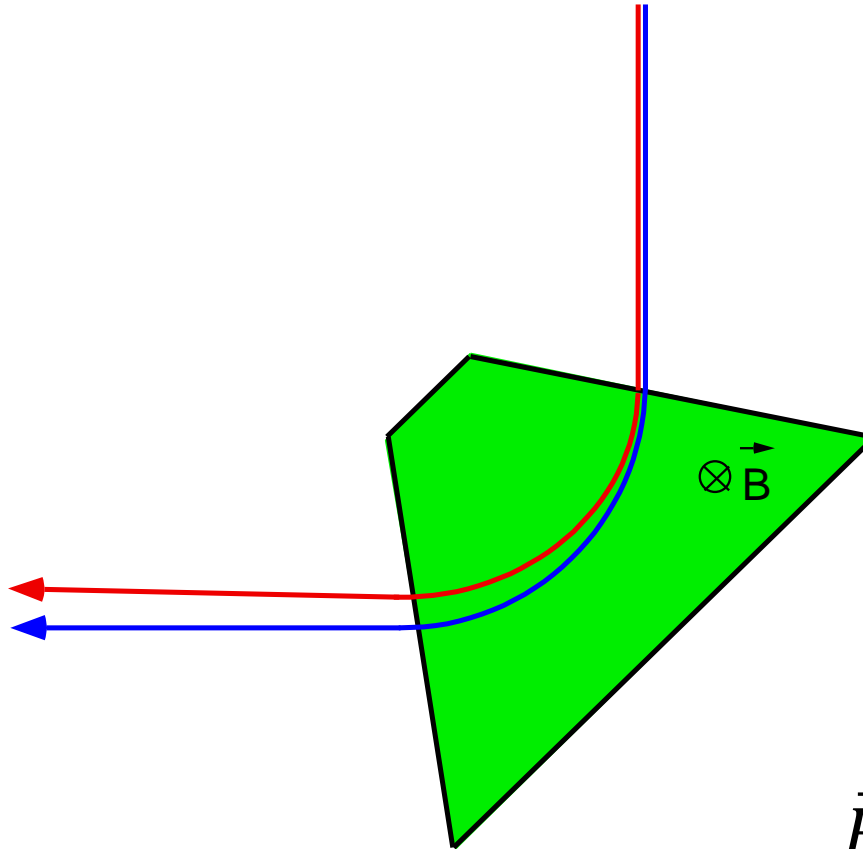


EELS vs. EDX

	<u>EELS</u>	<u>EDX</u>
Count rate	high	low
Background	high	low
Quantification	tricky	easy
Mapping	fast	slow
Spatial res.	atoms	columns
Bonding info	yes	no

Instrumentation

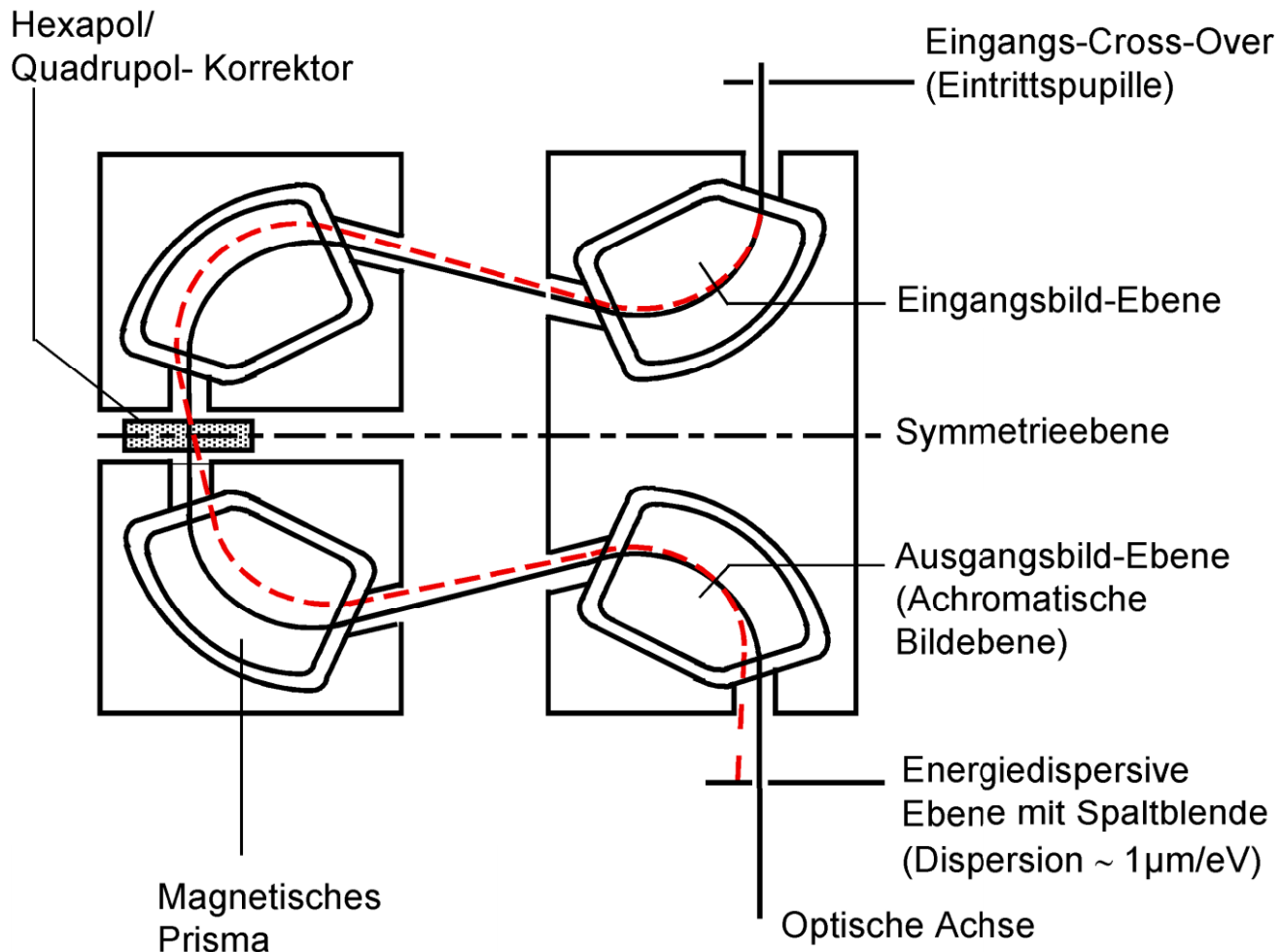
Energy Loss Spectrometer (magnetic prism)

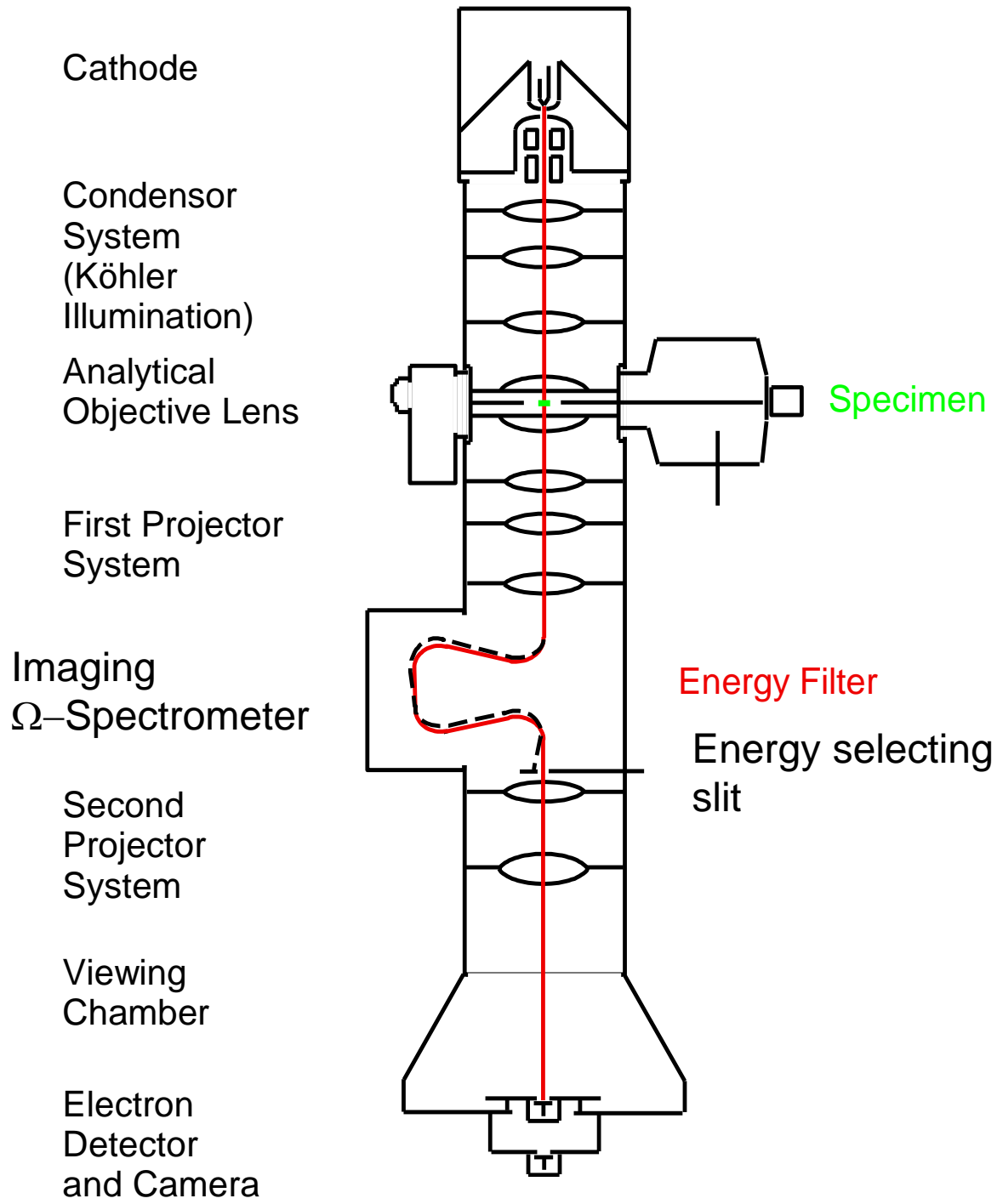


Lorentz Force

$$\vec{F}_L = -e(\vec{v} \times \vec{B})$$

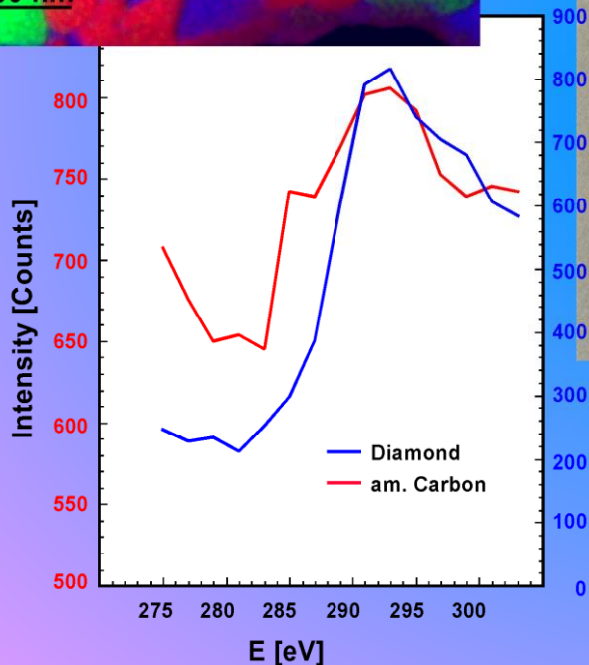
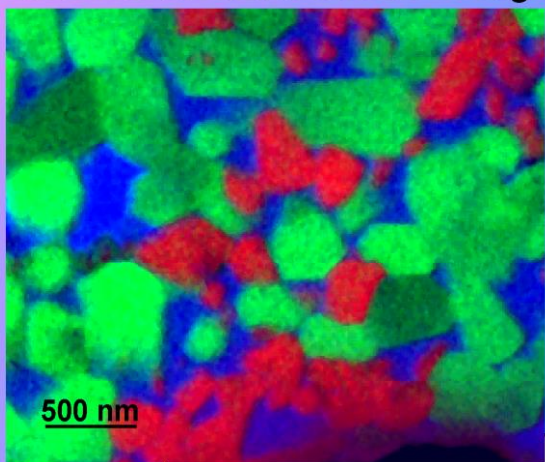
The Omega Energy Filter



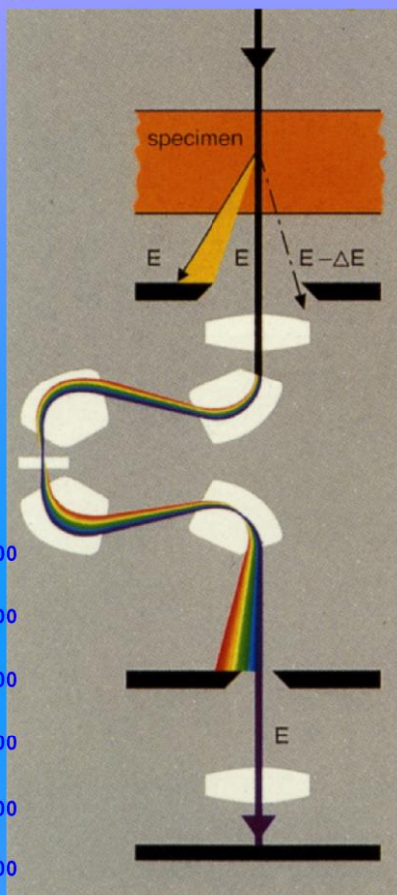


Energy Filtering Transmission Electron Microscopy

elemental distribution images

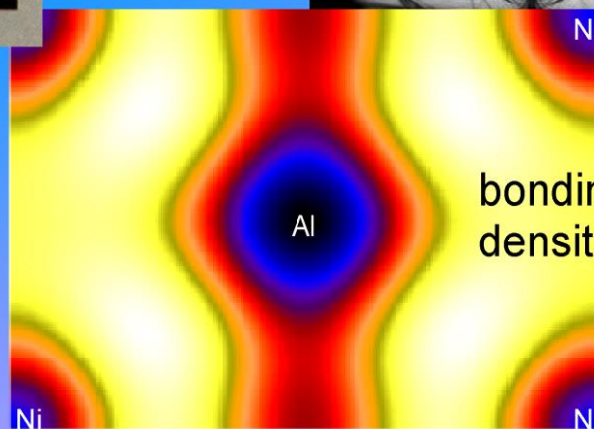
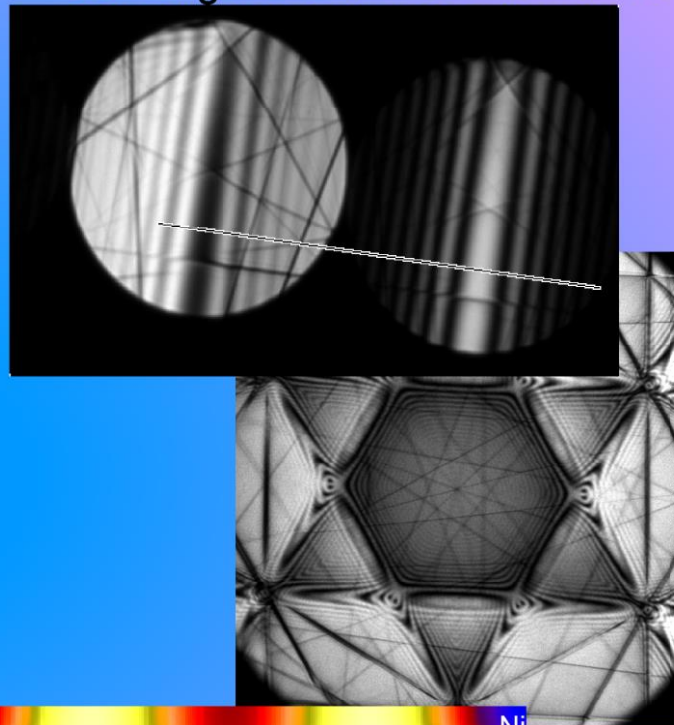


spatially resolved energy loss spectroscopy



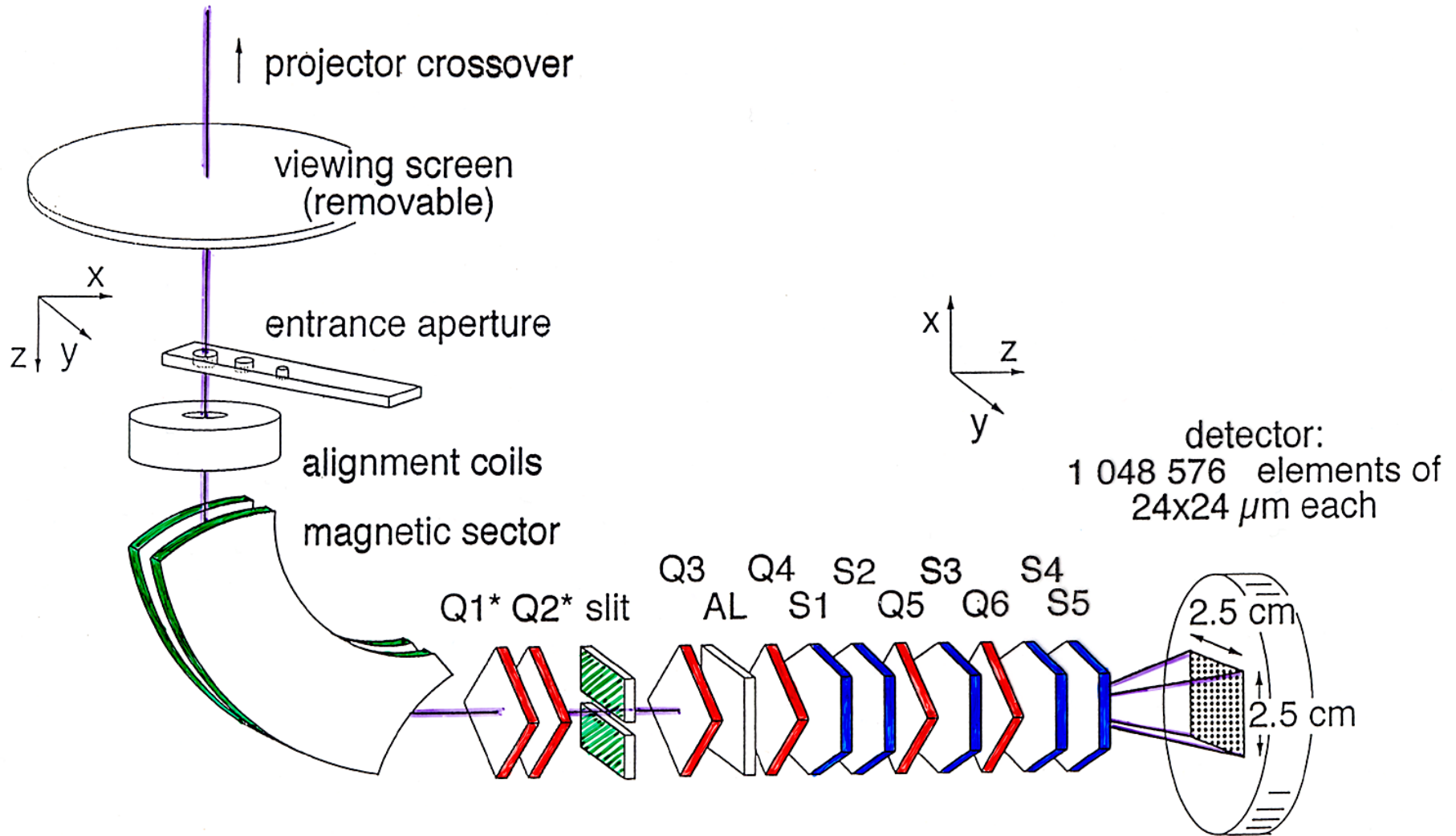
Ω -filter

convergent beam electron diffraction



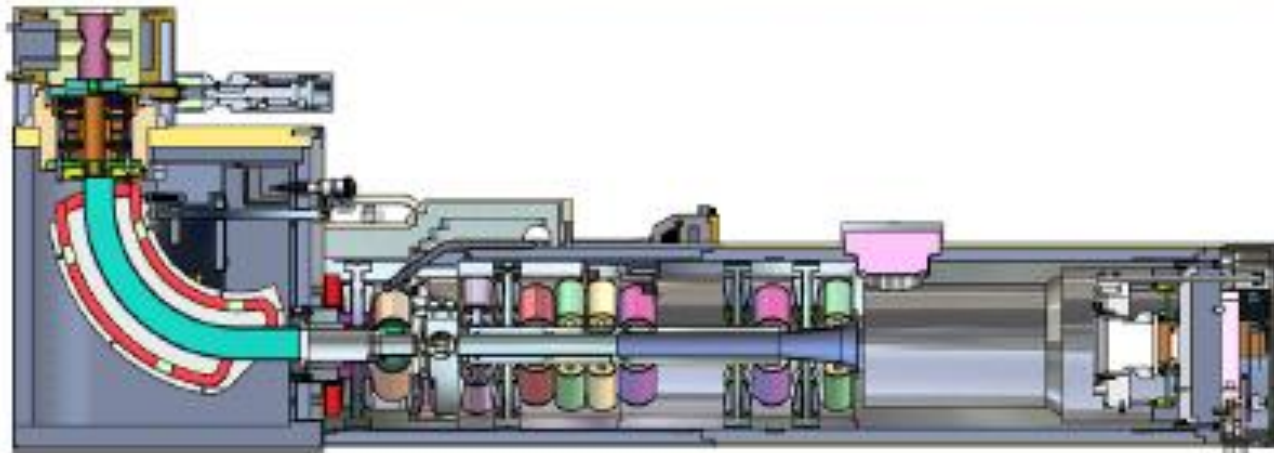
bonding charge densities

Optical elements of Gatan post-column filters



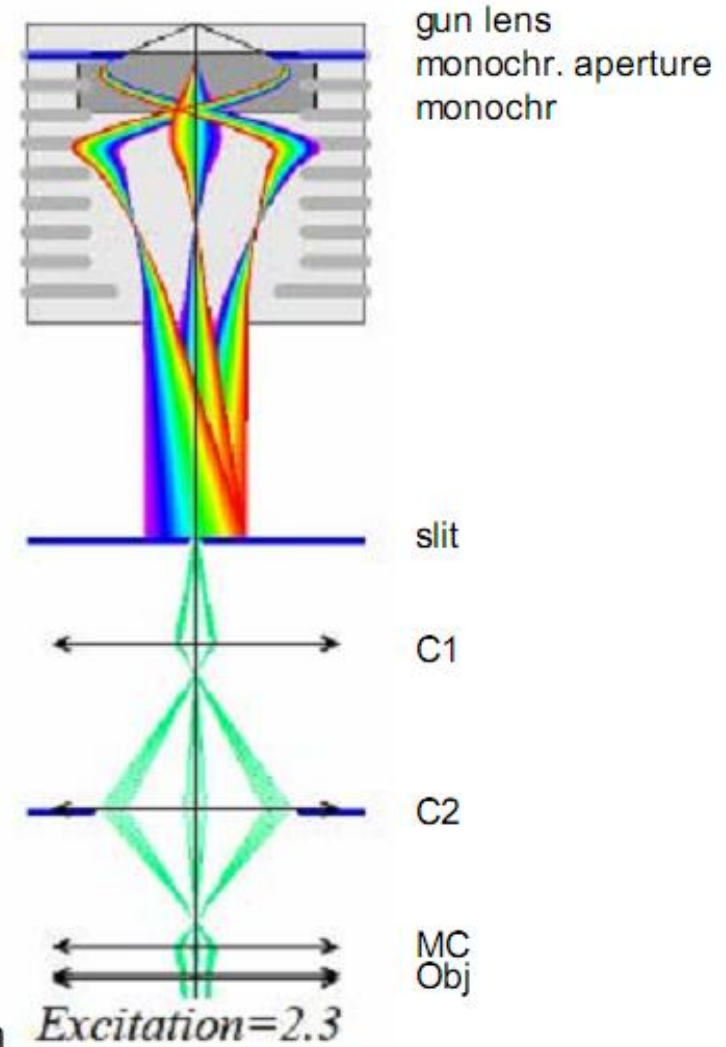
*200 kV and higher filters only

The Gatan Imaging Filter



Models: GIF 2000 series, new GIF Tridiem

Wien Filter Monochromator



2 crossed fields perpendicular to each other

Two forces act on the particles:

$$F_E = qE, \text{ electrostatic field}$$

$$F_B = qvB, \text{ magnetic field}$$

For electron moving with v and E parallel to optic axis the forces are balanced and the electron travels straight

Any other electron travelling with different v or at some angle to the axis execute a cycloidal motion

What is the best way to water flowers?

