EELS

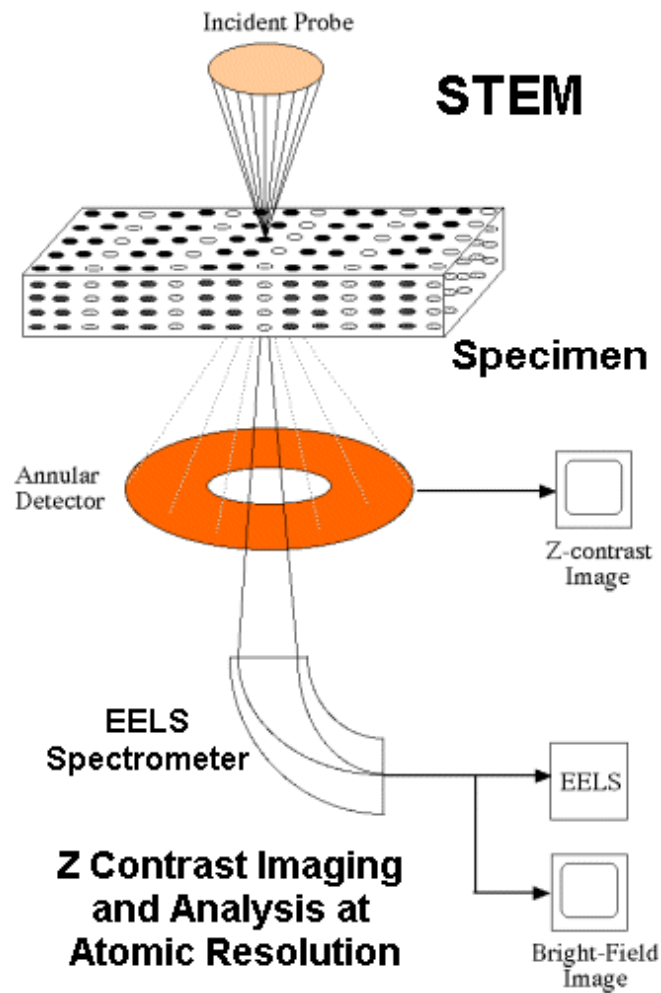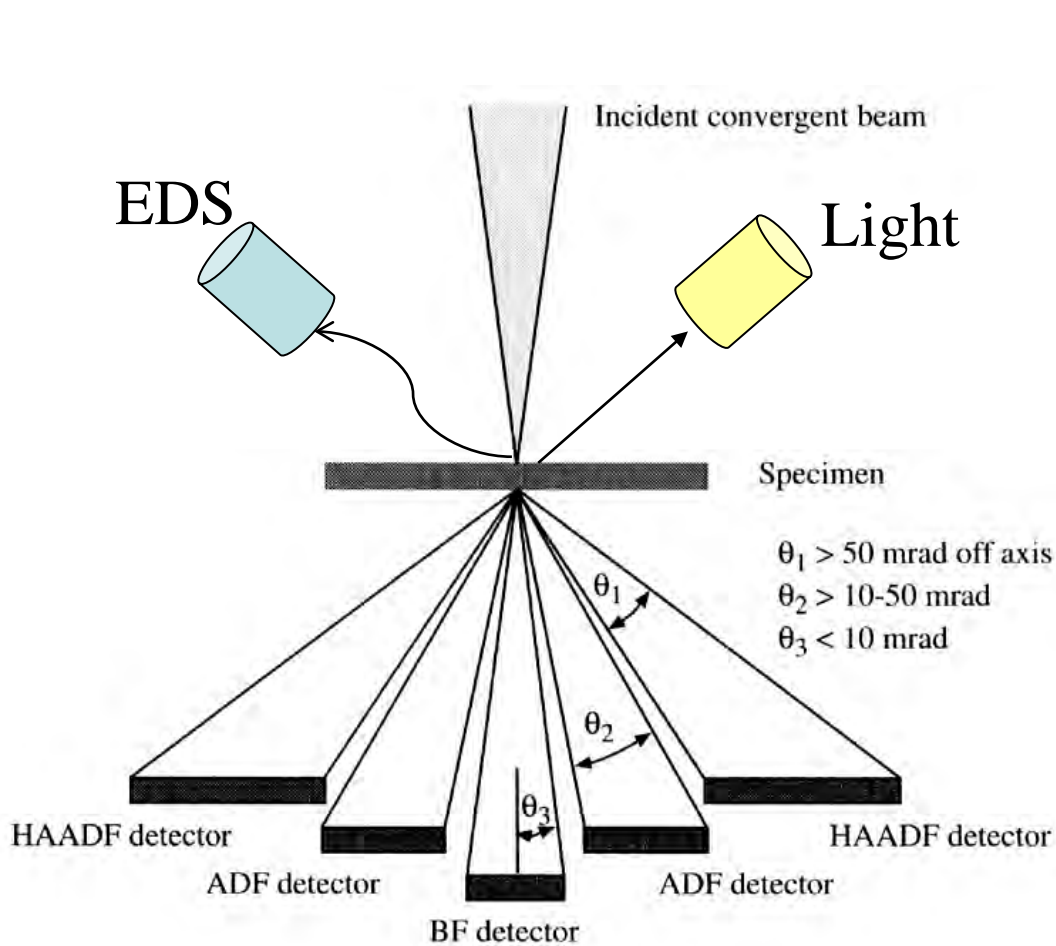## Electron Energy Loss Spectroscopy