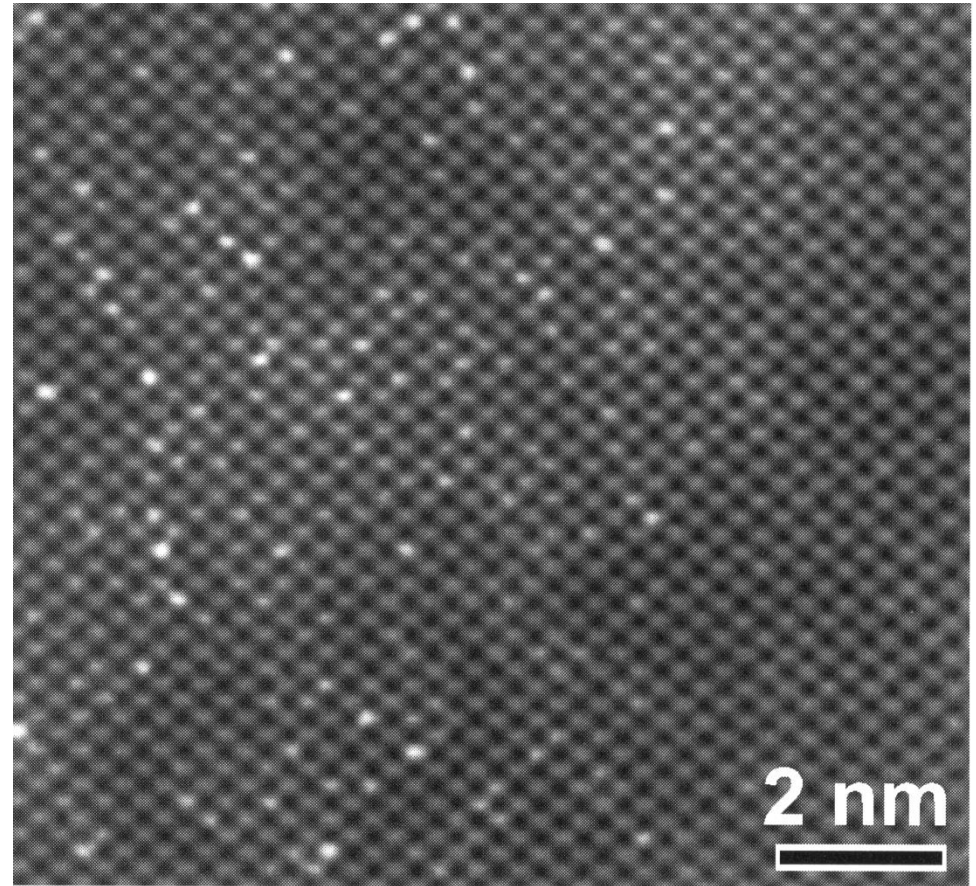
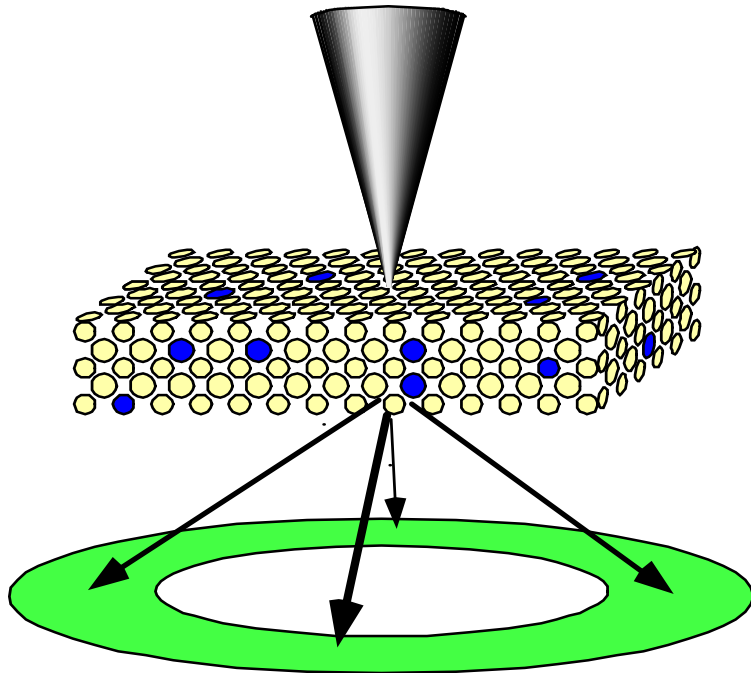


EFTEM



STEM

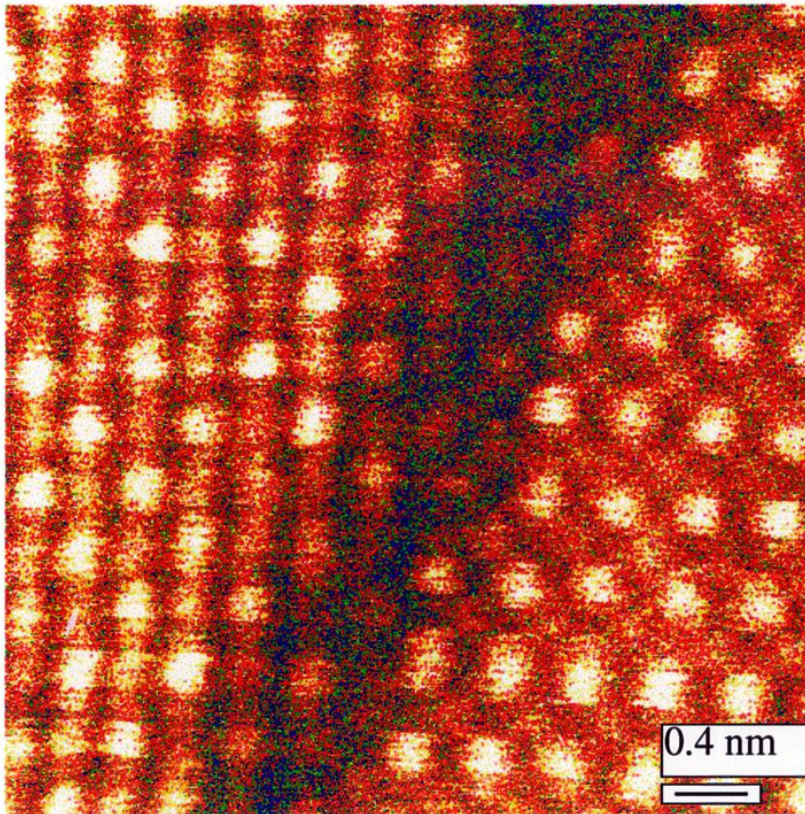
HAADF - STEM Imaging



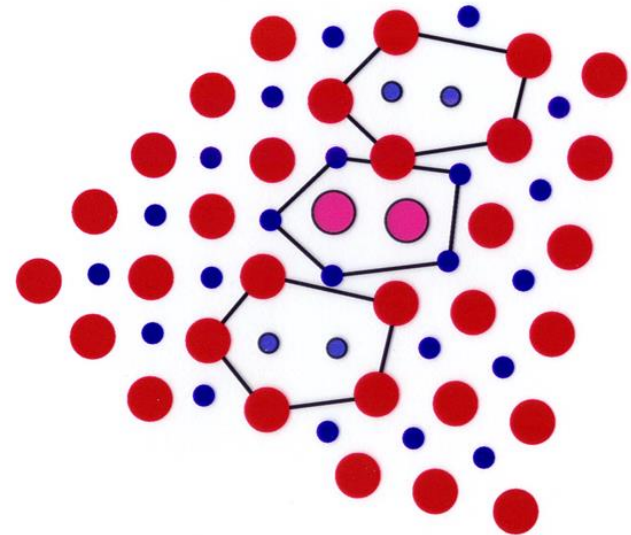
Example: individual Sb atoms in doped Si

Voyles, Muller and Kirkland, *Microsc. Microanal.* 10 (2004)

High Resolution Z-Contrast Imaging Mn-Doped GB in SrTiO₃

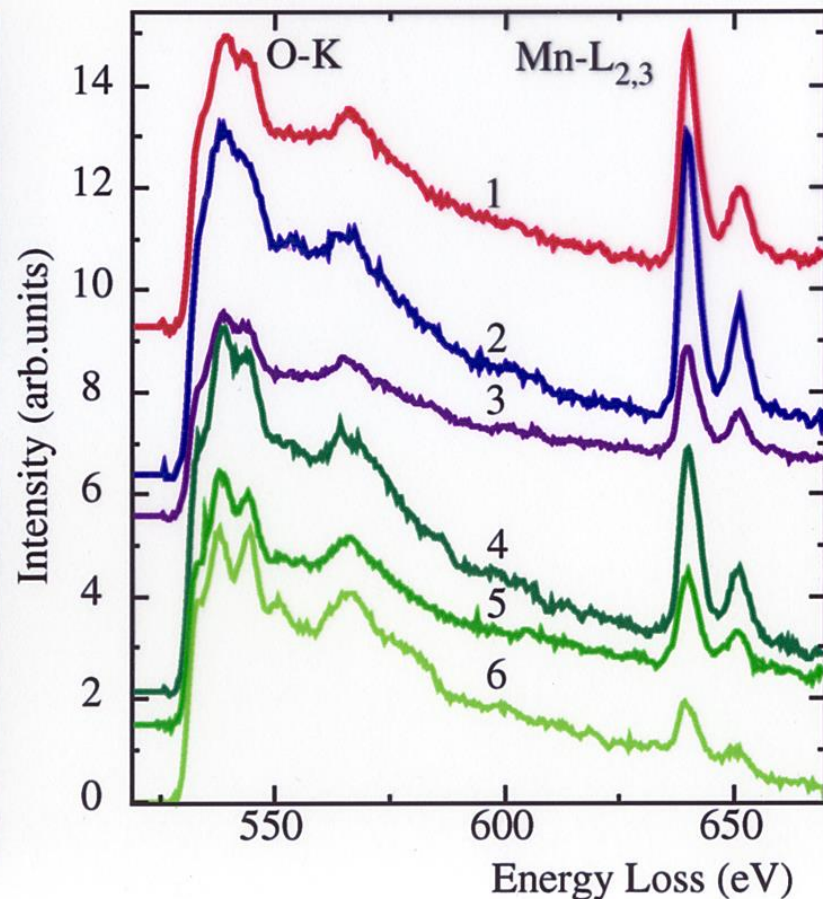
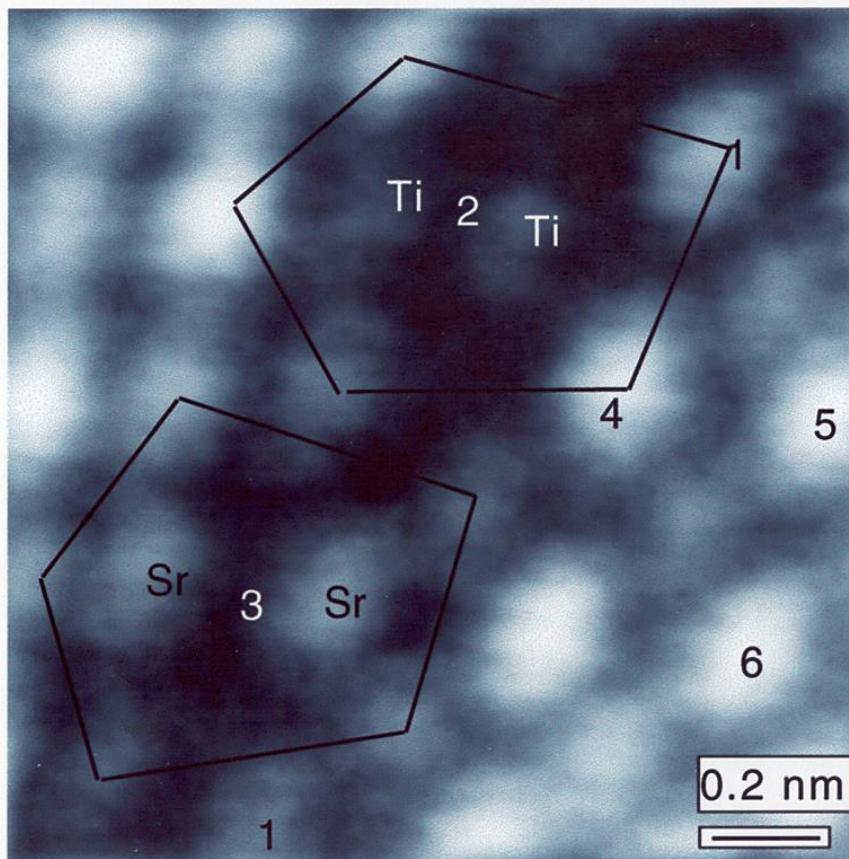


G. Duscher, Solid State Division, ORNL



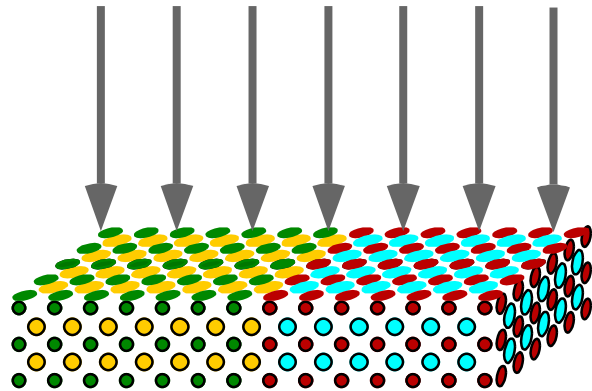
- full Sr column
- half filled Sr column
- full Ti - O column
- half filled Ti - O column

Atomic Column Resolved EELS at SrTiO₃ 36.7° Grain Boundary Doped with Mn

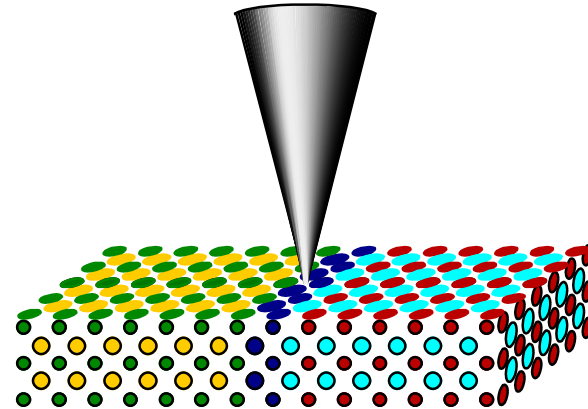


G. Duscher, Solid State Division, ORNL

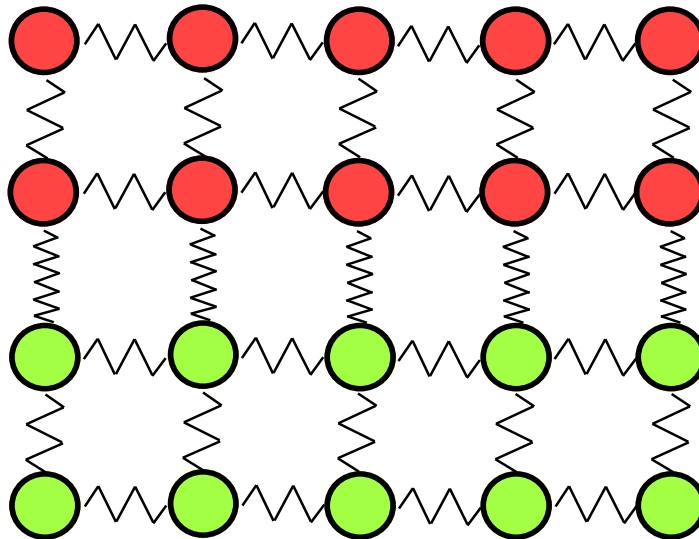
Structure



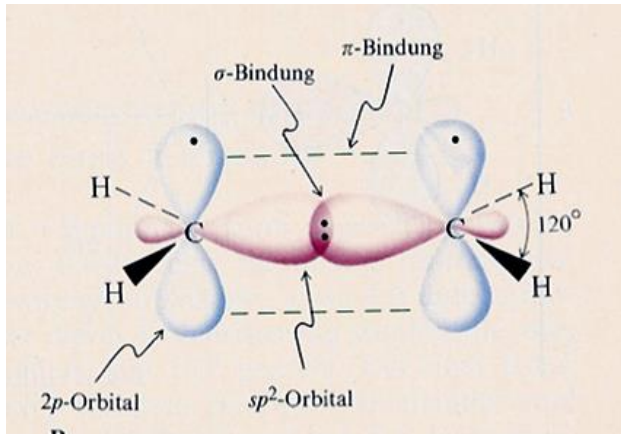
Chemistry



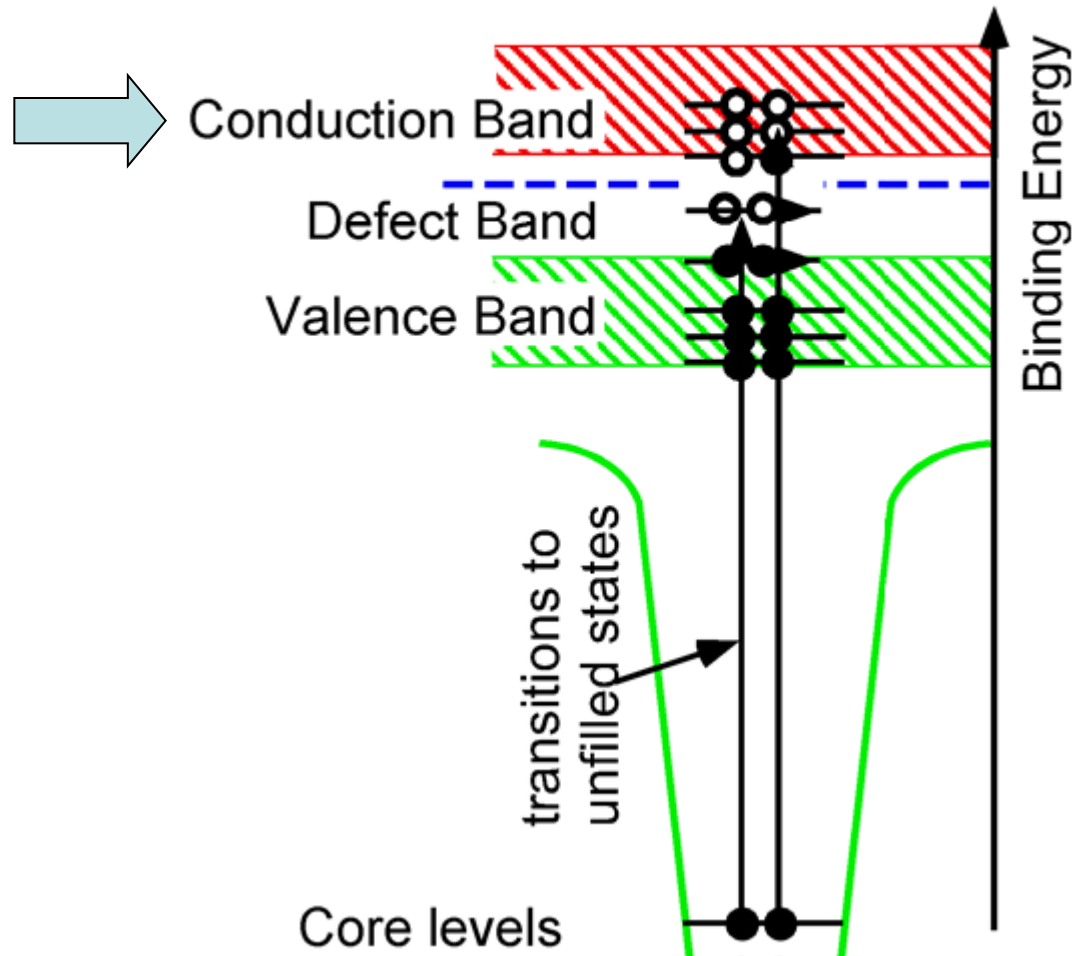
Bonding



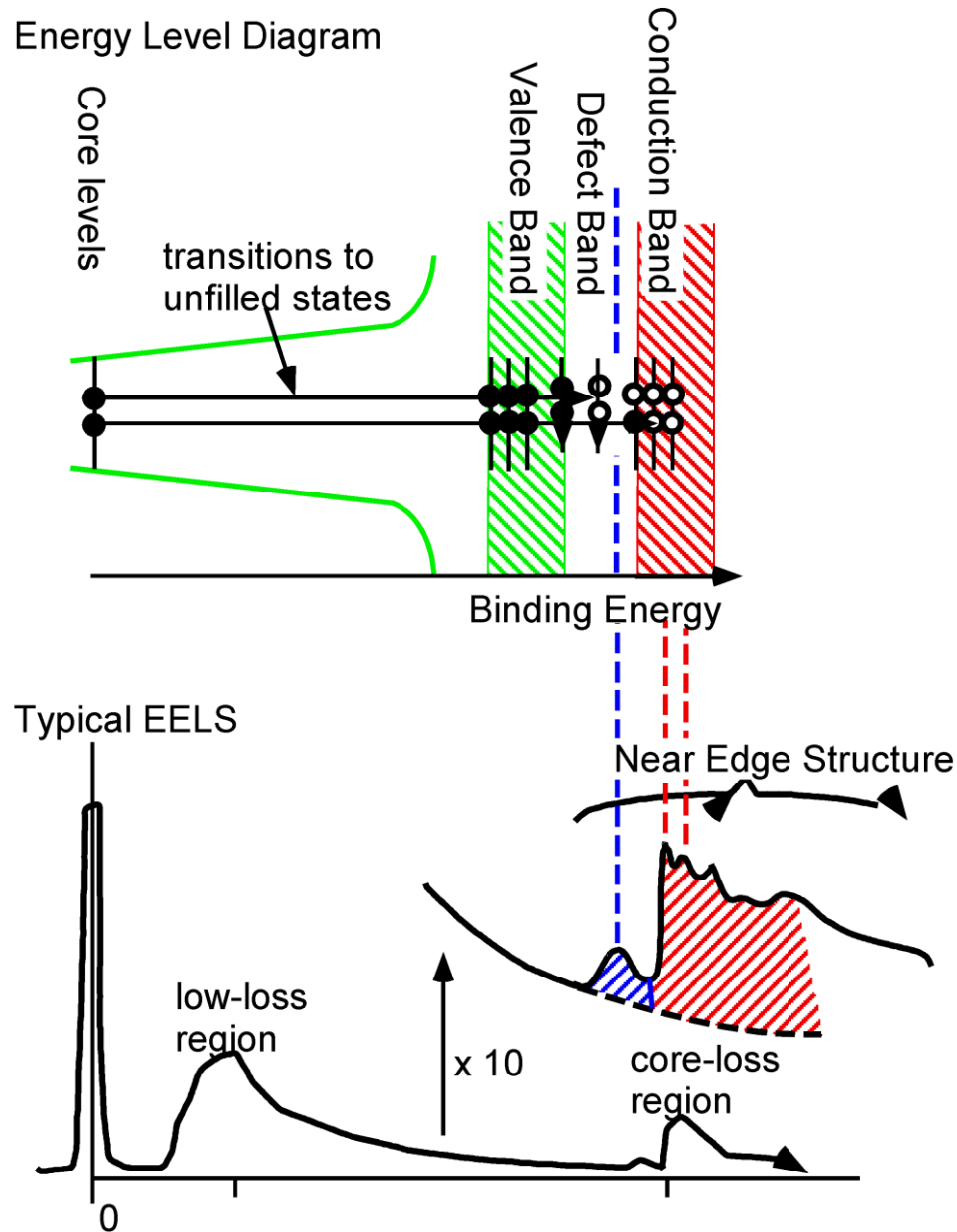
Electronic Band Structure



Energy Level Diagram



Energy Loss Near Edge Structure (ELNES)



ELNES-Interpretation

(one electron approximation)

1) Fermi's Golden Rule:

$$I(E) \propto |M(E)|^2 N(E)$$

- local density of unoccupied states (LDOS)

2) Dipole selection rule:

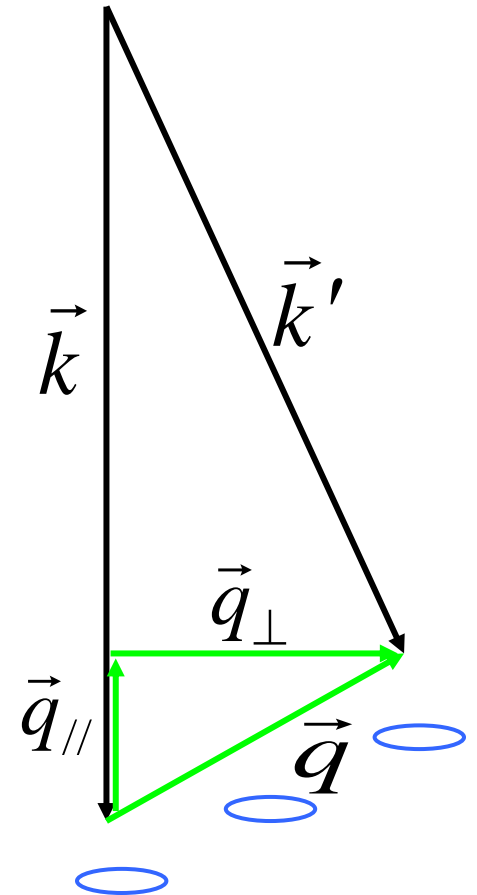
$$\Delta l = \pm 1$$

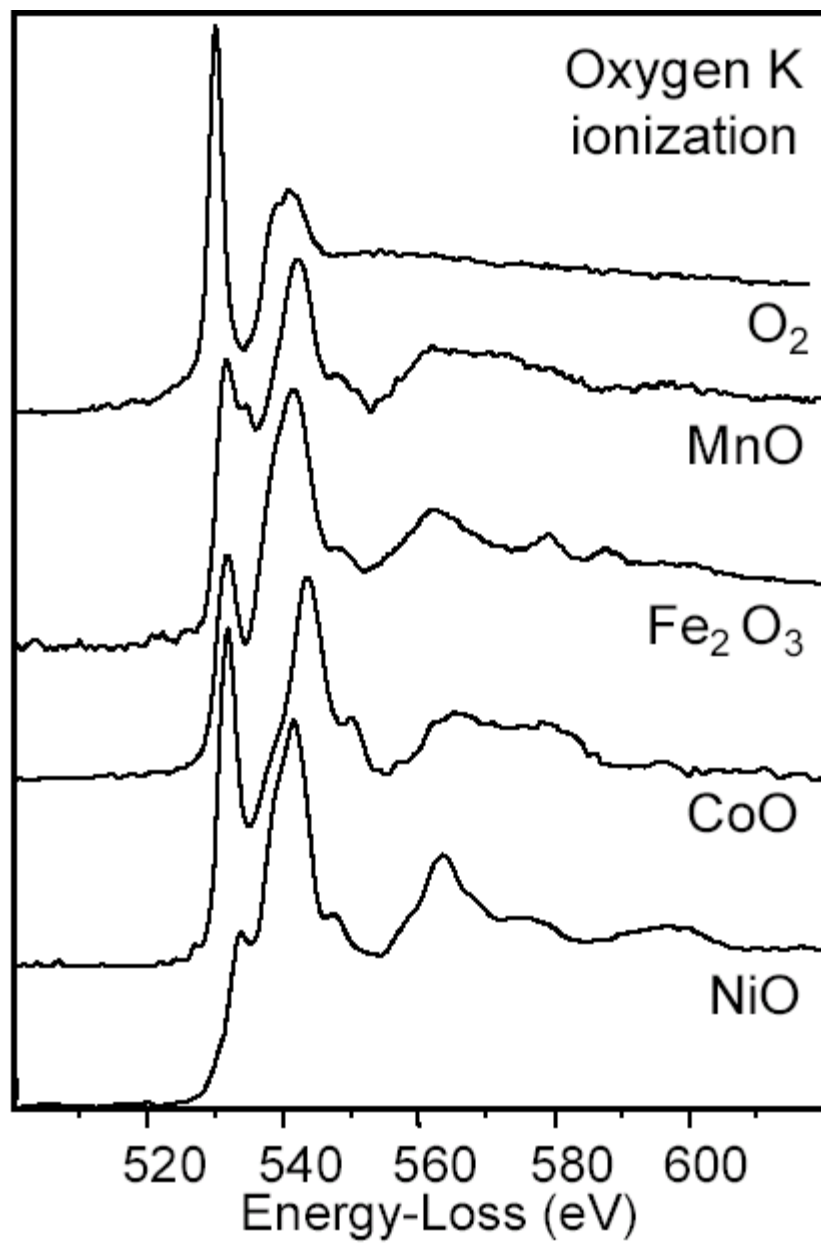
- symmetry projected DOS

3) Momentum resolved spectroscopy:

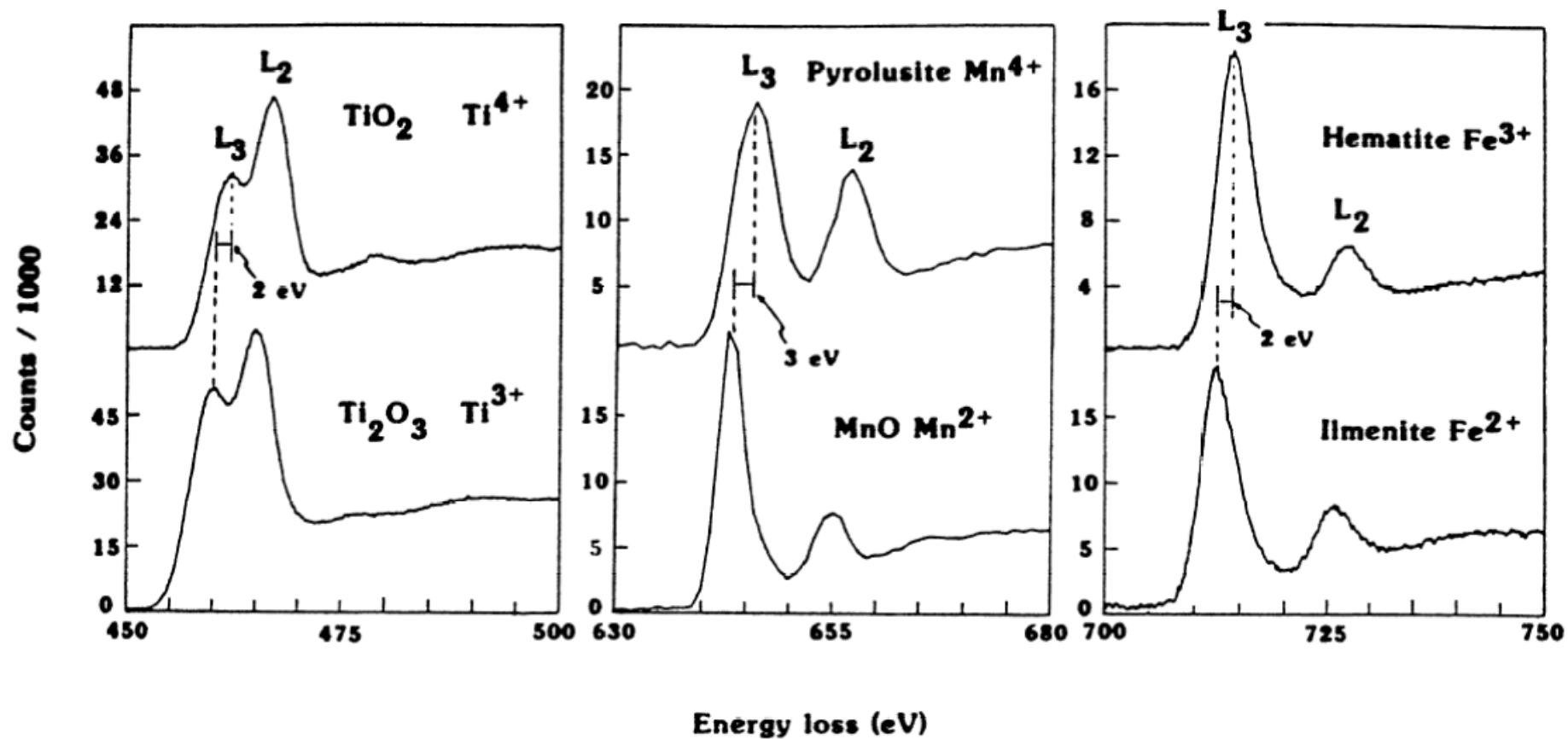
$$\vec{q} = \vec{q}_{//} + \vec{q}_{\perp}$$

- excitation into specific orbitals



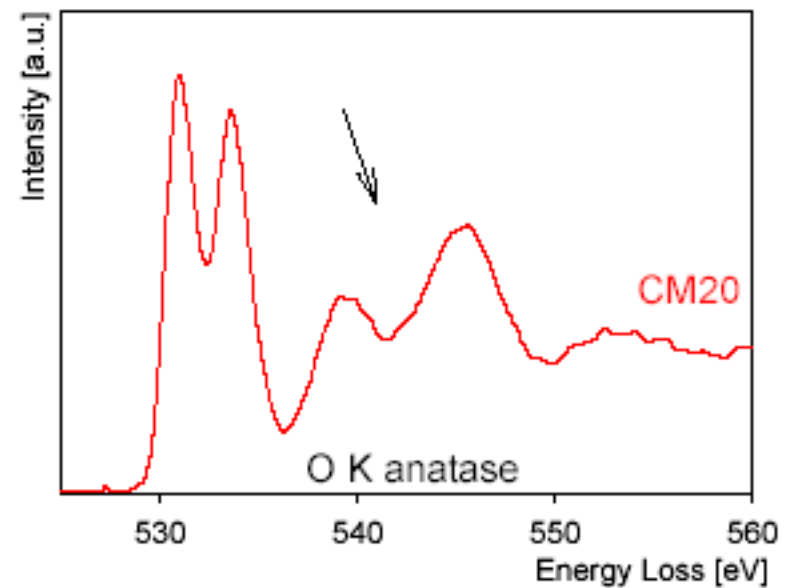
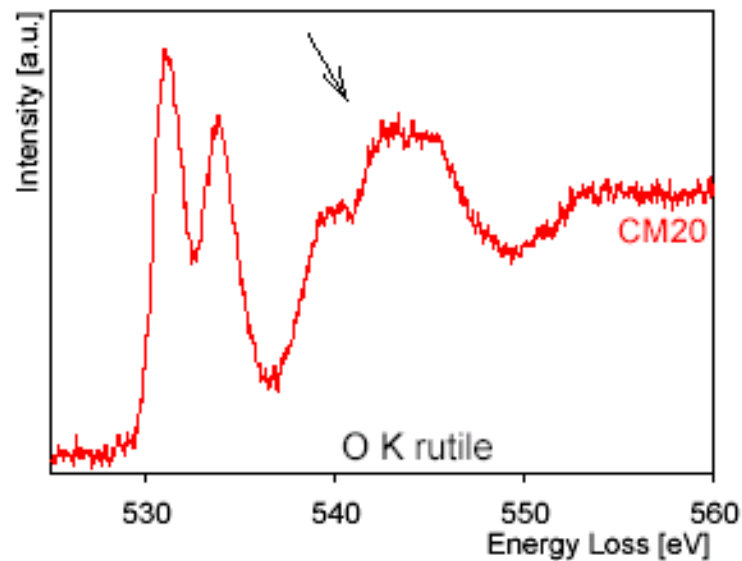
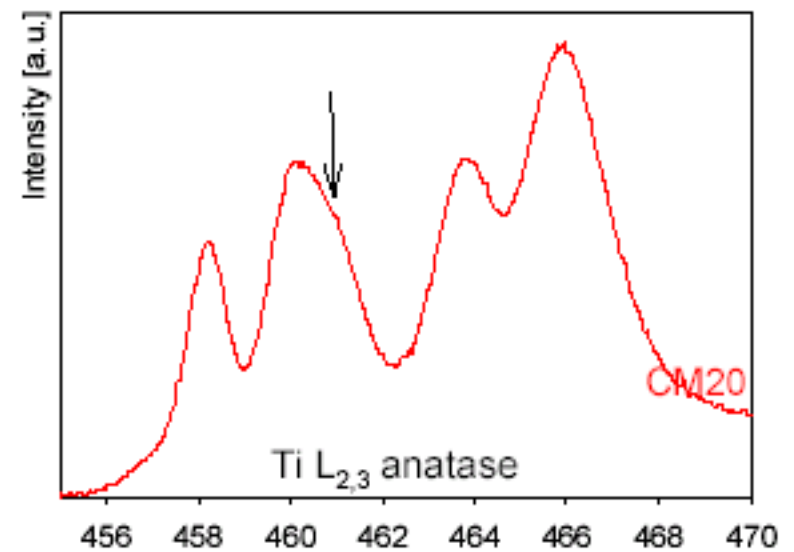
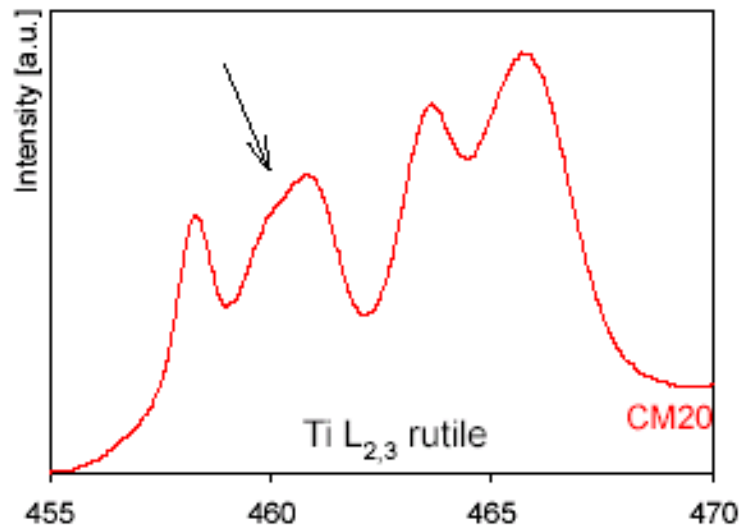


Chemical Shifts



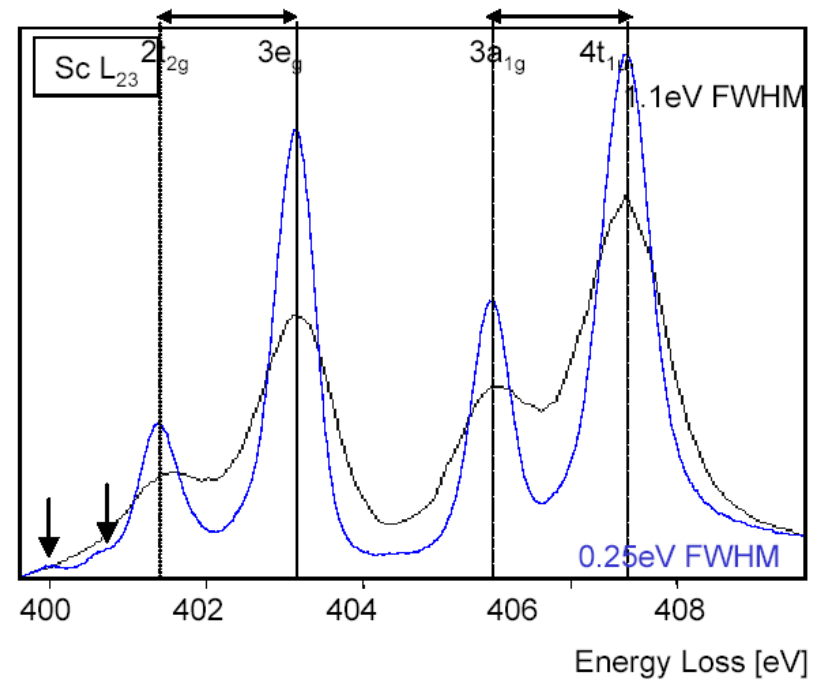
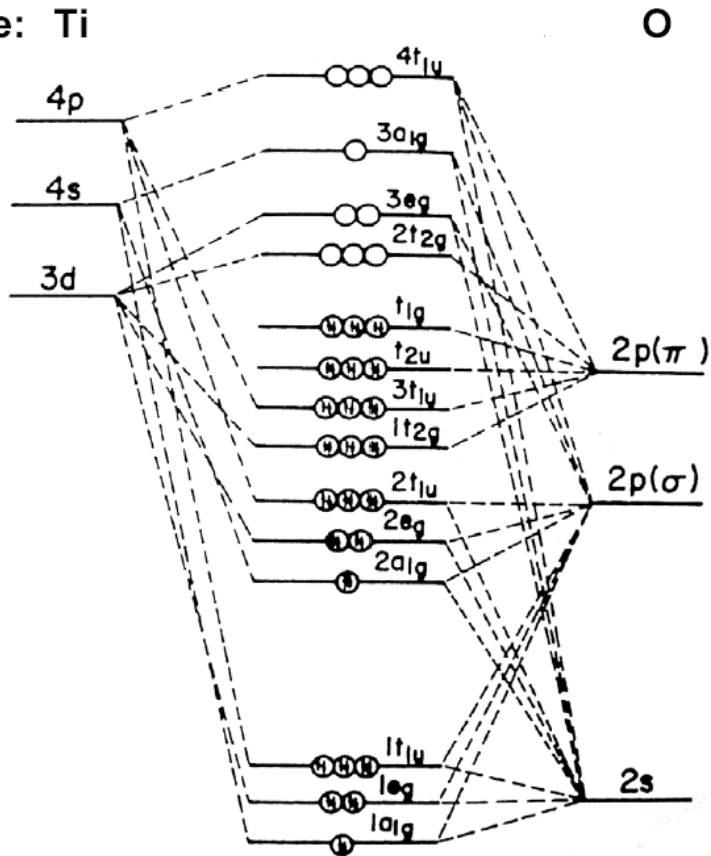
TiO₂ - Polymorphs

(F. Hofer, TU Graz)