(Thanks to Steve Pennycook, Quan Li, Charlie Lyman, Ondre Krivenak, David Muller, David Bell, Natasha Erdman, Nestor Zaluzec and others)
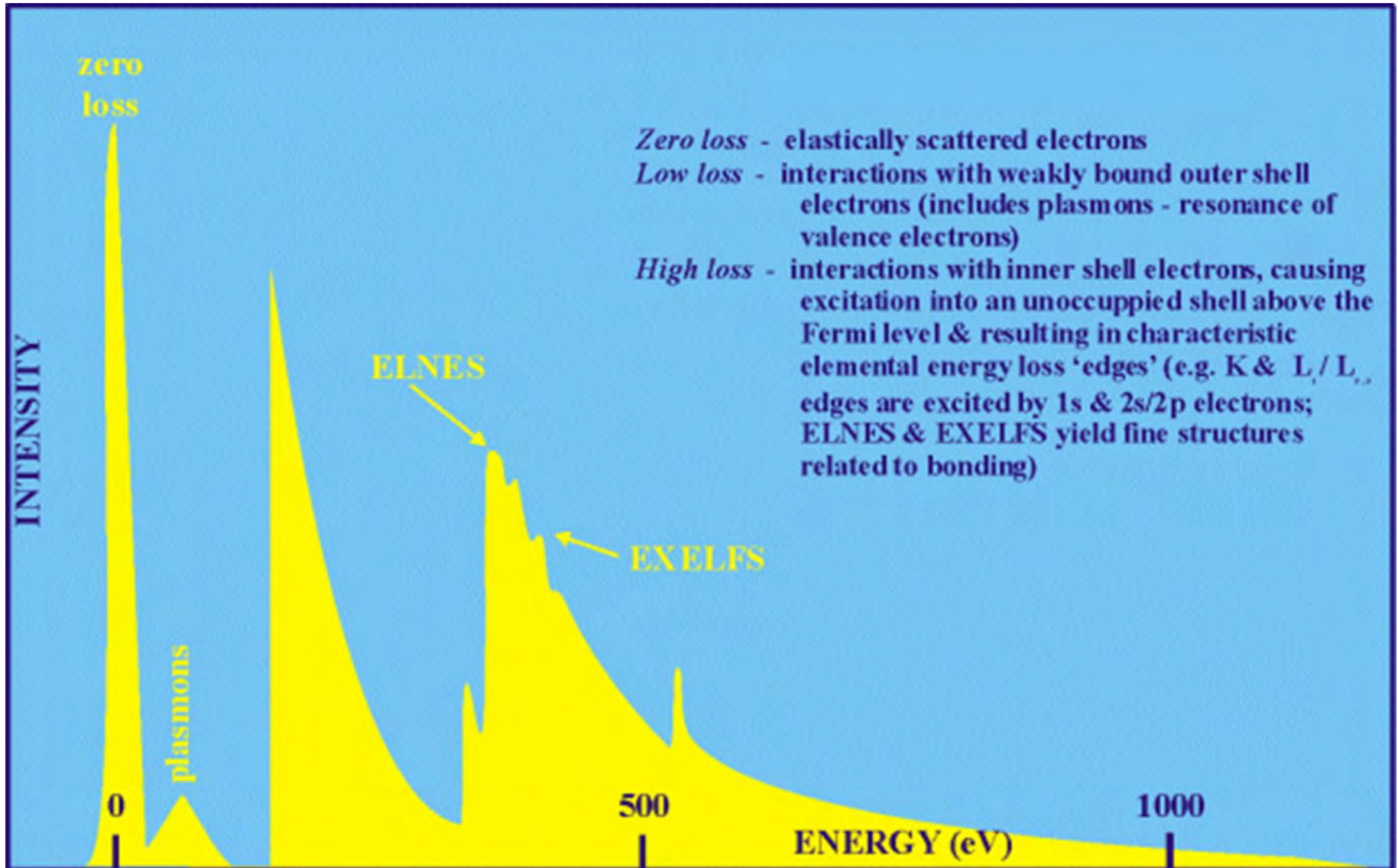
Generic Structure of STEM