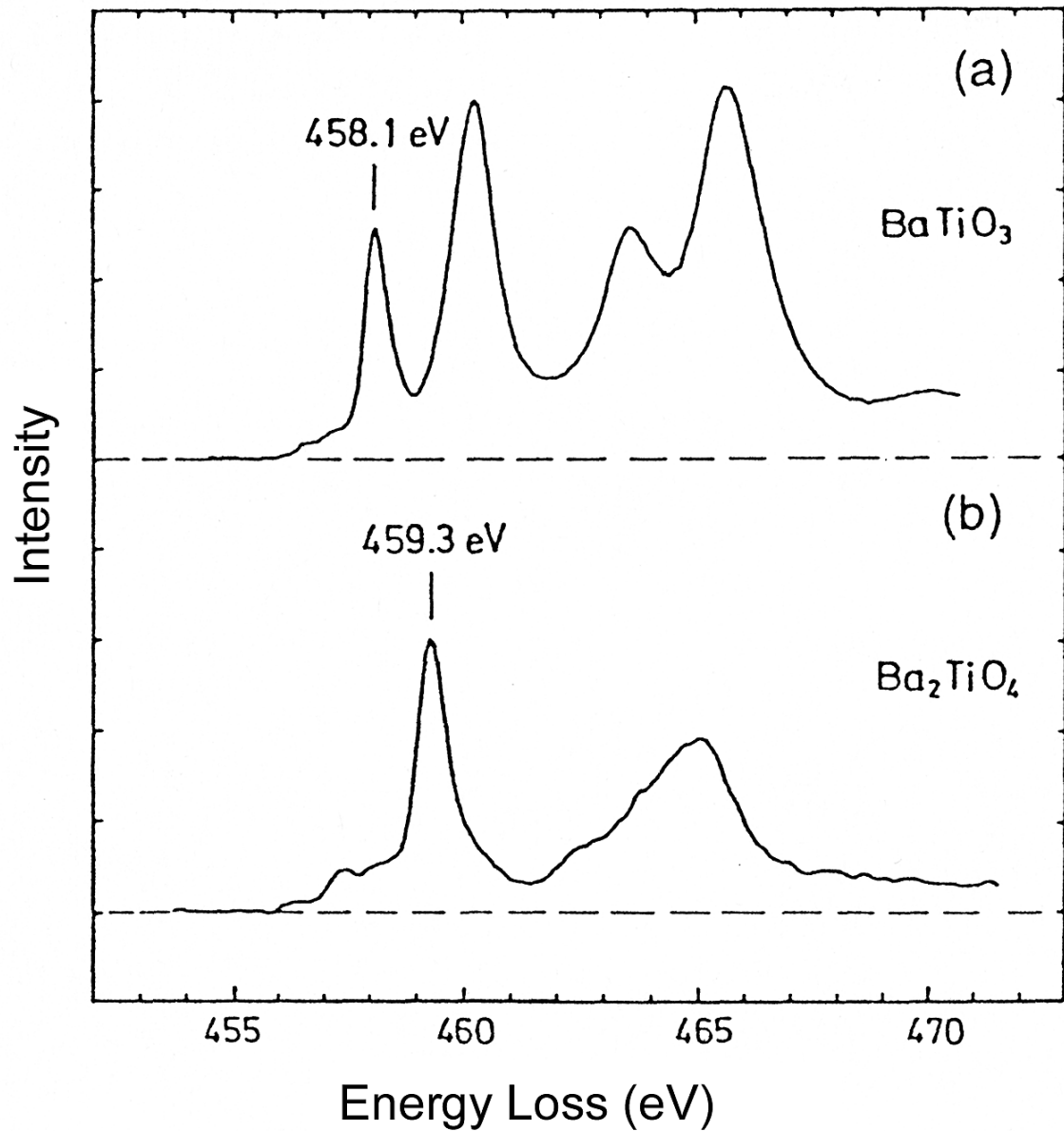


Molecular Orbital (MO) Term Scheme

Example: Ti



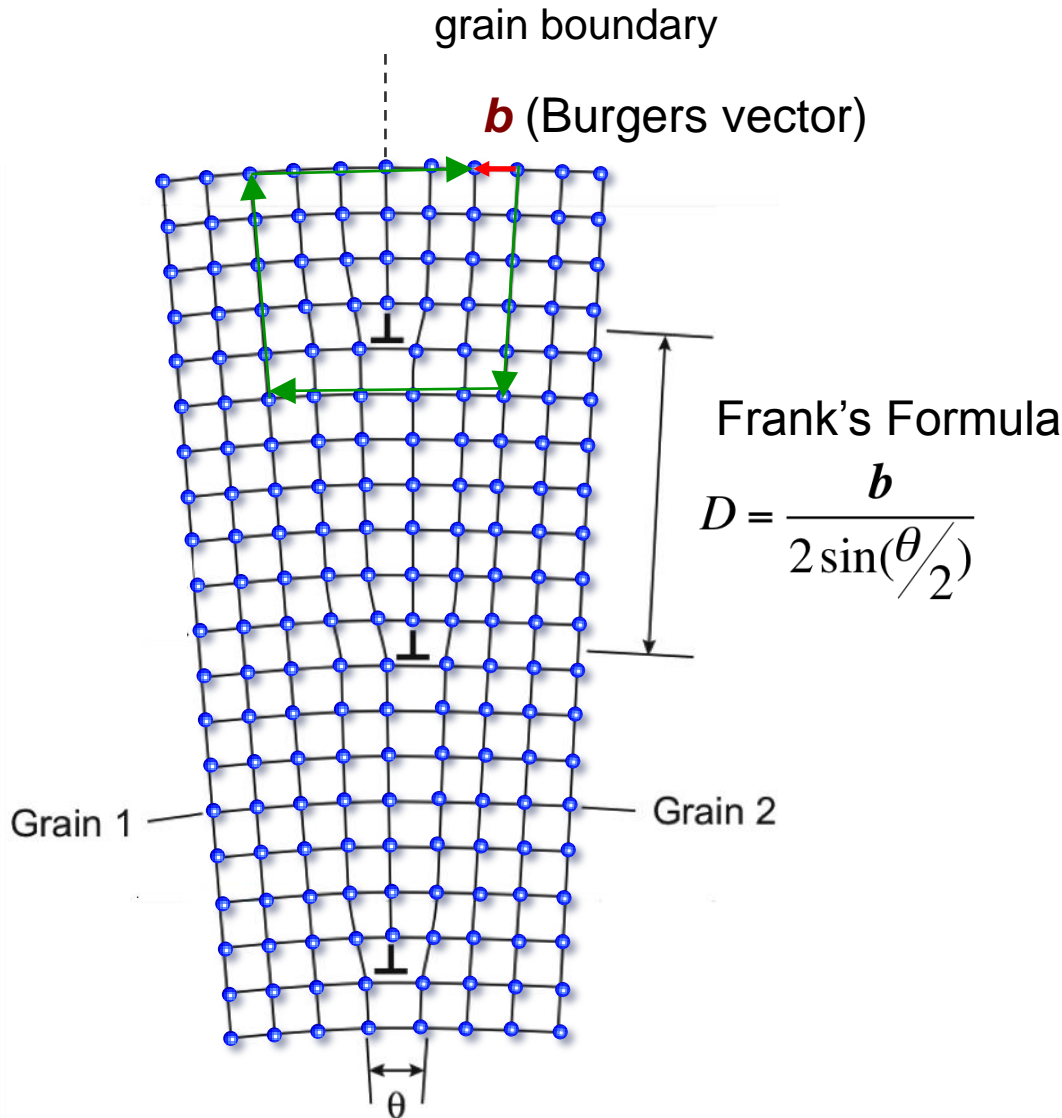
Tsutsumi et al., Phys. Rev. B, 15 (1977) 4638
 Leapman et al & Grunes 1983, 1984



BaTiO₃:
Ti in octahedral
coordination

Ba₂TiO₄:
Ti in tetrahedral
coordination

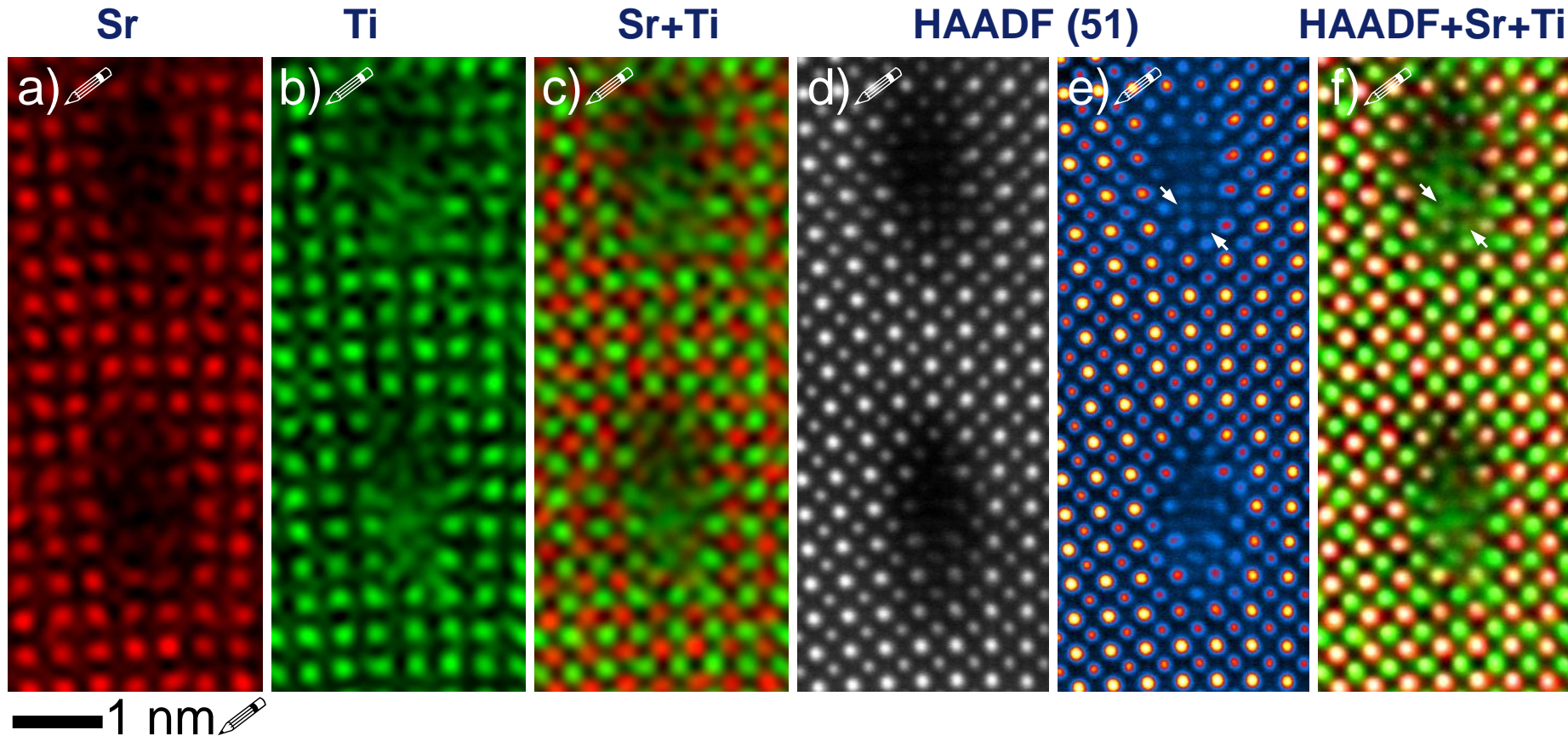
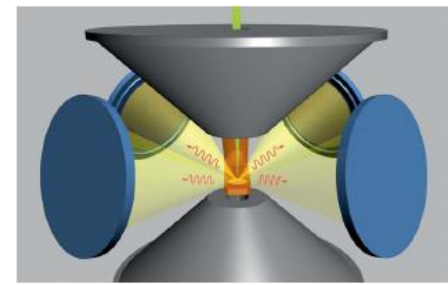
Dislocations at SrTiO₃ low-angle grain boundary



d) 

S.
epth
nip
d

EDX spectrum imaging @200 kV

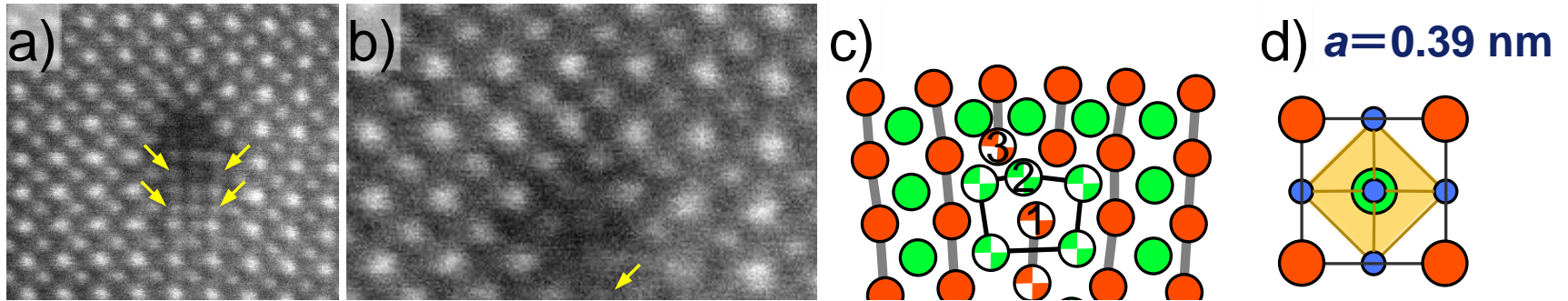


- EDX: Extra Ti-intensity at the tensional side of the dislocation cores
- HAADF: altered coordination at tensional side

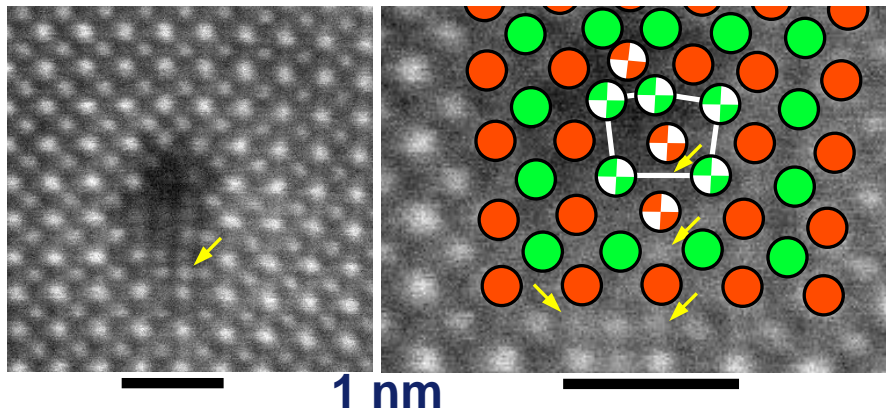
Core Structure

HAADF PICO@80 kV

PICO@80kV



- EDX: Extra Ti-intensity confirms the presence of the FCC TiO phase at the tensional side of the dislocation cores
- Result of strain energy (lattice constant of FCC TiO: 0.42 nm, SrTiO₃: 0.39 nm).

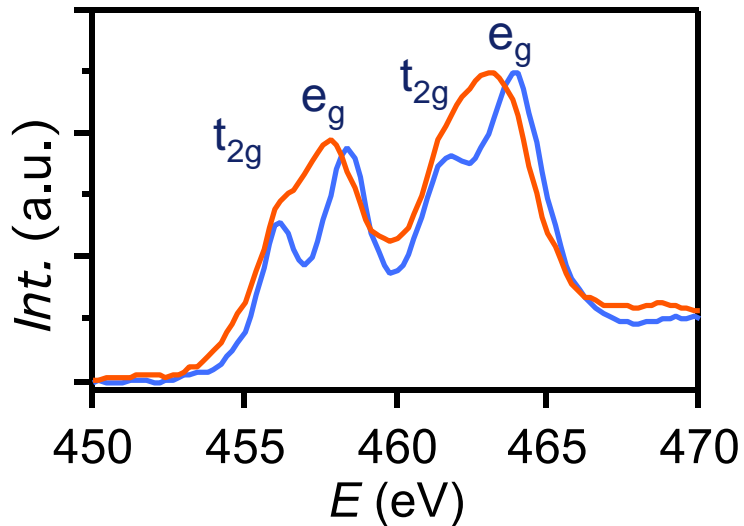


Edge-sharing TiO₆ octahedra associated with the FCC TiO phase at the tensional side of the dislocation cores

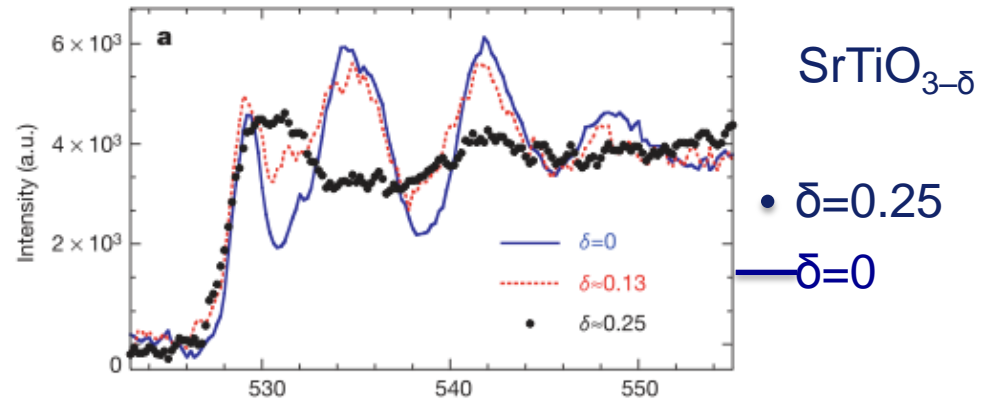
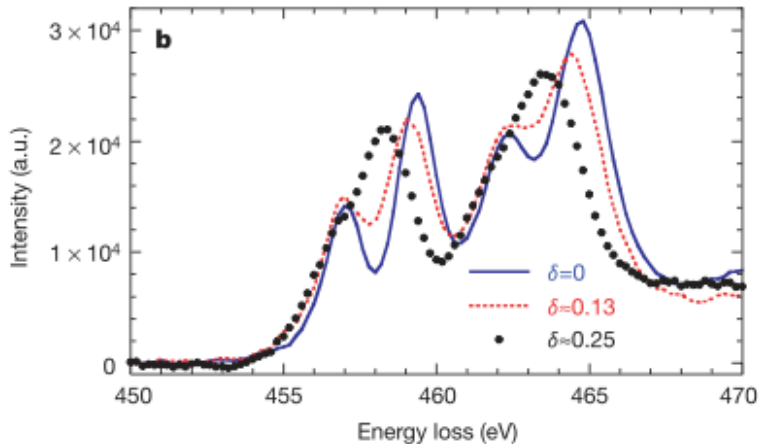
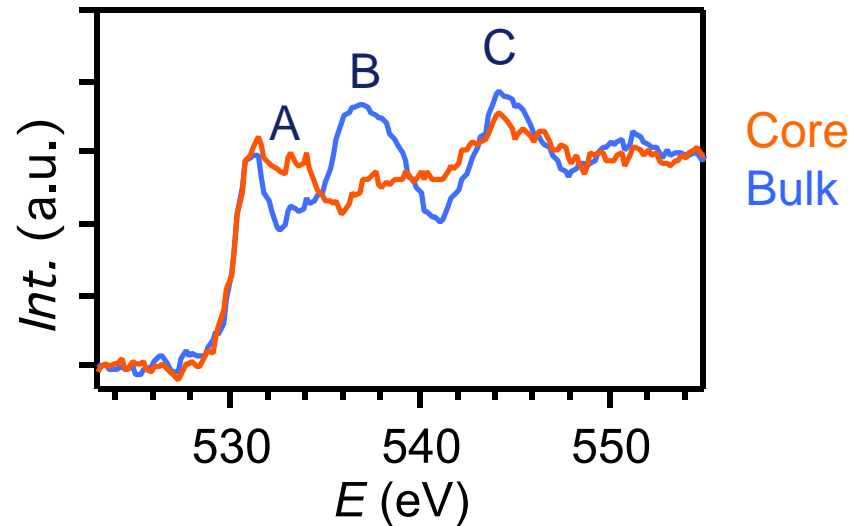
$a=0.42$ nm 
 JÜLICH
FORSCHUNGSZENTRUM

Energy loss near edge fine structure

Ti L_{2,3} (2p→3d)



O K (1s→2p)

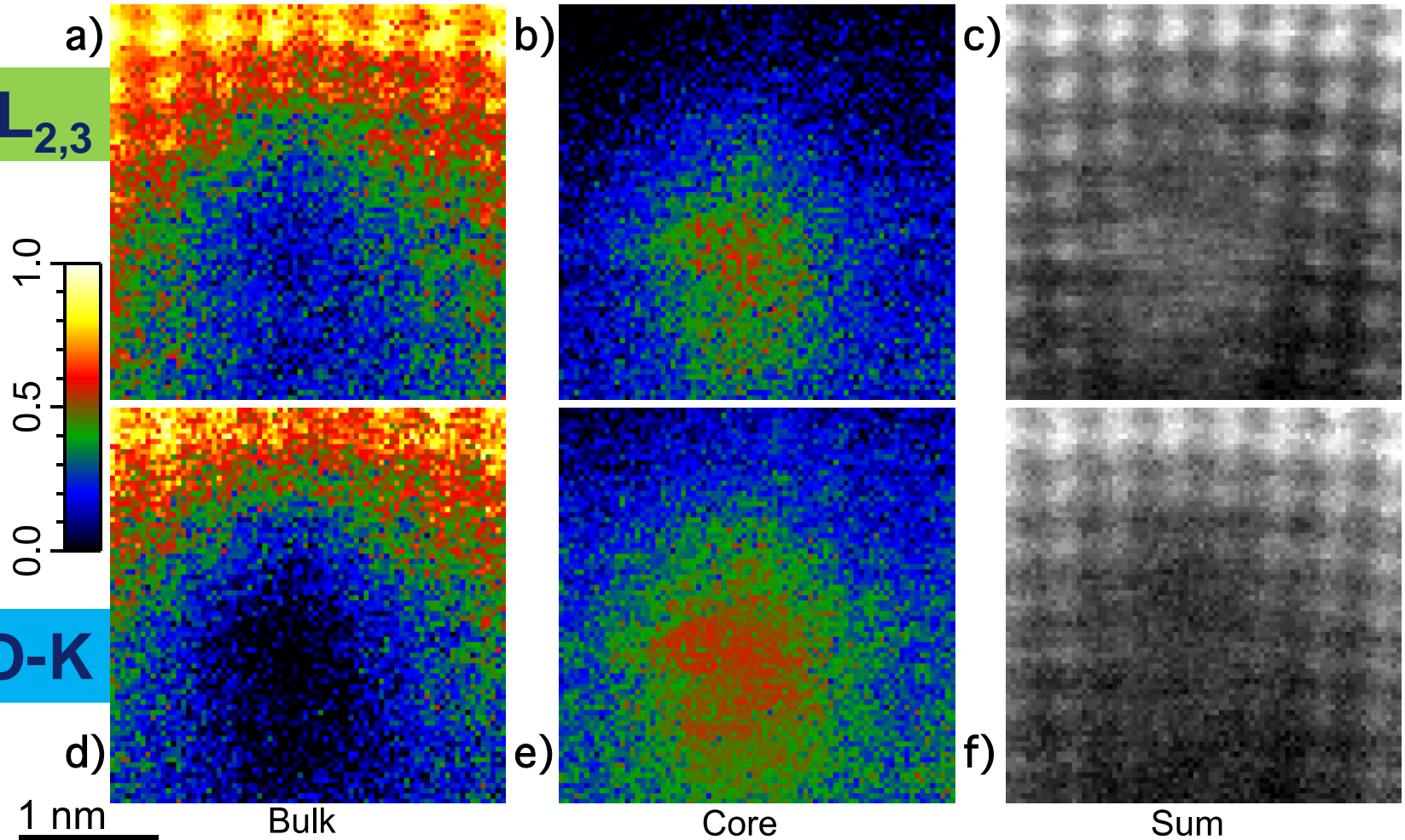


δ estimated by the free carrier density (Hall effect)

— Ref. D. A Muller *et al.* Nature v430,p657.

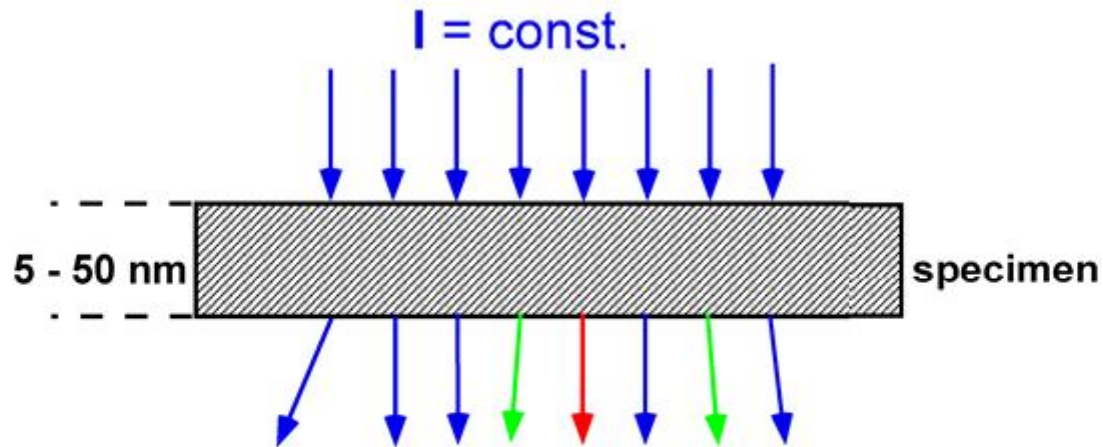
Valence/Bonding state mapping

Ti-L_{2,3}



Reduction of Ti-valency state makes dislocation core electrically active!

Analytical TEM: Electron Intensity Distribution



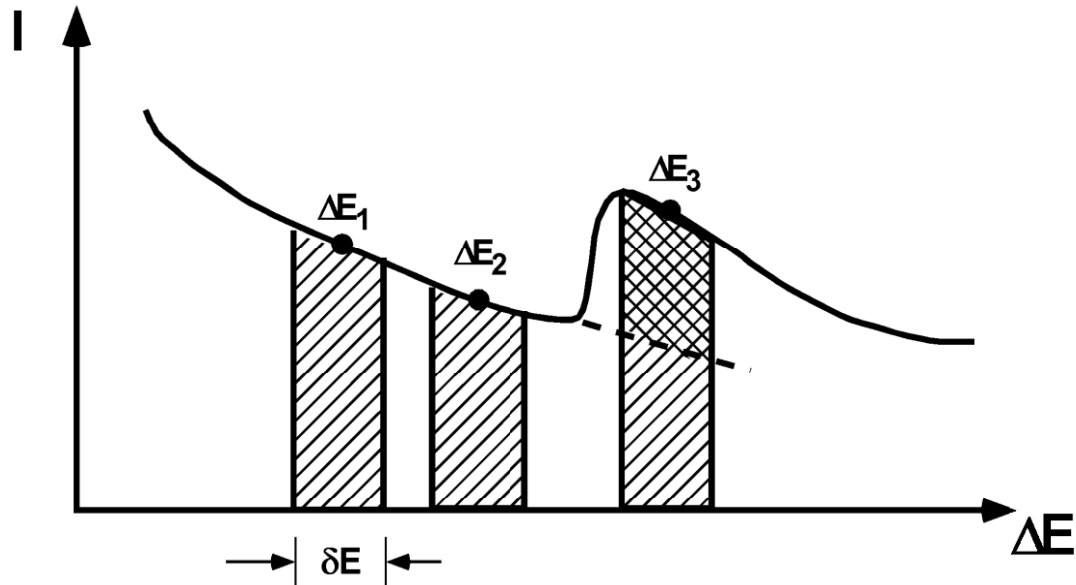
$$I = I(x, y, \theta_x, \theta_y, \Delta E)$$

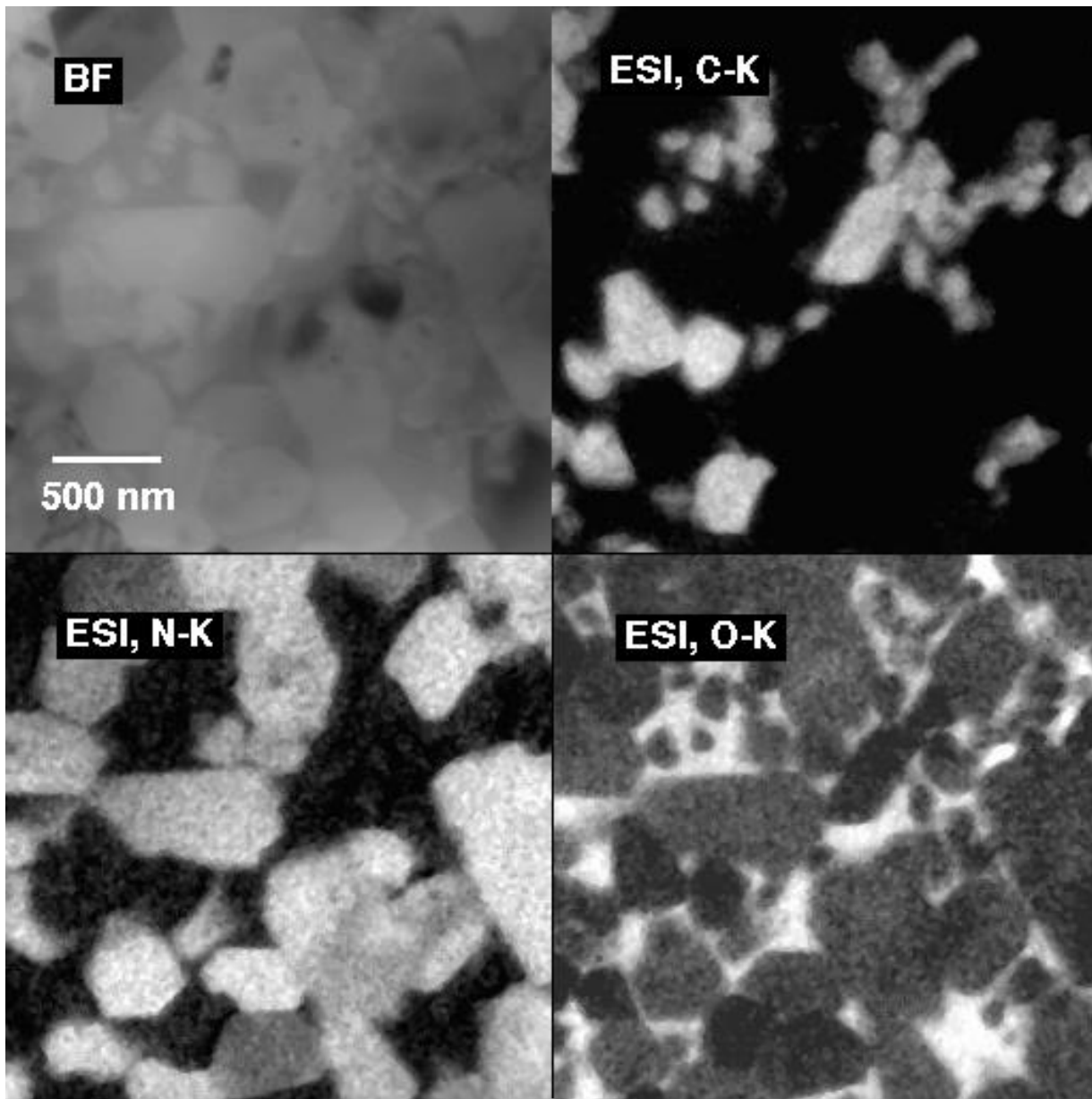
conventional TEM EELS

Electron Spectroscopic Imaging (ESI)
Diffraction (ESD)

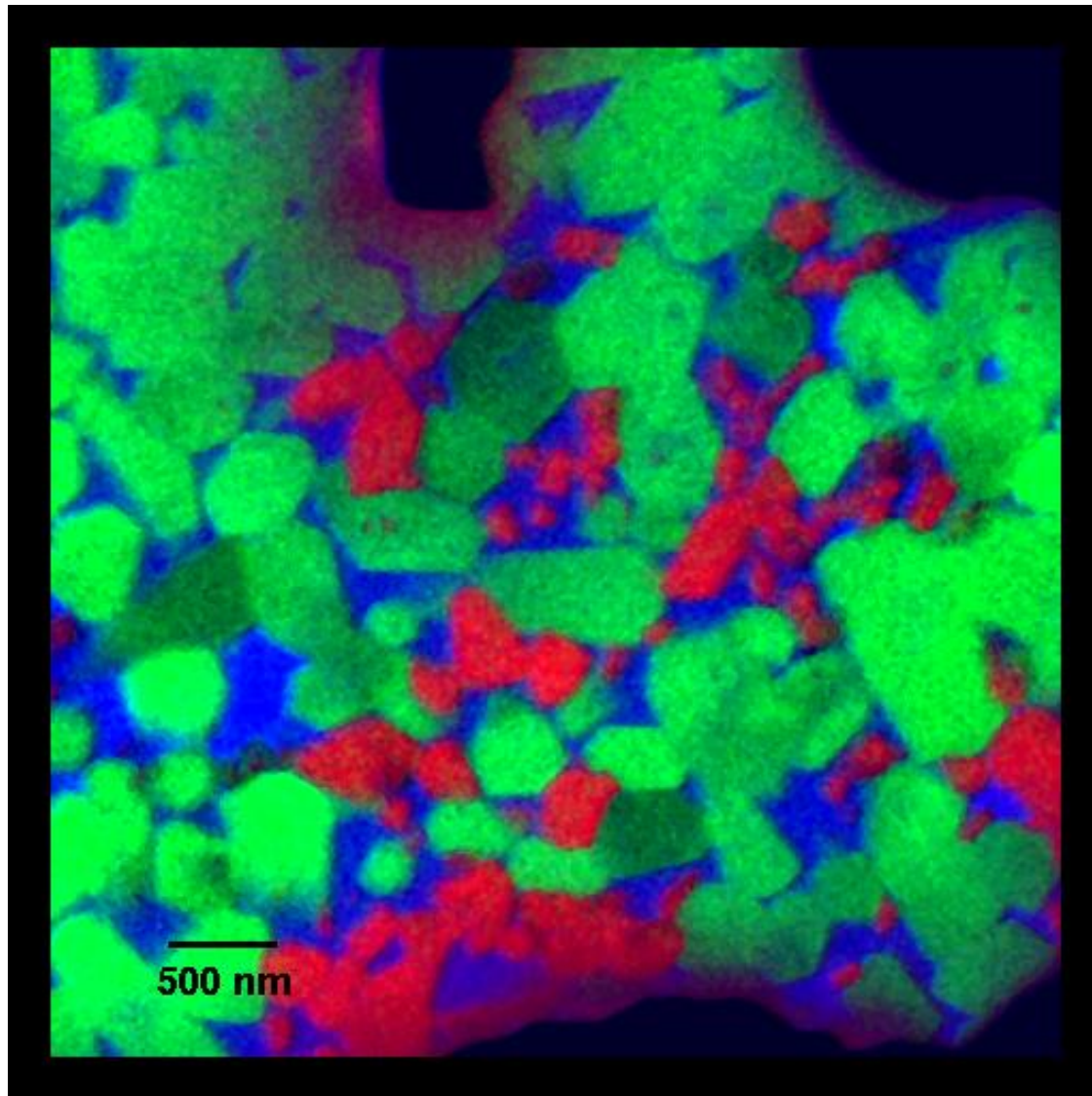
Energy Filtering TEM

Elemental Distribution Images: Three Window Technique





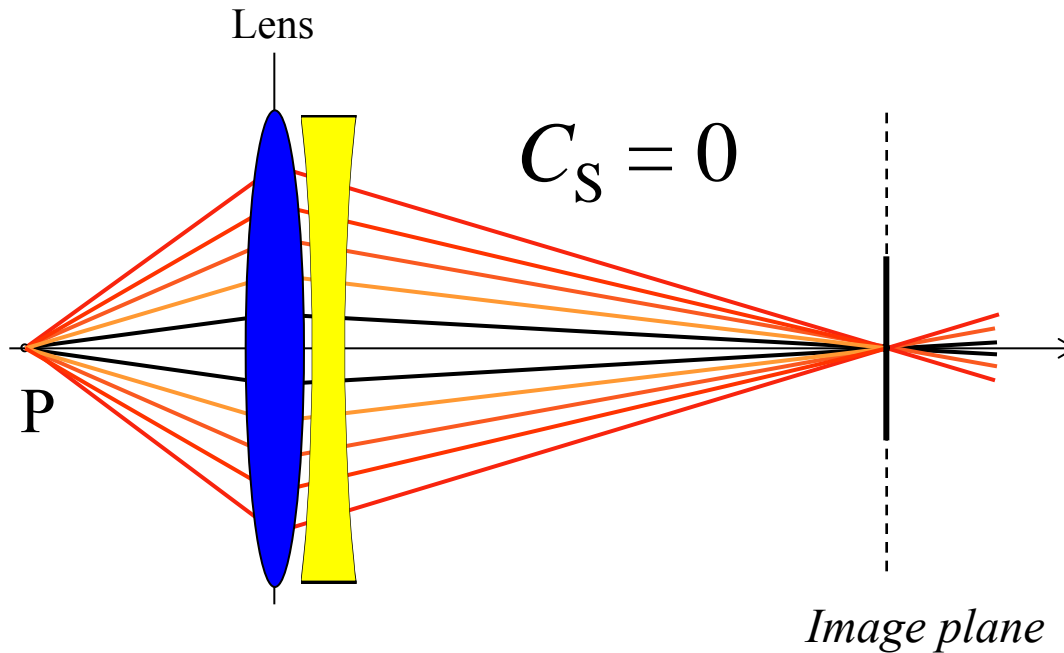
Sintered polymer derived $\text{Si}_3\text{N}_4/\text{SiC}$ -composite



red: C, green: N, blue: O

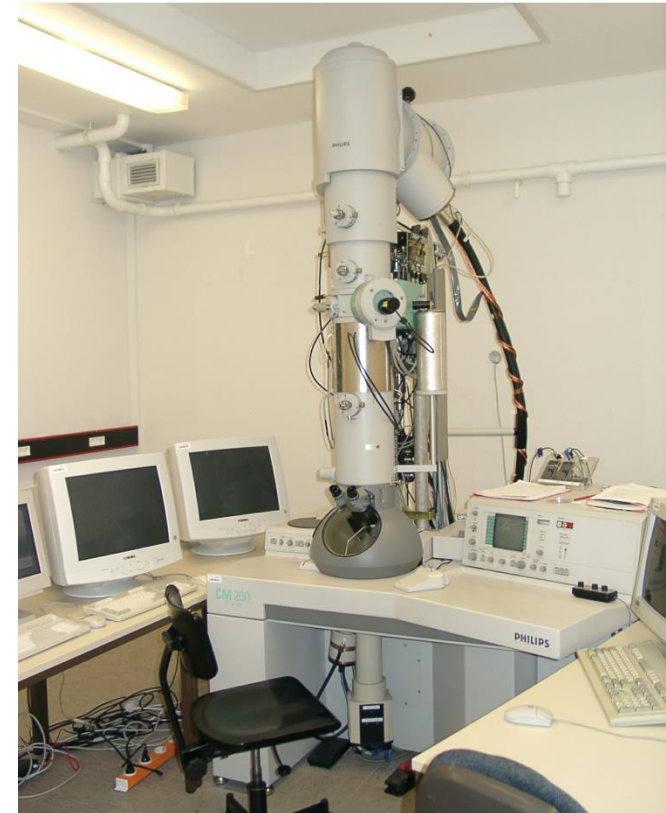
Sintered polymer derived Si₃N₄/SiC-composite

Aberration corrected electron optics



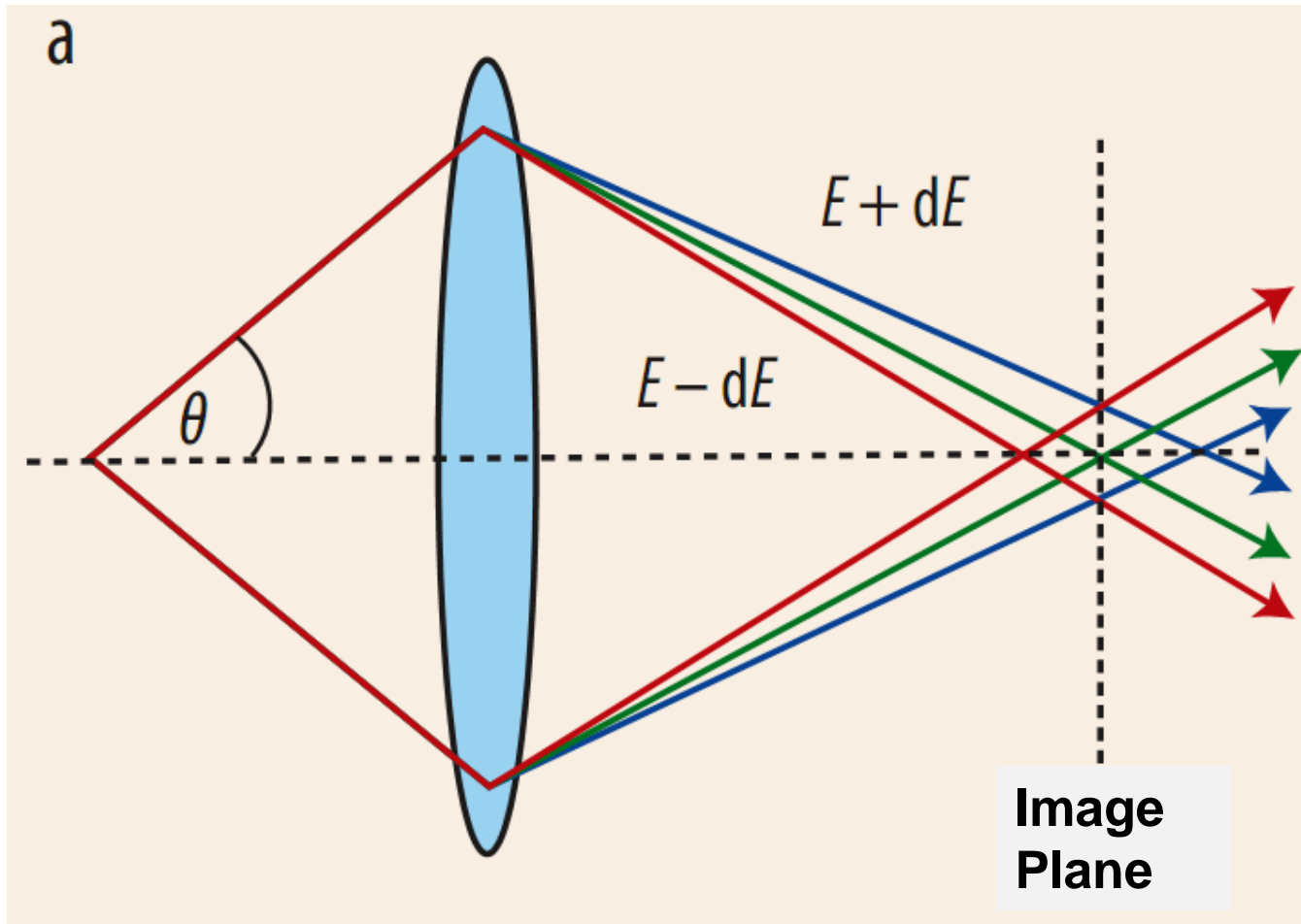
- TU Darmstadt (H. Rose)
- EMBL Heidelberg (M. Haider)
- Forschungszentrum Jülich (K. Urban)

Volkswagen Stiftung

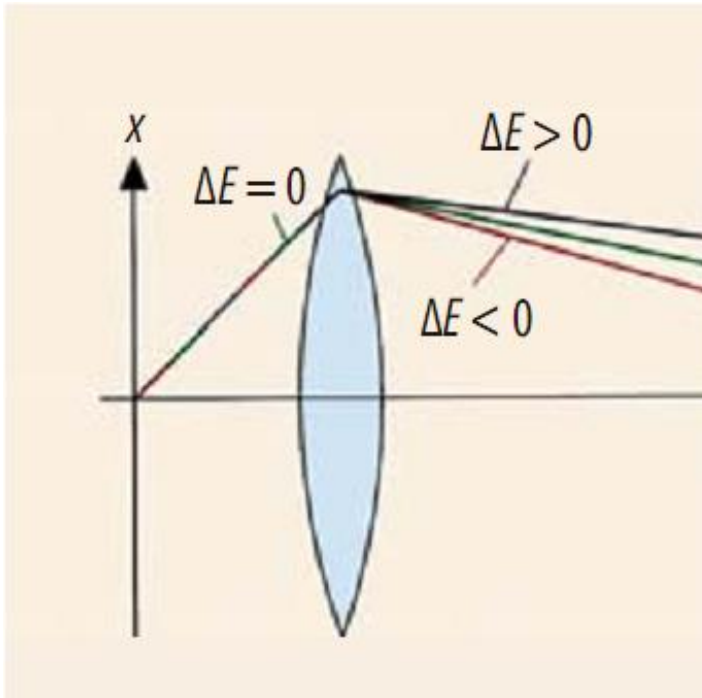
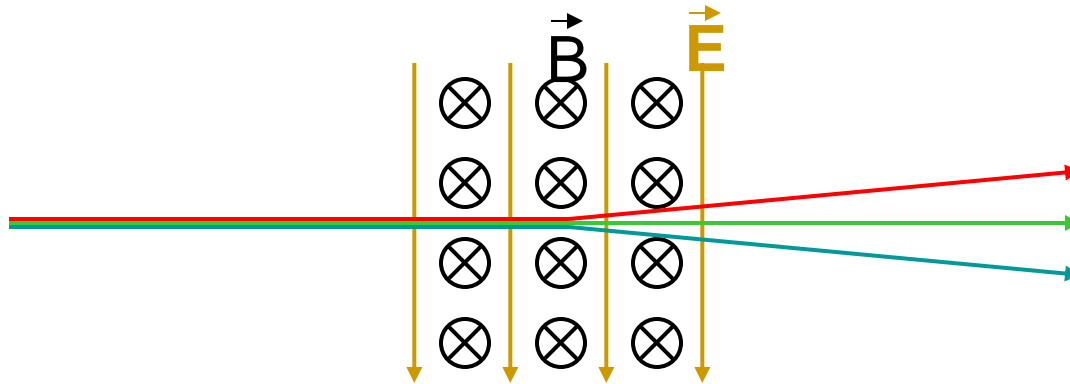


Haider, Rose, Urban et al.
Nature 392, 768 (1998)