Incident convergent beam

EDS

Light

Specimen

$\theta_1 > 50$ mrad off axis
$\theta_2 > 10\text{-}50$ mrad
$\theta_3 < 10$ mrad

θ_1

θ_2

θ_3

HAADF detector

ADF detector

BF detector

ADF detector

HAADF detector

Incident Probe

STEM

Specimen

Annular Detector

Z-contrast Image

EELS Spectrometer

Z Contrast Imaging and Analysis at Atomic Resolution

EELS

Bright-Field Image

What Matters?

Initial State	Final State/Detector
• Core Electron	• ~~X-ray~~
• Valence Electron	• ~~Light~~
• Selection Rules	• ~~Heat/Sound~~
• Bonding	• Electrons which have lost energy
• Local Environment	• Background
• Sample	• Efficiency for different elements/modes
	• $$ On detector

Spectrum

zero loss

plasmons

ELNES

EXELFS

Zero loss - elastically scattered electrons
Low loss - interactions with weakly bound outer shell electrons (includes plasmons - resonance of valence electrons)
High loss - interactions with inner shell electrons, causing excitation into an unoccuppied shell above the Fermi level & resulting in characteristic elemental energy loss 'edges' (e.g. K & L₁ / L₂,₃ edges are excited by 1s & 2s/2p electrons; ELNES & EXELFS yield fine structures related to bonding)

INTENSITY

0   500   1000

ENERGY (eV)

Comparison

- *EDS*
  - *Low collection efficiency (small solid angle)*
  - *Good peak/background*
  - *Good for high-Z elements*
  - *SEM (~500 nm) or TEM (~10 nm)*
  - *Stray x-rays in the column can be mistaken for trace elements*
- *EELS*
  - *TEM only & thin samples*
  - *High collection efficiency (~90%)*
  - *Poor peak/background (esp in thick samples)*
  - *Best for low-Z elements (large signals)*
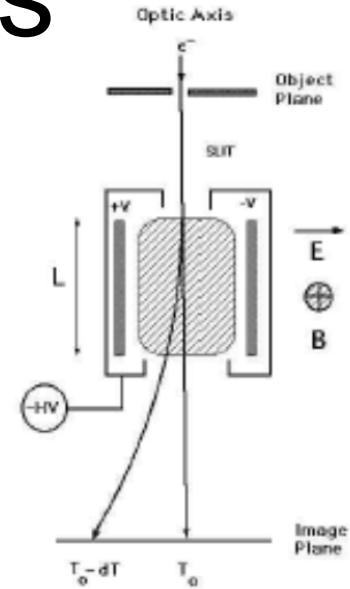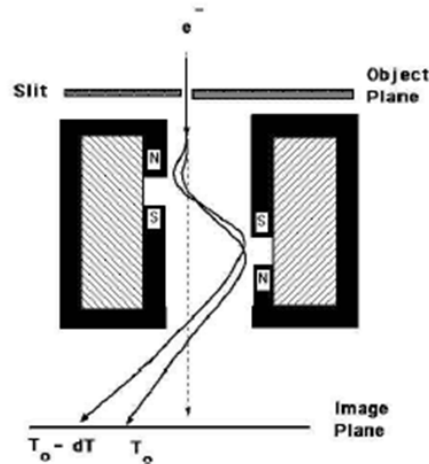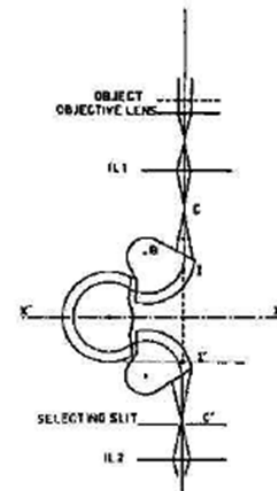 - *Bonding information for $Z < 33$*
  - *High spatial resolution (0.1 – 1 nm)*