Chromatic Aberration

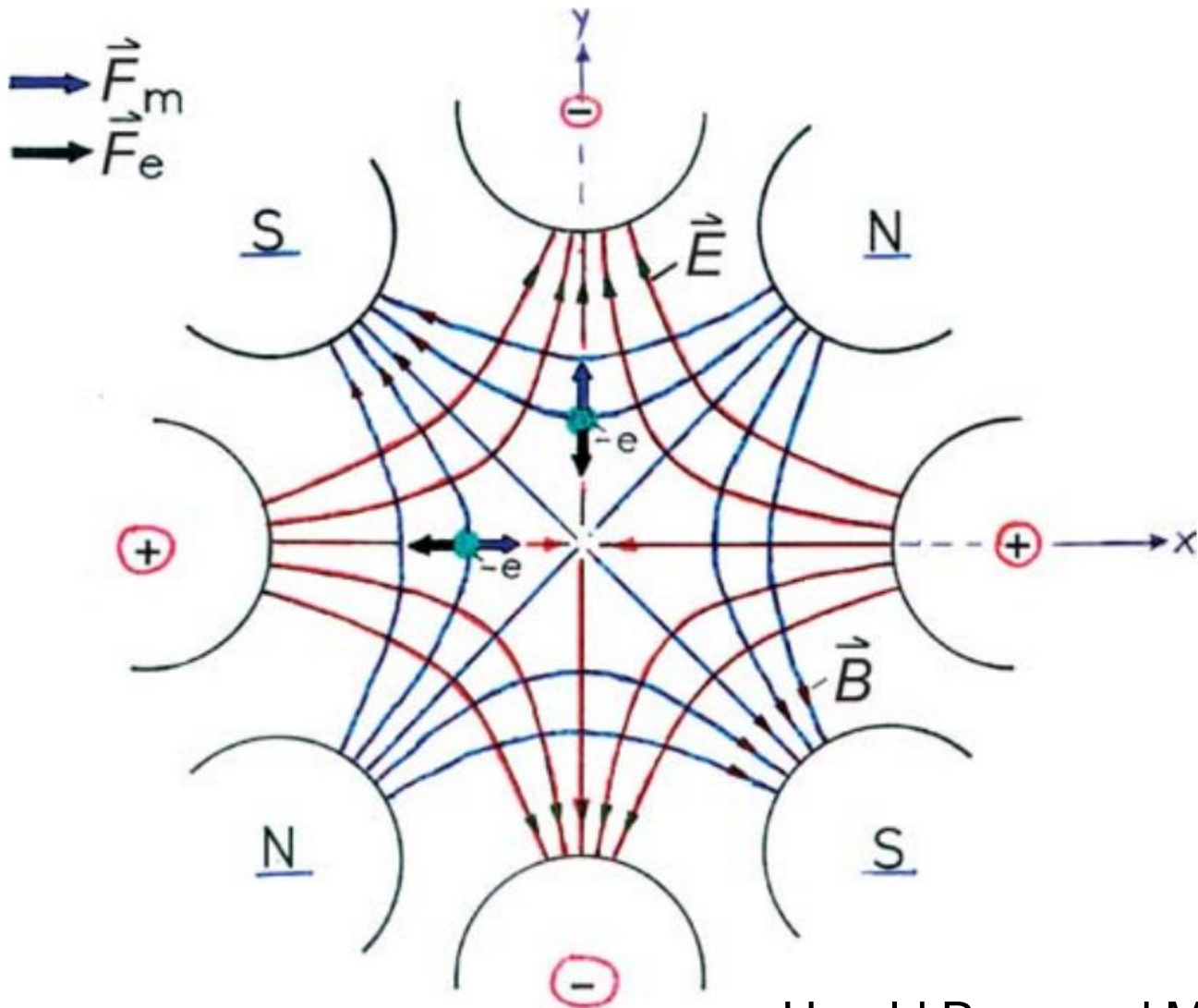


Correction Principle: Wien Filter

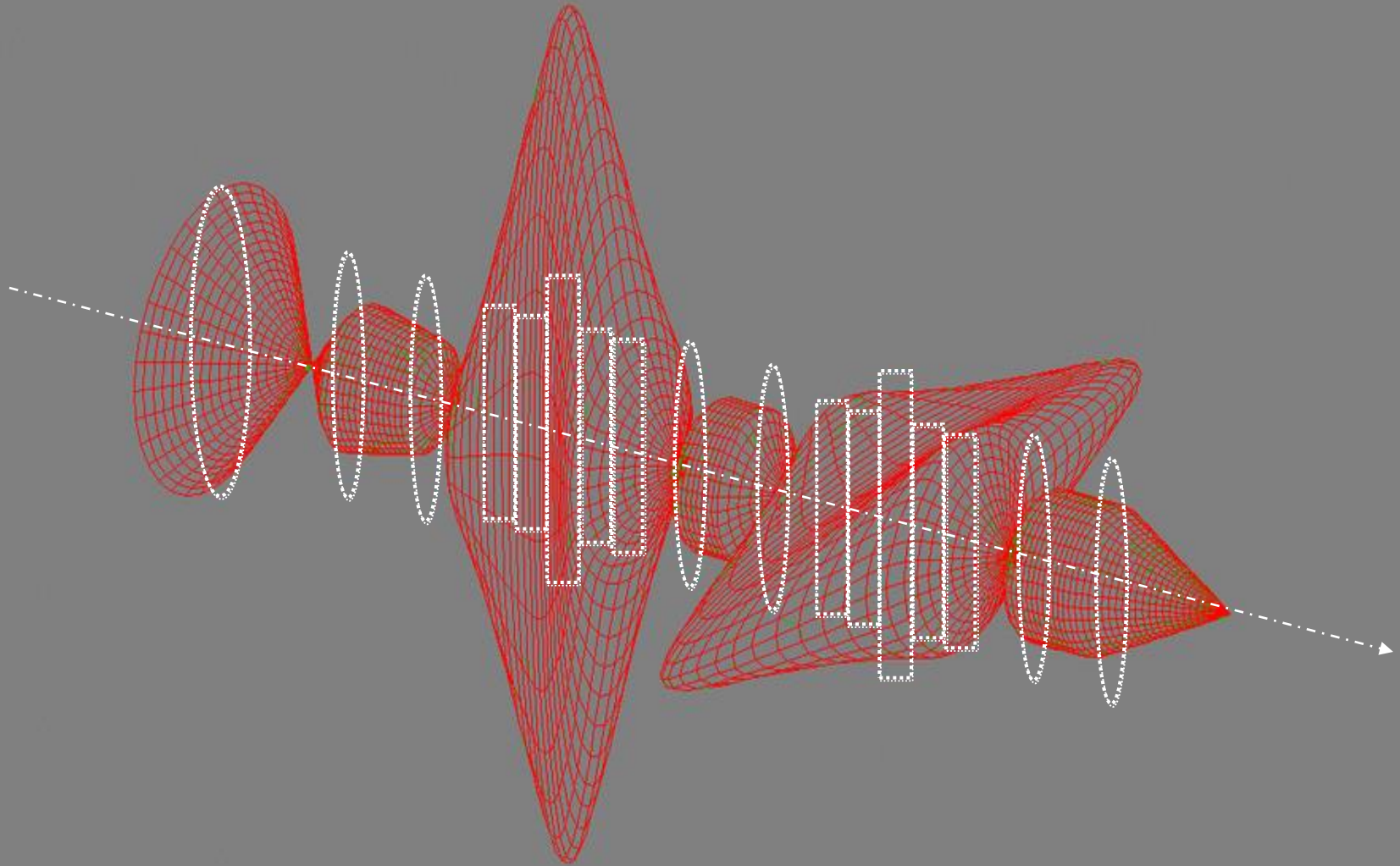


Harald Rose and Max Haider

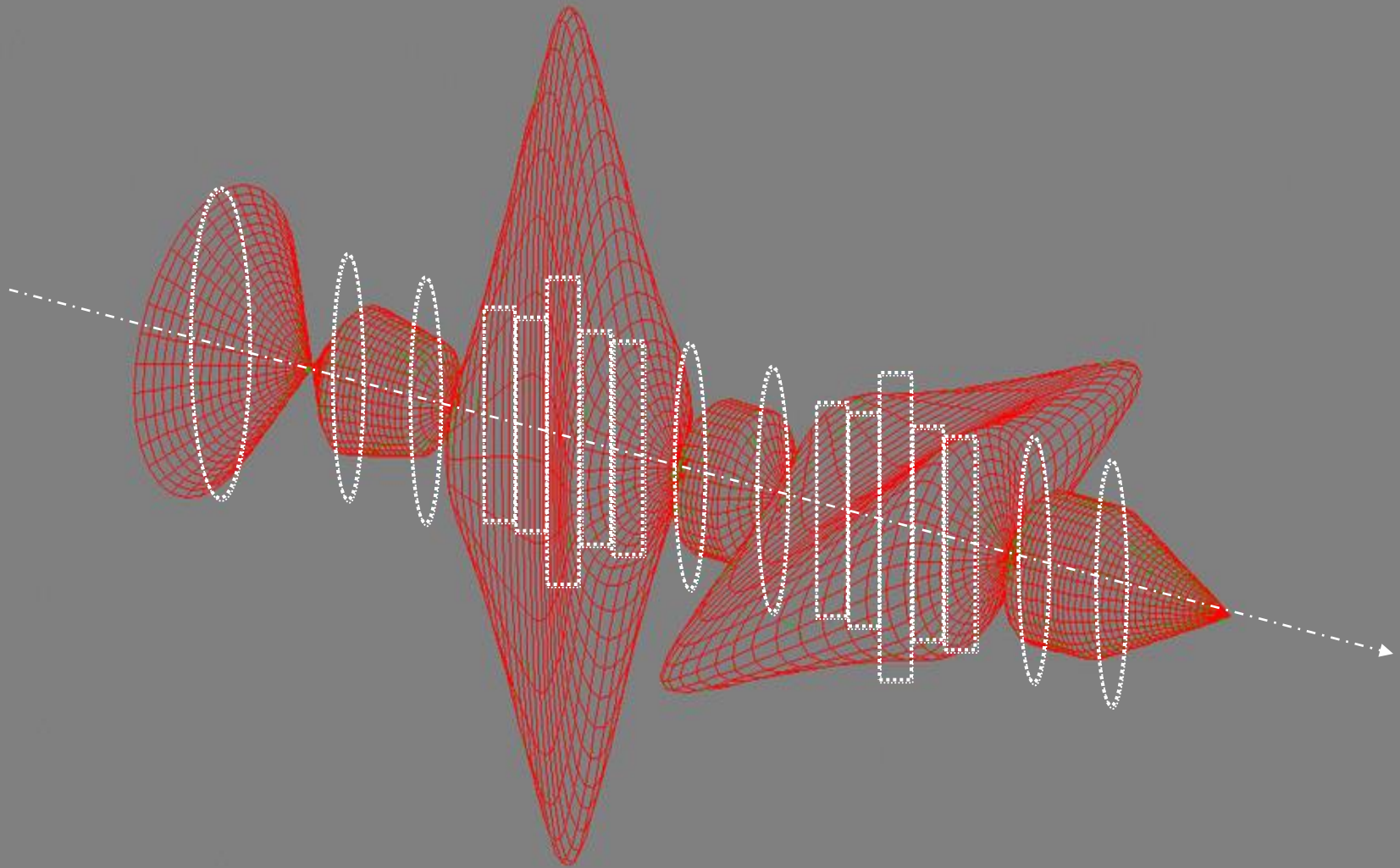
Correction Principle: Crossed Electrostatic/Magnetic Quadrupoles



Harald Rose and Max Haider



Cc-Corrector: 10 multipole elements + 4 coupling lenses



Cc-Corrector: 10 multipole elements + 4 coupling lenses

CCOR in Heidelberg, CEOS



828 mm,
470 kg,
160 channels



PICO upgrades



2011

2012

2013

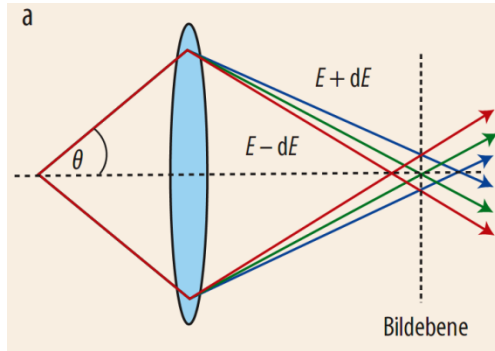
2014

2015

CCOR
power supplies

CCOR → CCOR+
and power supplies

Chromatic Aberration



$$d_c = \frac{1}{2} C_c \frac{dE}{E} \theta$$

Biggest impact of Cc-correction expected for:

- large energy spread dE (EFTEM)
- low accelerating voltages (low E)



Energy Filtering TEM

EFTEM resolution:

$$d_{\text{tot}} = \sqrt{d_c^2 + d_s^2 + d_d^2 + d_{\text{del}}^2}$$

Spherical Aberration	0
Chromatic Aberration	0
Diffraction Limit	$d_d = 0.6 \frac{\lambda}{\theta}$
Delocalisation	$d_{\text{del}} = 0.5 \frac{\lambda}{\theta_E^{3/4}}$

21%



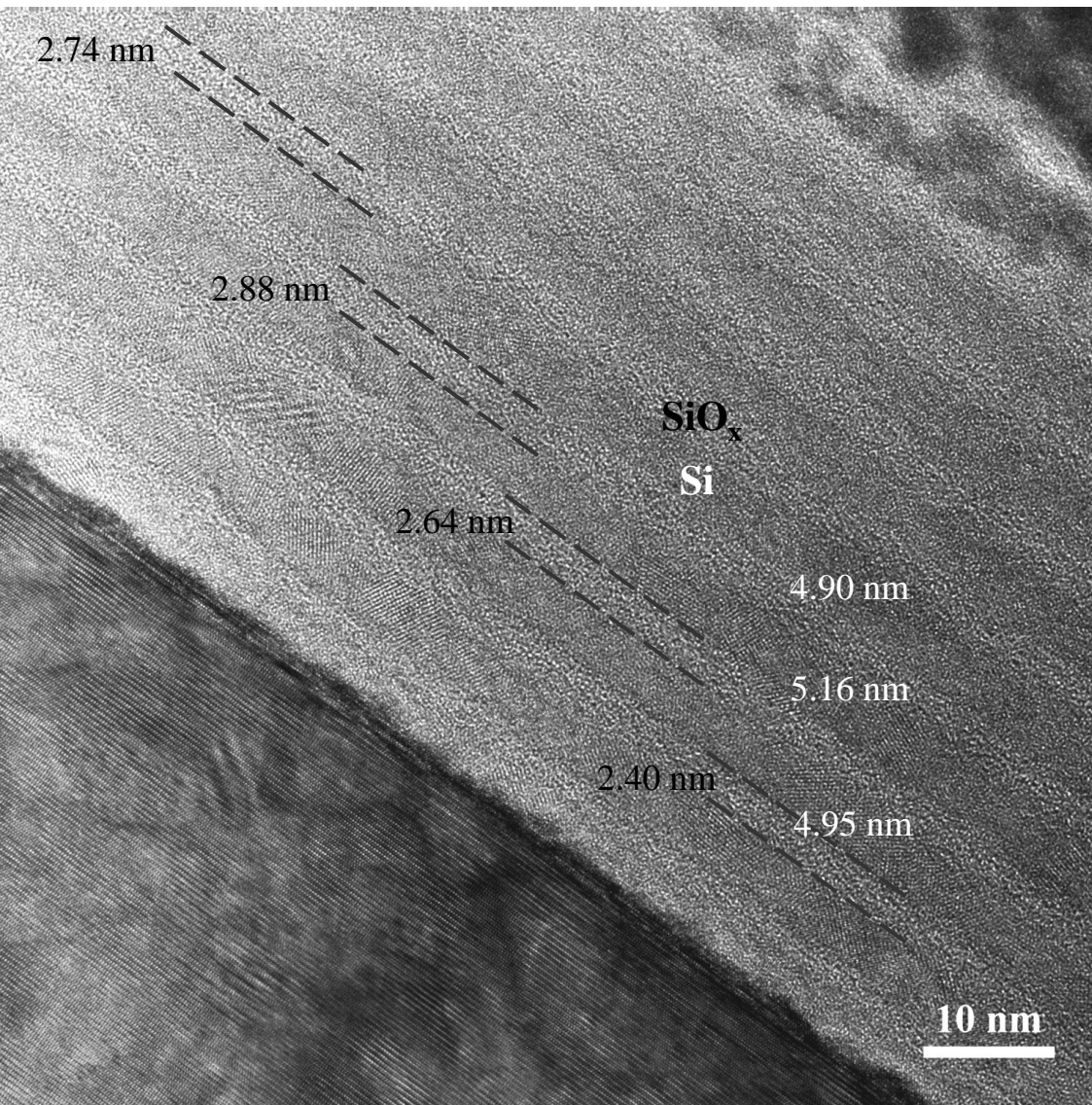
BMBF-project
SINOVA

21%

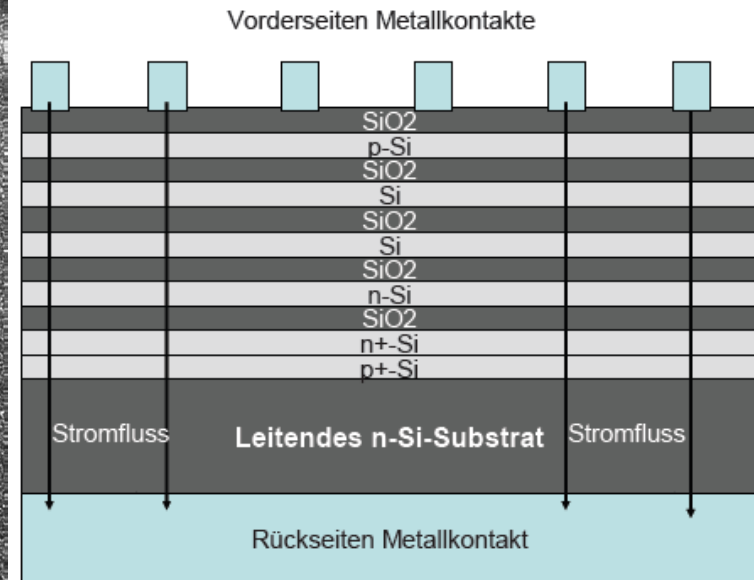
60%



Design Concept

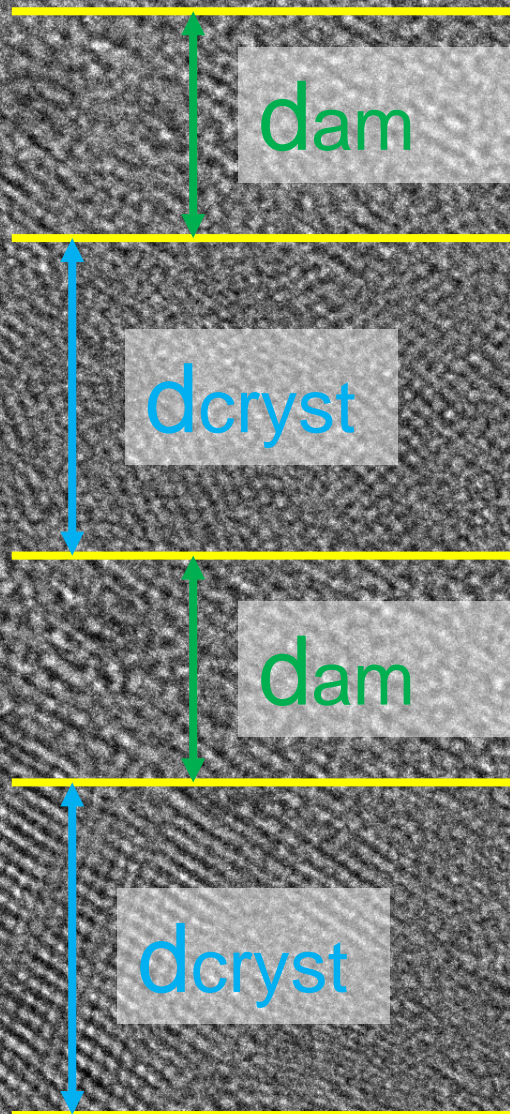


Vertical Transport



**Si/SiO₂-Superlattices:
Fabrication by RPECVD at
250°C and
Rapid Thermal Annealing at 900
to 1100°C**


PICO



5 nm

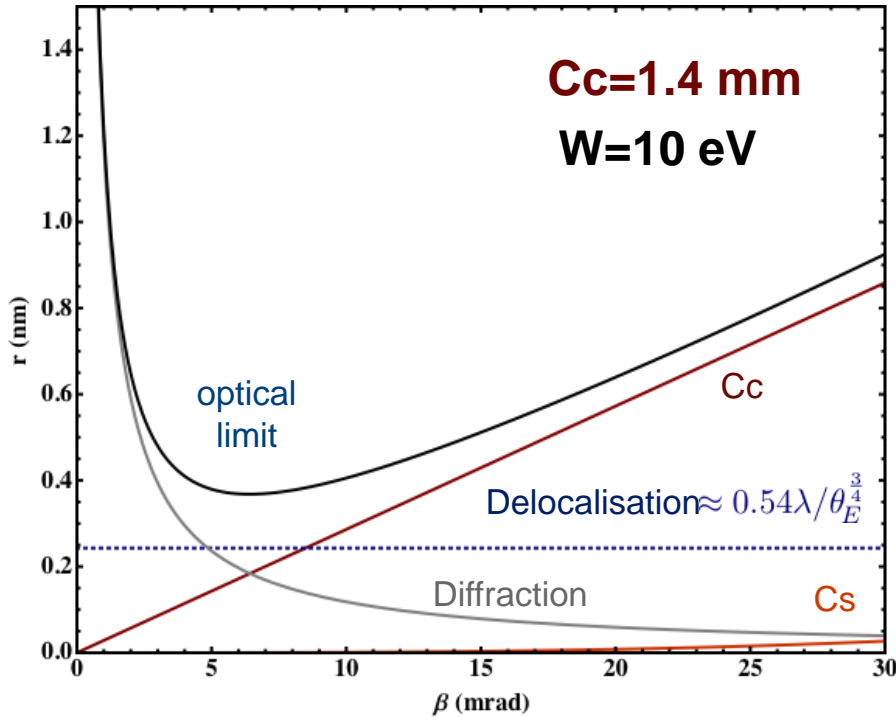
**PICO: Energy Filtering TEM
Si-L edge, 3 window meth.**

5 nm

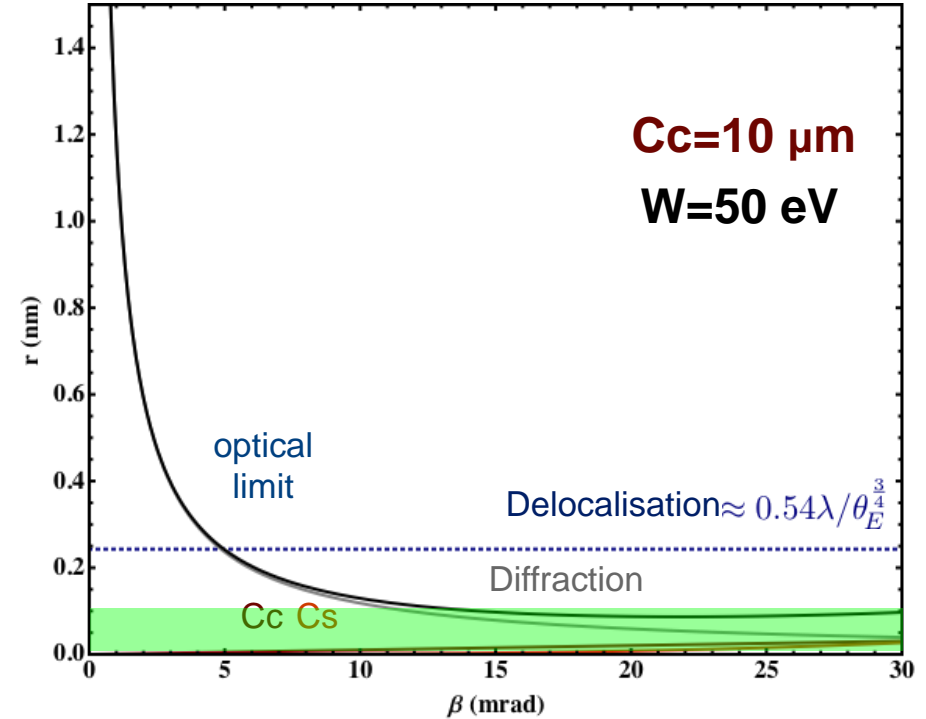
A horizontal white line representing a scale bar of 5 nm.