Spectrometers

Mollenstedt Analyzer

Castaing-Henry Filter

Wien Filter

Cylindrical Magnetic Analyzer

Omega Filter

Nestor Zaluzec, ANL

entrance
aperture

QX QY
SX SY
ALIGN

90° prism

beam trap
aperture

photodiode
array

TE cooler

electrically
isolated
drift-tube

Q1 Q2 Q3 Q4
and
transverse
deflector

electron
shield

YAG
scintillator

fiber-optic
window

E_0

Objective
Aperture

2

1

3

4

$E_0 - \Delta E$

Dispersion
plane
(selection
slit)

25-hole mask

Retractable TV-rate camera

1k x 1k/2k x 2k/10k x 10k multiScan CCD camera

3rd-order filter aberration corrector

Large 5 mm entrance aperture

Pre-filter optical configuration

Patented
alignment mask

Dispersion and focusing section

Automated filter tuning
Mature application software

Projection section

MICROSCOPY suite

2nd-order corrected prism design

Multipole projector optics for optimum detector
coupling for EFTEM and EELS

High-speed CCD detector with unique cinema
mode for rapid EELS acquisition

Drift tube

Quadrupole/Sextupole/octupole lenses

Piezo-controlled energy-selecting slit

Electron energy filter/spectrometer configurations in TEM

Post-column filtering

In-column filtering

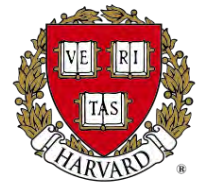bias electrode

filament

acceleration tube and beam deflection coils

electrostatic gun lens

condenser lenses, C1 & C2

STEM objective aperture

condenser stigmators and deflection coils (STEM scan coils)

condenser mini-lens (off)

specimen

objective lens (on), objective stigmator (on) and objective mini-lens (off)

deflection coils

collector aperture

post-specimen lens system, stigmator coils and deflection coils

removable annular dark-field detector

GIF for EELS, brightfield and energy-filtered CBED

FEG STEM at UIC

LIBRA 200® C_s and Monochromator

FEG
+ Monochromator

Condenser
(C1, C2 & C3)

Objective

C_S Corrector

Projector 1
(P1, P2 & P3)

Corrected
Omega Filter

Projector 2
(P4, P5 & P6)

Viewing chamber
+ Detectors

Monochromator

CEOS
Corrected Electron Optical
Systems GmbH

dispersive
plane (slit)

• Dispersion free
• Ease of use
• 30% of intensity at
0.2eV

Nion U-HERMES™* STEM and Iris EELS

*__U__ltra-__H__igh __E__nergy __R__esolution __M__onochromated __E__ELS-__S__TEM

Iris spectro-meter

Side-entry stage with liquid N2 cooling

C3-C5 aberration corrector

Nion monochromator

100 or 200 kV CFEG

Chromatic Correction (12-poles)

Prism

Beam trap (motorized)

Dispersion magnification (constant power)

Interface/ Geometric Correction (16- and 12-poles)

Optional Detectors

Primary Detector

Iris high resolution electron energy loss (and gain) spectrometer

The EELS and the monochromator employ extensive aberration correction and several stability-enhancing schemes, and reach better than 1 in 10^7 stability .

Experimental XEDS, XPS, and EELS data from the Copper L shell. Note the differences in energy resolution, and spectral features.