Maryam Beigmohamadi, Jörg Jinschek

Cs corrected



Cs and Cc corrected

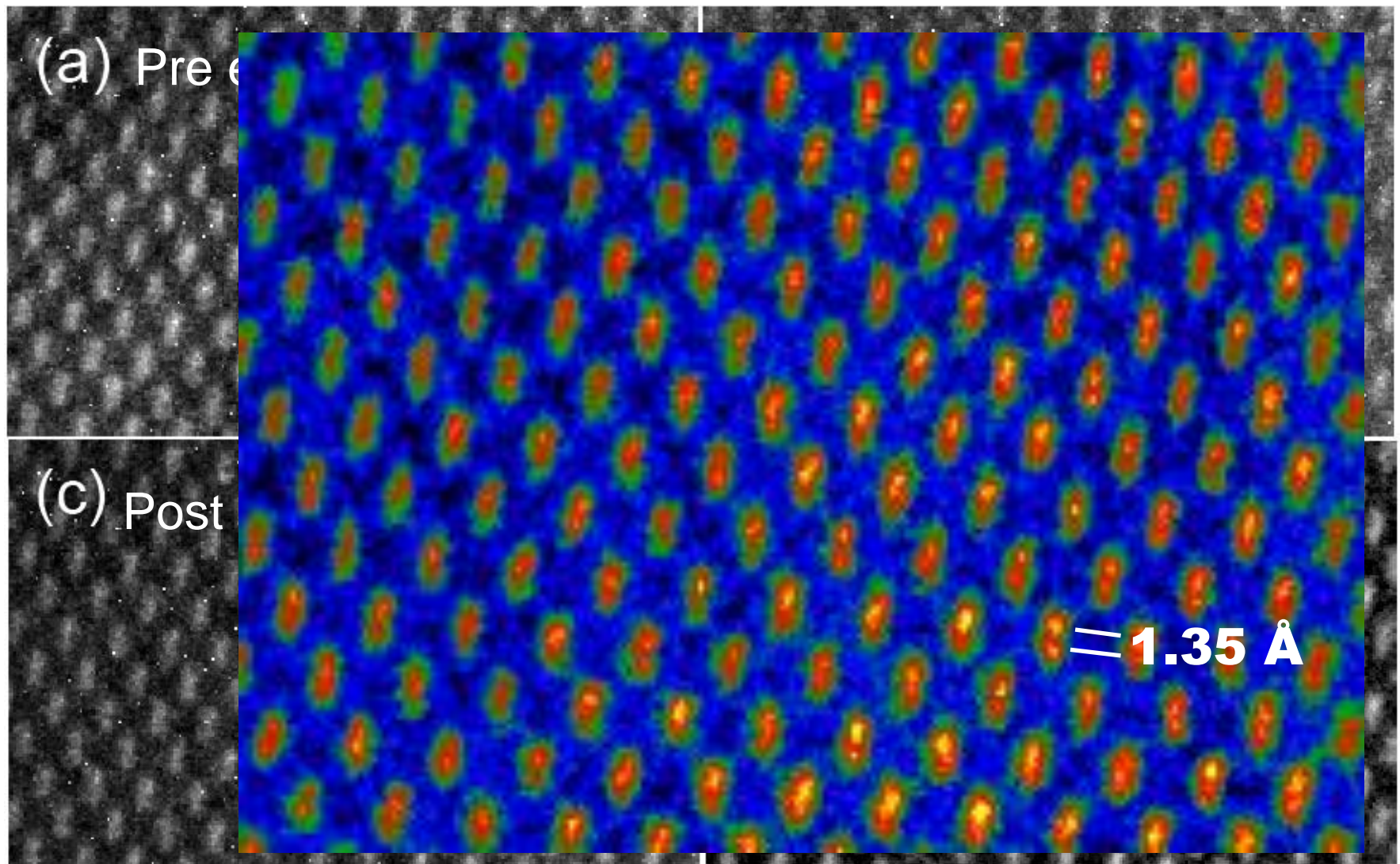


- > optical resolution better than delocalisation
- > large windows possible

As in Krivanek et al, J. Microsc. **180** (1995) 277
R. F. Egerton, J. Electr. Microsc. **48** (1999) 711.

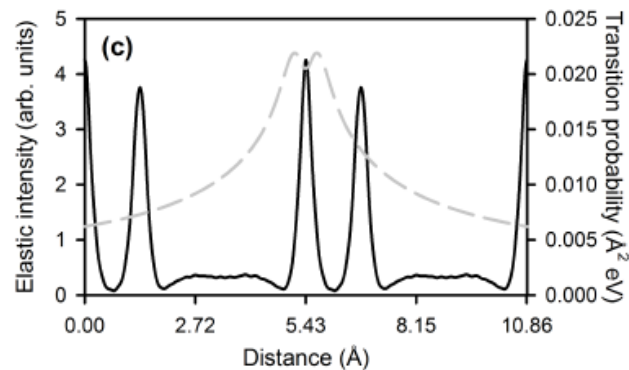
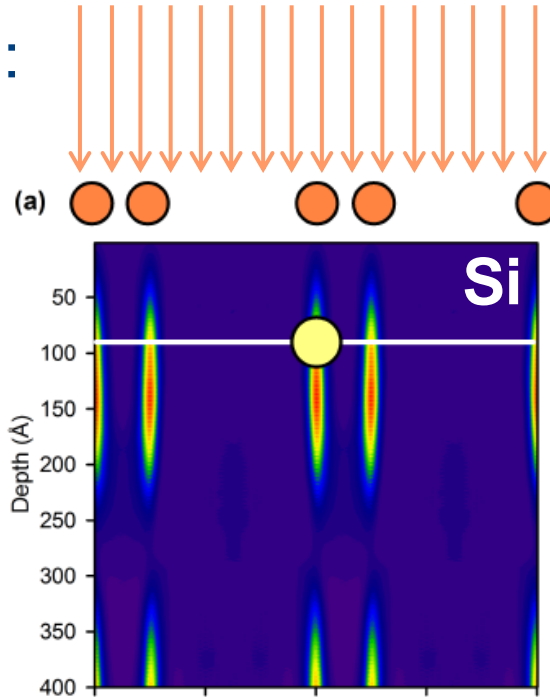
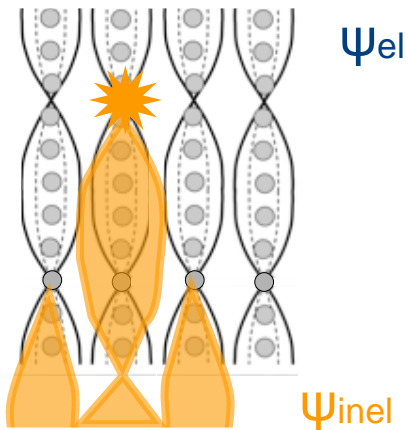
High Resolution EFTEM of Si

EFTEM, Si-L edge at 99 eV, energy window 40 eV



Knut Urban, Jörg Jinschek,
Les Allen, J. Mayer, Phys. Rev. Letters **110**, 185507 (2013)

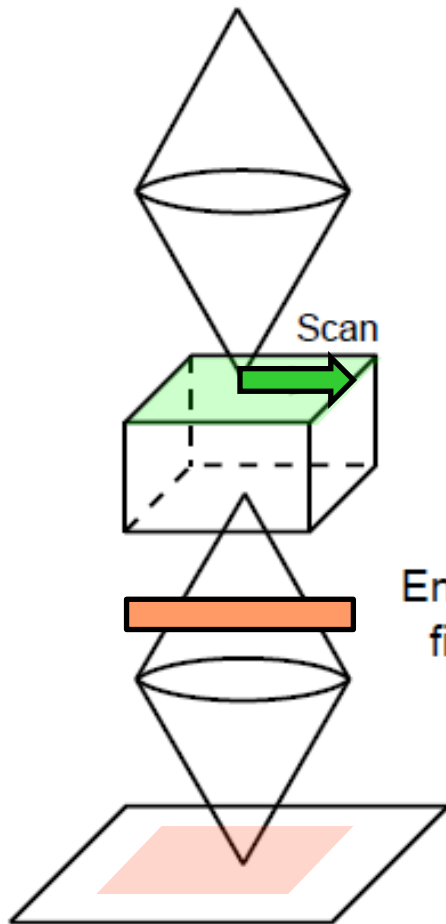
Elastic Wave Field: Channeling and Pendellösung



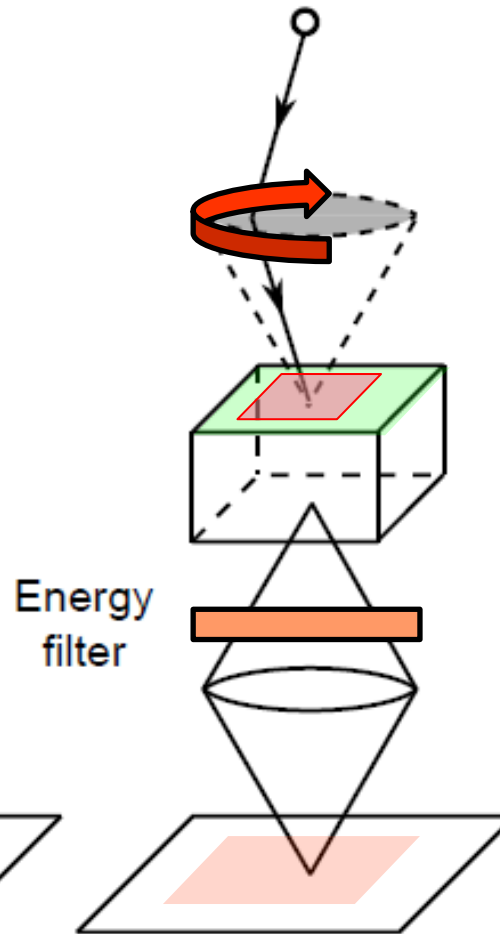
Knut Urban, Jörg Jinschek,
Les Allen, J. Mayer, Phys. Rev. Letters **110**, 185507 (2013)

EFISTEM vs. hollow cone illumination and STEM

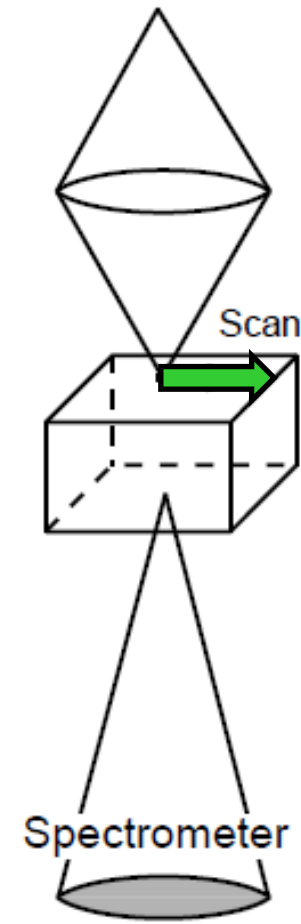
(a) EFISTEM



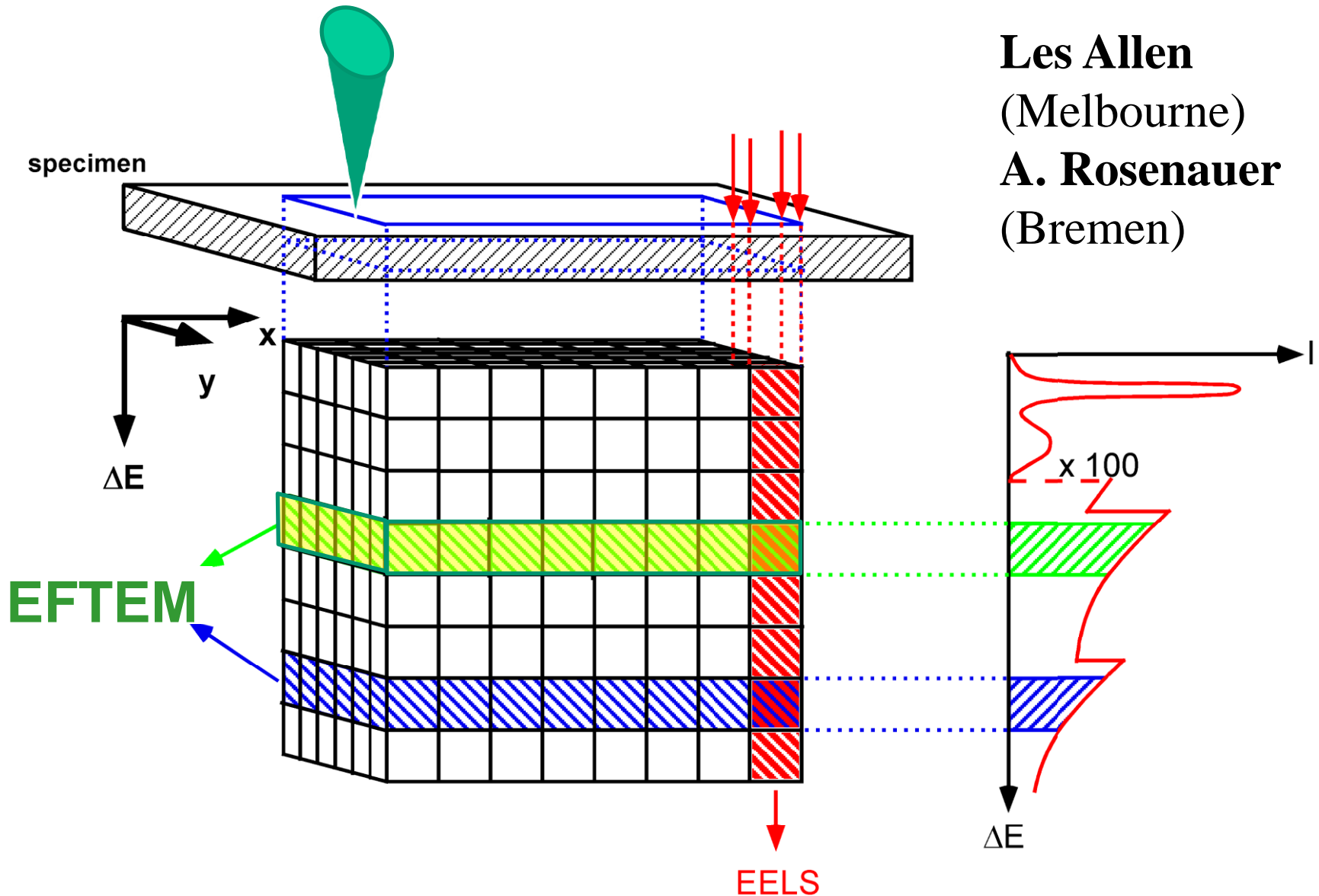
(b) Precession EFTEM
(over solid angle)



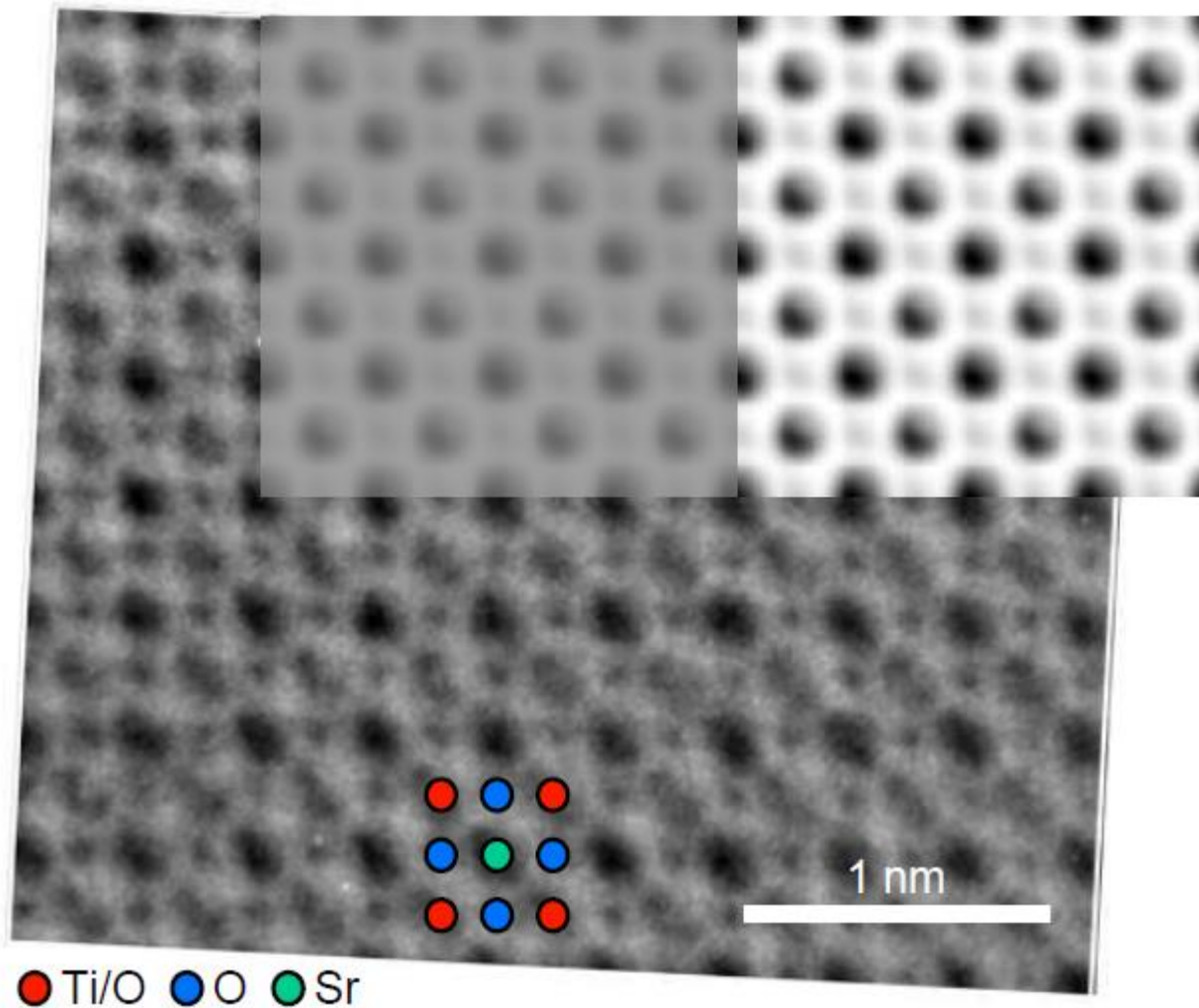
(c) STEM EELS



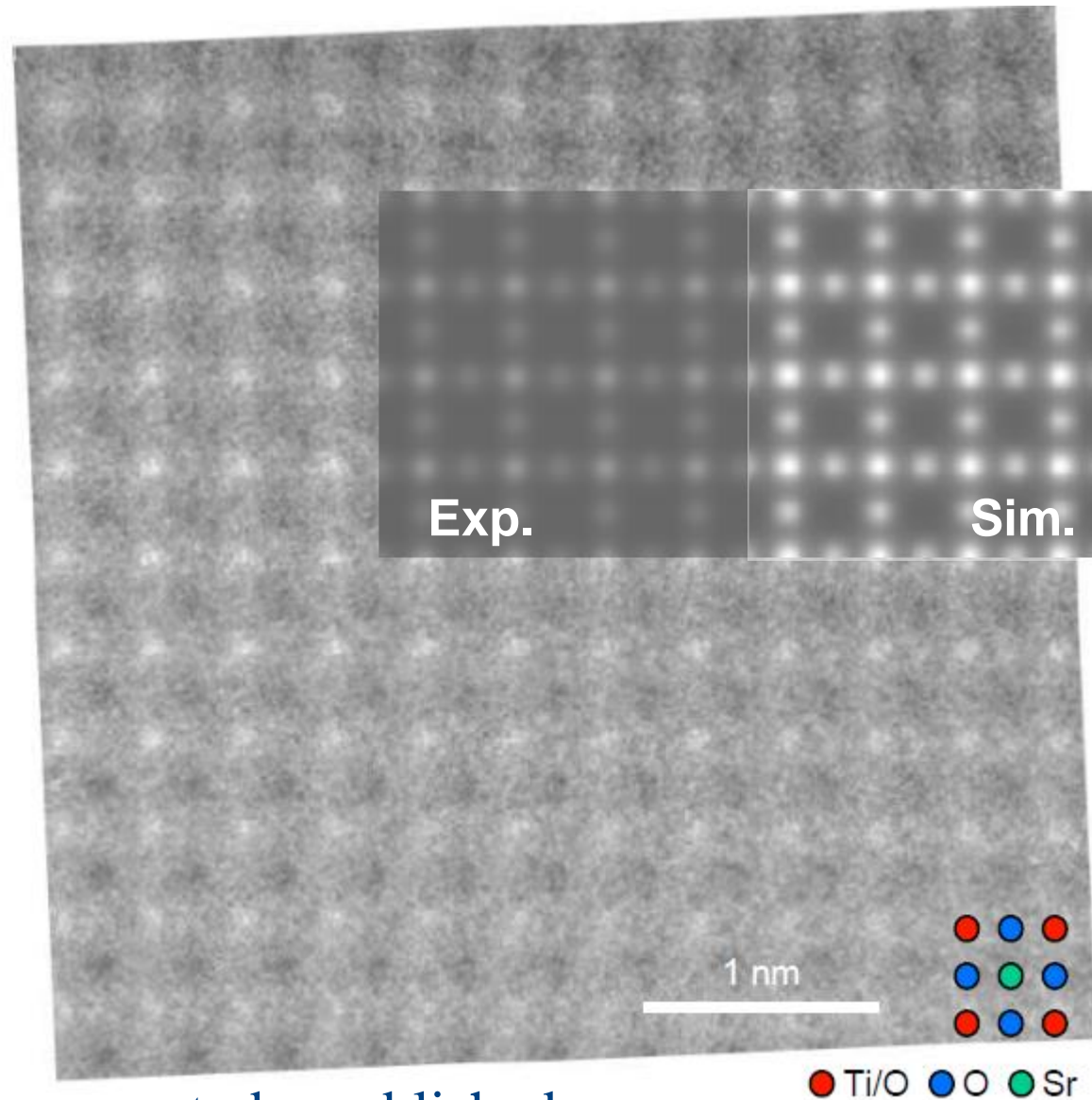
Energy Filtering Image STEM (EFISTEM)