Nestor Zaluzec, ANL

Energy Levels and Energy-Loss Spectrum

from Williams and Carter, *Transmission Electron Microscopy*, Springer, 1996

Basic formalism I

- Ignore diffraction effects, not really right but OK for now
- Consider inelastic scattering as completely incoherent – 99% correct
- Ignore relativistic effects, not correct and over the last decade they have been shown to be critical
- Assume that processes are not dependent upon the electron energy, good for swift electrons
- Consider a simple probability P(dE,q), for dE change in energy and q wavevector change
- Many simplifications if we integrate over all q, collection angle (experimental variable)

Basic Geometry of EELS

Loss
Probability
$P(dE, q)$

Incident
electron

Loss
electron

q,
almost
normal

Basic formalism II

$$\frac{dI(E,q,z)}{dz} = \int I(E - E', q - q', z)P(dE', dq')dE'dq'$$

Simplest case when energies do not overlap leads to a Poisson distribution solution:

$$I(E, q, t) = \exp\left(-\frac{t}{\lambda}\right)\delta(E) + tP(dE, q)\exp\left(-\frac{t}{\lambda}\right)\delta(E - dE) + \cdots$$

$$I(E - ndE, nq, t) = \left(\frac{1}{n!}\right)t^n P^n(dE, q)\exp(-t/\lambda)$$

$$1/\lambda = \int P(dE, q)dEdq$$

We call λ the mean free path. Note that the zero-loss peak has an intensity of exp(-t/λ), so if we divide by this we get tP(dE,q) for single scattering

With multiple scattering the result is slightly more complicated, but one can do a log deconvolution to clean up the data

Al specimen

Plasmon Peaks

A

Thin sample

I_0

I_P

B

Thick sample

I_0

I_{P_1} I_{P_2} I_{P_3}

Figure 38.2. (A) The low-loss spectrum from a very thin sample of pure Al showing the intense zero-loss peak (I_0) and a small plasmon peak (I_P) at about 15 eV. (B) The low-loss spectrum from a thick specimen of pure Al showing several plasmon peaks.

$$I(E - ndE, nq, t) = (\frac{1}{n!})t^n P^n(dE, q)\exp(-t/\lambda)$$

Basic formalism III

$$Probability = C \int \psi_{initial} \, \hat{O} \psi^*_{final} \, dr$$

Interaction Term

Depends upon how many initial states there are, $\psi_{initial}$, and final ψ^*_{final}.

Also, there are effects due to removal of an electron from the initial state which leads to a core-hole, and relaxation of the electrons

Energy Levels and EELS

Plasmons

- Coulomb interaction between fast electrons of microscope & electrons in solid

- Creates a shock wave (similar to a ship through water)

- Resonant frequencies of bulk electrons leads to plasmon losses – also dielectric components

e

Shock Wave

Al → free electron metal

Fe → Transition metal

1b Plasmon peak

NiO – ZrO$_2$ interface

NiO

ZrO$_2$

6 nm interface

Ni M$_{2,3}$

+3.0 nm

+1.8 nm

+0.6 nm

−0.6 nm

−1.8 nr

−3.0 nr

Inter- and Intra Band Transitions

Low loss spectrum from Al and Al compounds
→ The differences in the spectra are due to differences in bonding

Band gap differences manifesting itself in the low loss region of the EELS spectrum

1a Low loss region before Plasmon peak

Intraband transition characteristic of Polystyrene

Core Losses

Idealized edge

Edge superimposed on plural scattering

Bonding Effects

EXELFS

ELNES

Diffraction Effects from atoms surrounding the ionized atom

Thick Specimen → Combination of ionization and plasmon losses

Ionization loss

Plasmon loss

Transmission Electron Microscopy by David B. Williams and C. Barry Carter, Plenum Press, New York, 1996.

Near edge structure

- Depends upon
  - Dipole rule ($\Delta l = \pm 1$)
    - Hence s$\rightarrow$ p, p$\rightarrow$d but not s$\rightarrow$s
  - What states are open
    - Changes with valence and bonding