SrTiO₃: EFISTEM zero loss



SrTiO₃: EFISTEM oxygen map

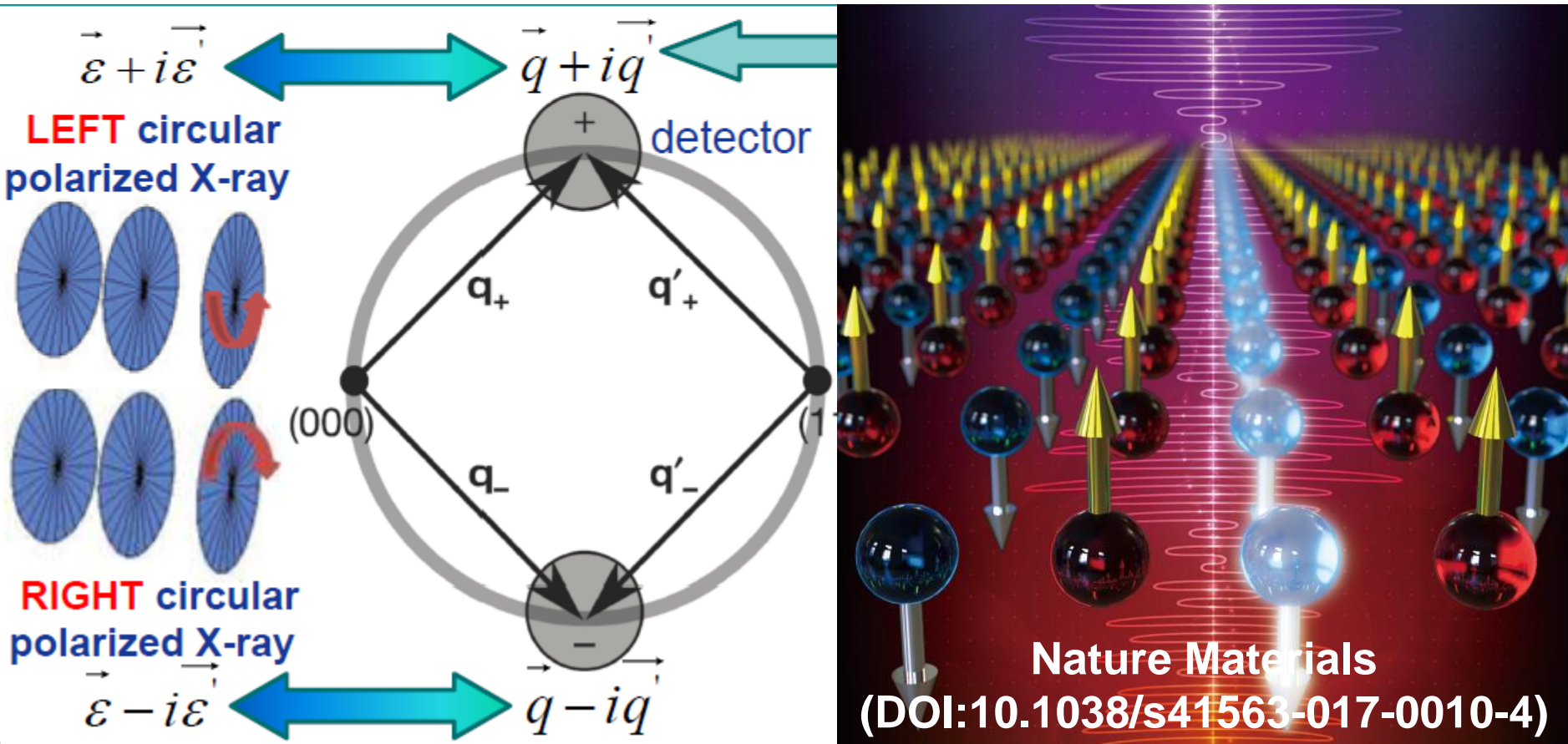


Ultramicroscopy, to be published

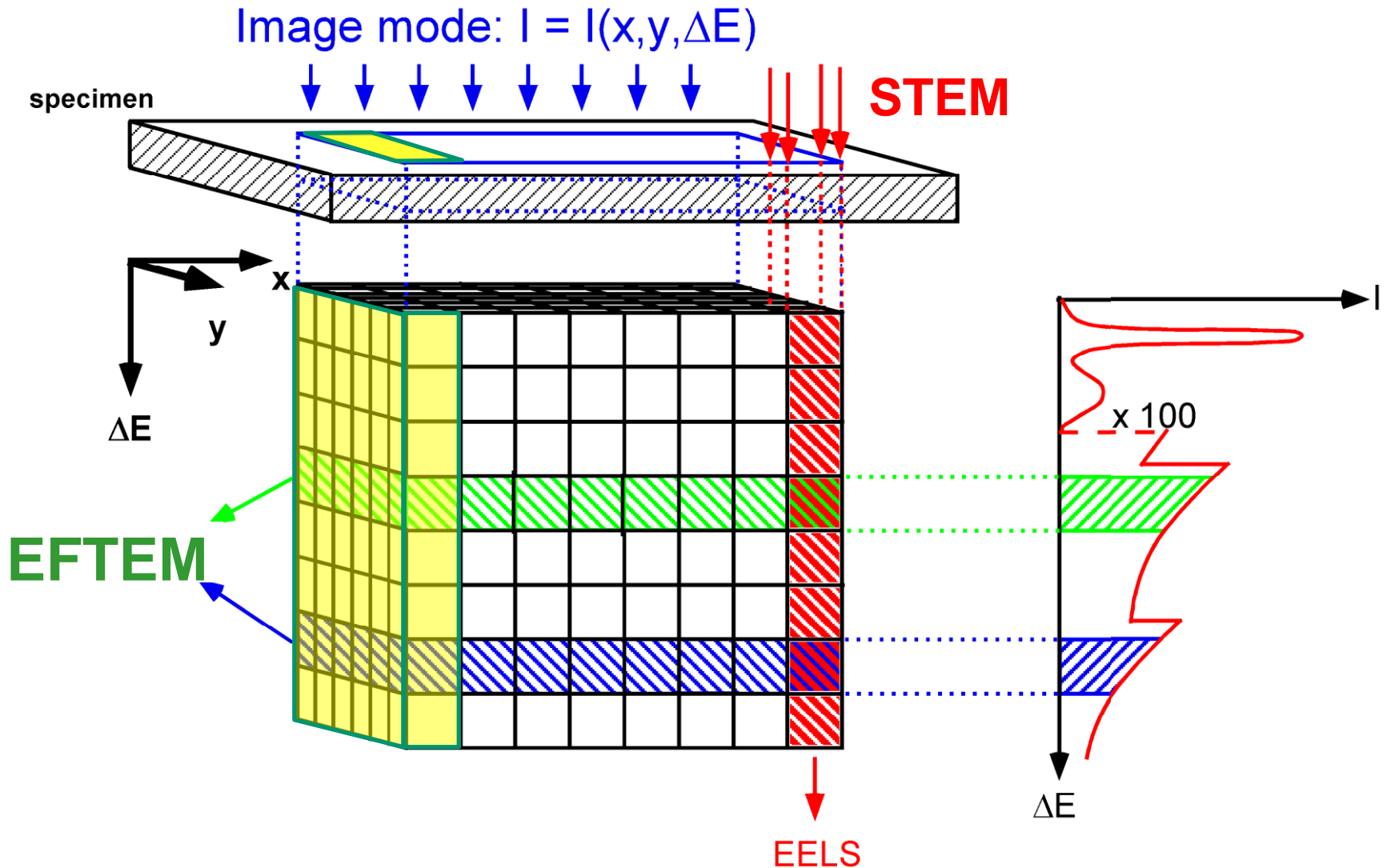
Electron Magnetic Circular Dichroism (EMCD) Electron Energy-loss Magnetic Chiral Dichroism

Tsinghua University: Xiaoyan Zhong, Zechao Wang, Hanbo Jiang

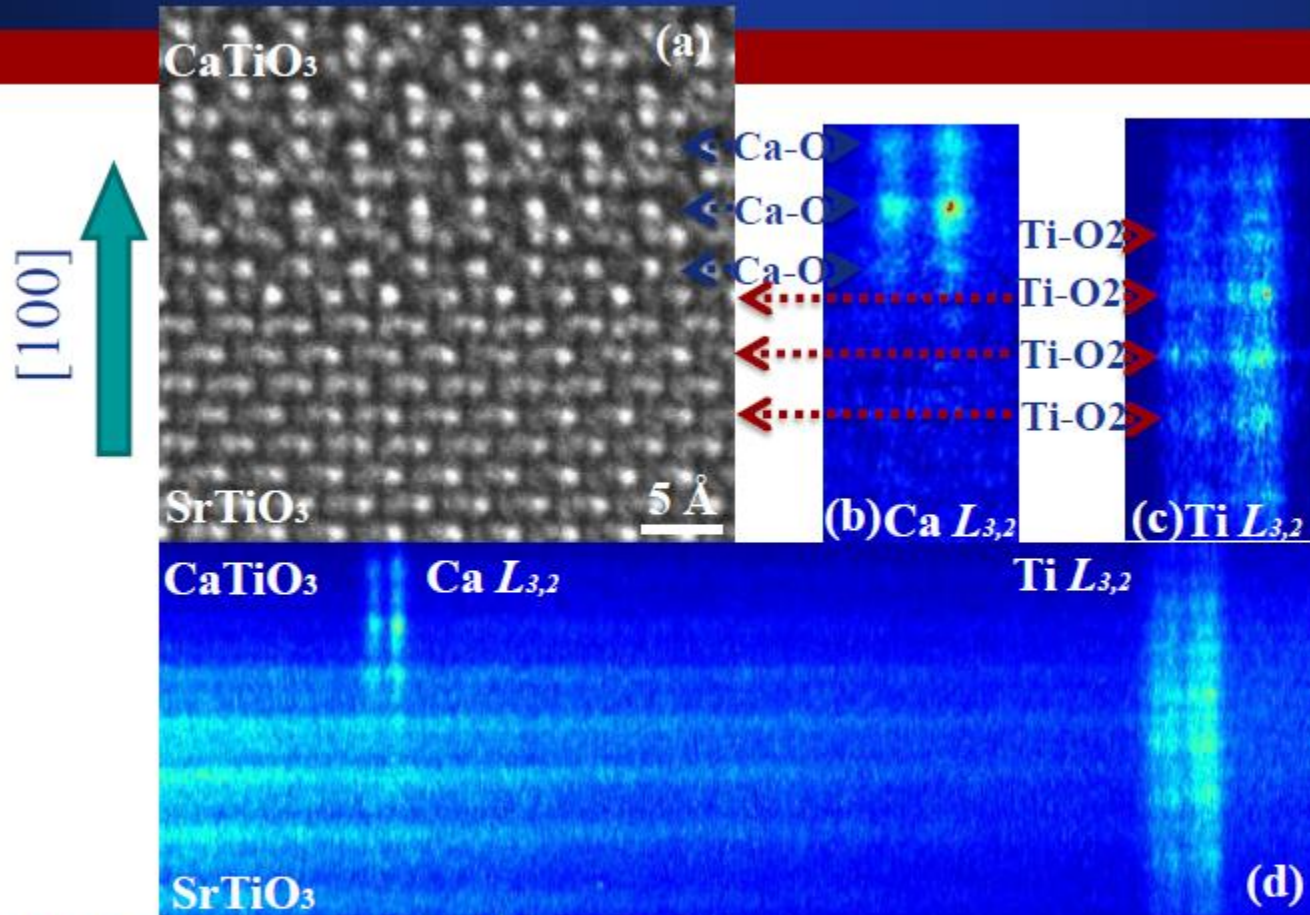
Ernst Ruska-Centre: Amir Tavabi, Lei Jin, Juri Barthel, Les Allen



Energy Loss Spectroscopic Profiling (ELSP)



Atomic Resolution ELSP of $\text{CaTiO}_3/\text{SrTiO}_3$ interface



**Cc corr.
needed!**

a: HRTEM of $\text{CaTiO}_3/\text{SrTiO}_3$ interface

b&c: Ca and Ti edge ELSP after background subtraction

d: raw ELSP data without background subtraction under (100) 3beam condition

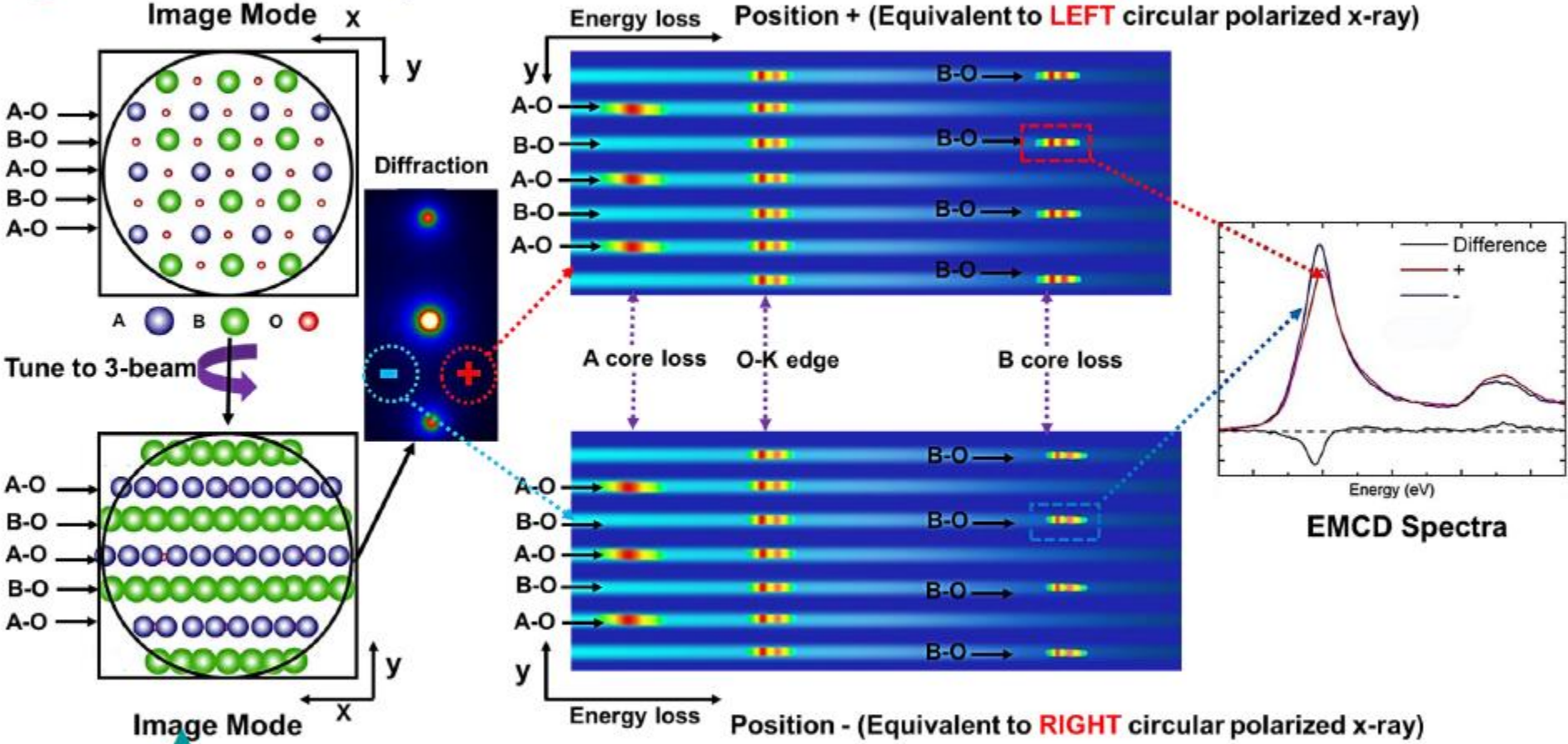
Ca edge and Ti edge are mainly localized at Ca-O and Ti-O2 crystal planes respectively. There is no much delocalization at Ca $L_{3,2}$ edge at CTO/STO interface.

Material: $\text{Sr}_2\text{FeMoO}_6$ Room-Temperature Ferrimagnetic T_c : 426K

Schematic of Atomic Scale ELSP+EMCD (SFMO)



External Magnetic Field direction (2T) strong enough to get SFMO saturated along z axis, EMCD measure M_z , spin direction of all Fe atoms // external field



In SFMO case, the B site contained the ordered Fe and Mo atom

Position +

Atomic Scale EMCD in SFMO

Layer 1
Layer 2

(a)

O-K

Fe-L

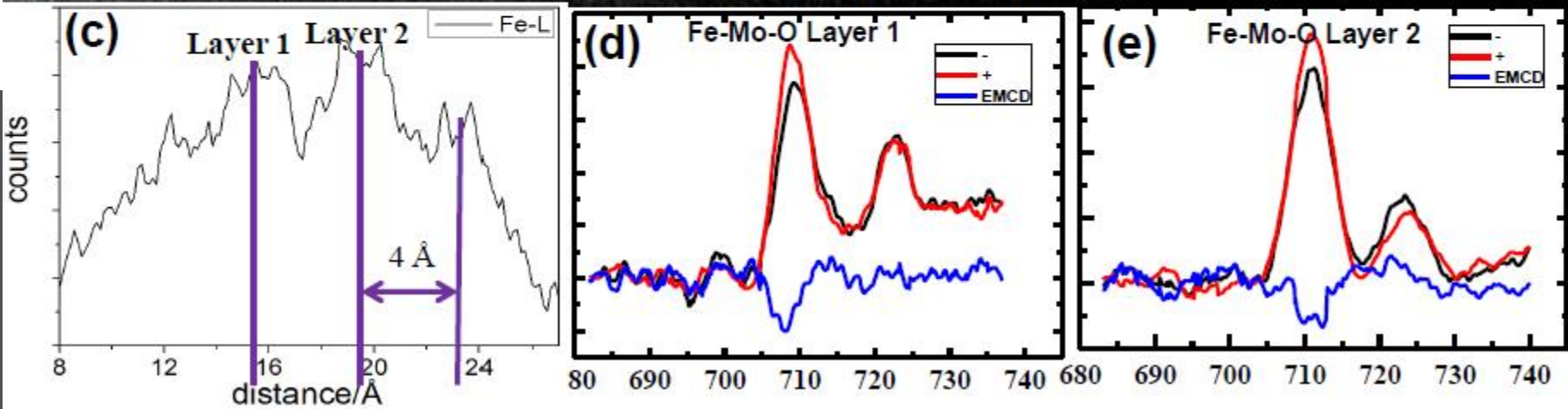
Position -

(b)

O-K

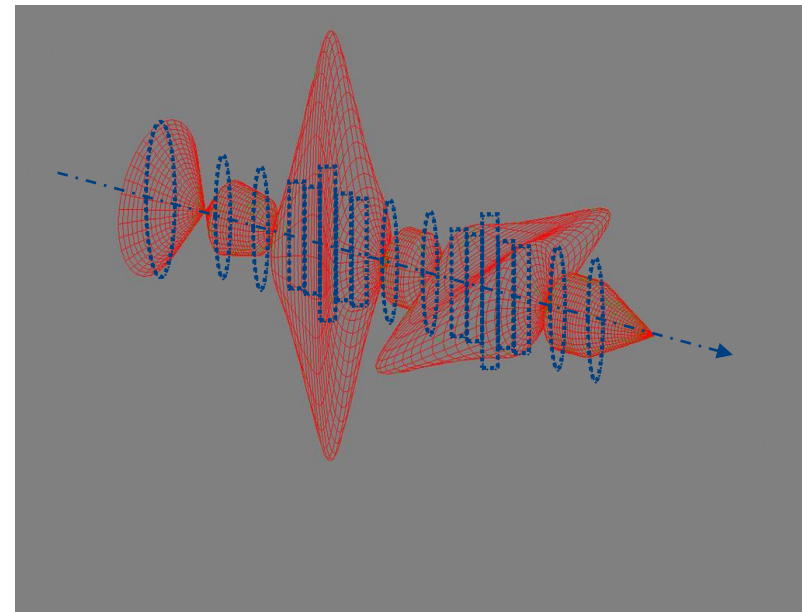
100s exposure time

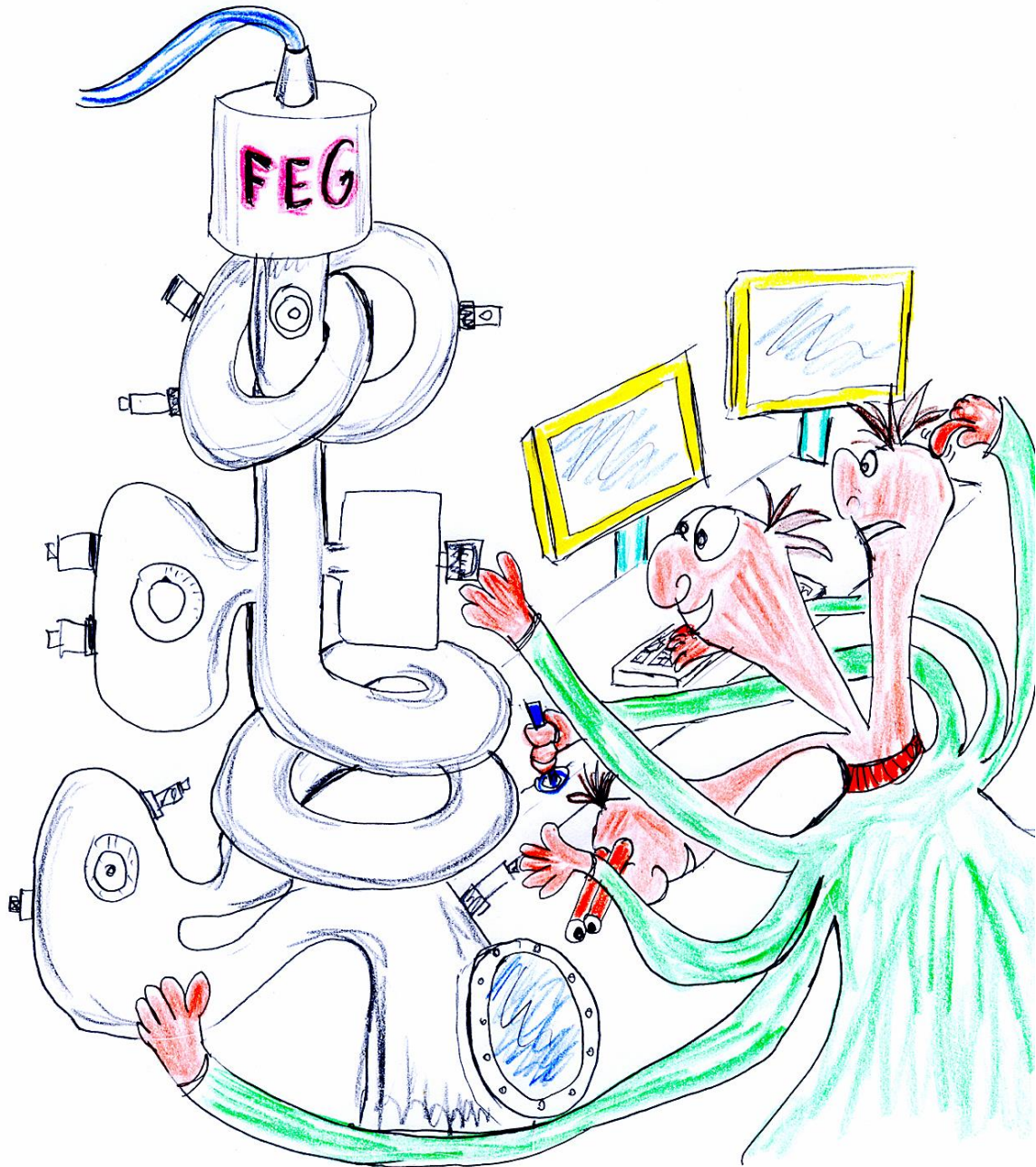
Fe-L

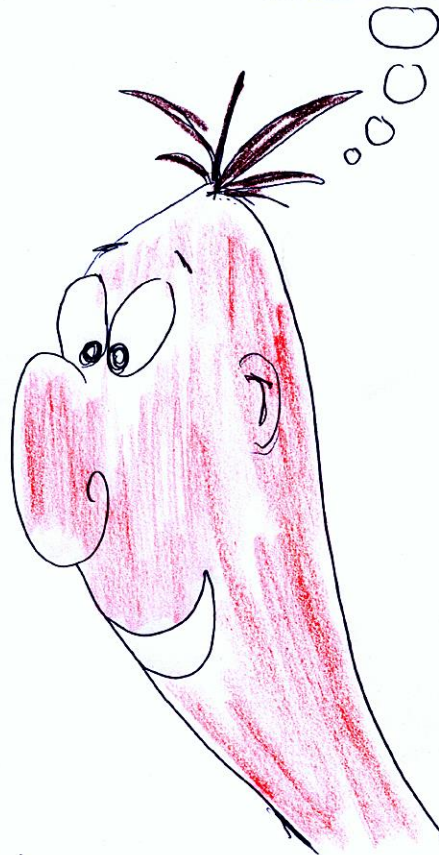
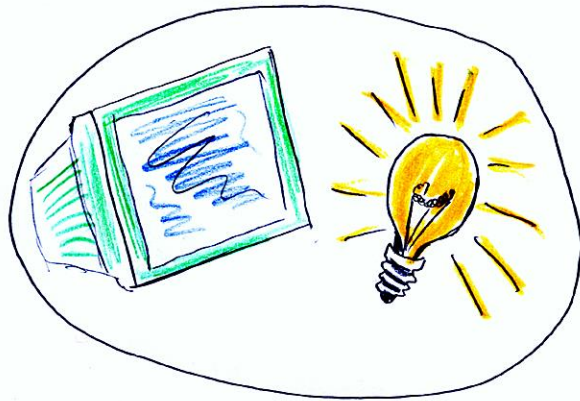


Conclusions

- Despite technical complexity, the Cc-corrector does not harm the TEM performance in any mode
- The resolution in many different TEM-modes can greatly be improved
- Low voltage HRTEM:
resolution improvement to 16λ
- Examples in spectroscopy:
atomically resolved
EFTEM + EFISTEM,
atomic scale EMCD







solution ...