Extended structure

Photoelectron

Back Diffraction – constructure or constructive

The L edge of transition metals (d-level occupancy)
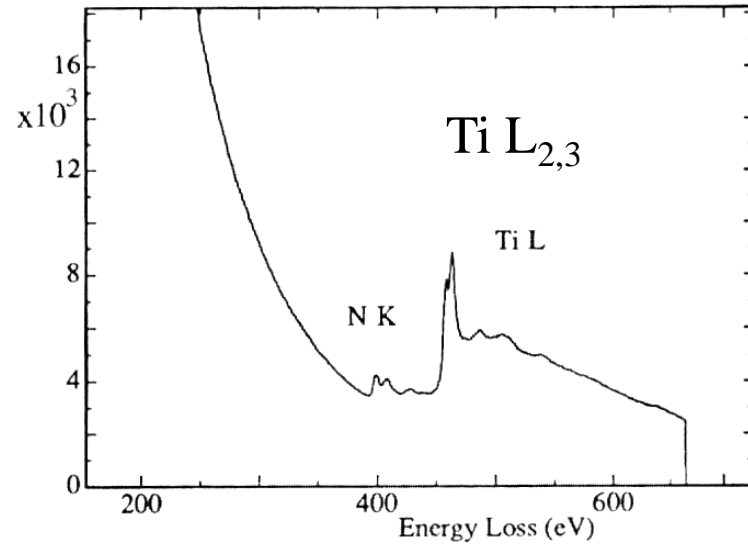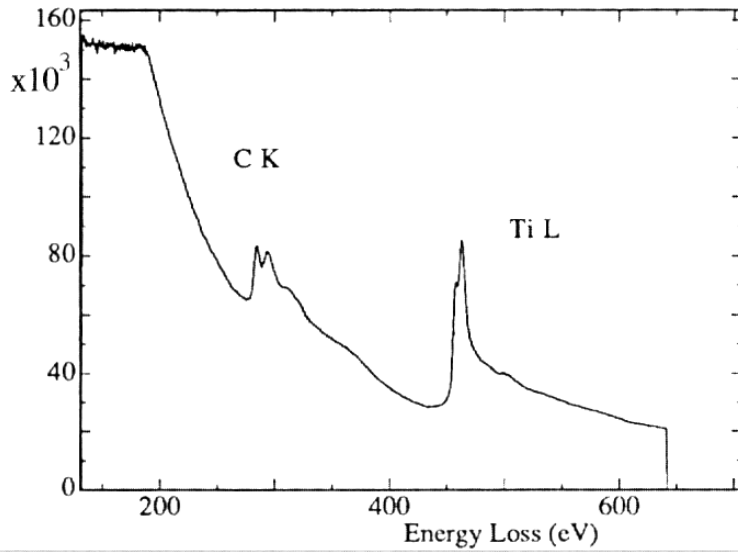
Chemical bonding

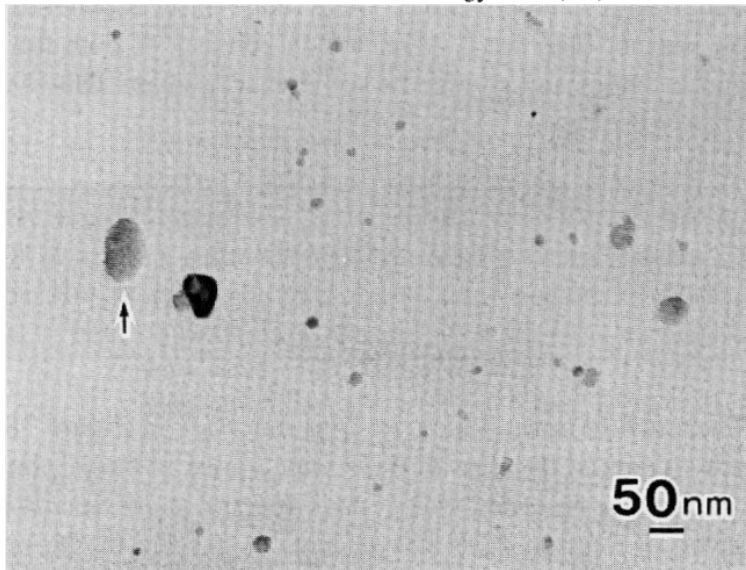**Cu is d^{10}, no states available
In CuO, there are empty levels**

Diamond, graphite and fullerene all consist of only carbon. All of these specimens have absorption peaks around 284 eV in EELS corresponding to the existence of carbon atoms. From the fine structure of the absorption peak, the difference in bonding state and local electronic state can be detected. The sharp peak at absorption edge corresponds to the excitation of carbon K-shell electron (1s electron) to empty anti-bonding π -orbital. It is not observed for diamond, because of no π bonding.
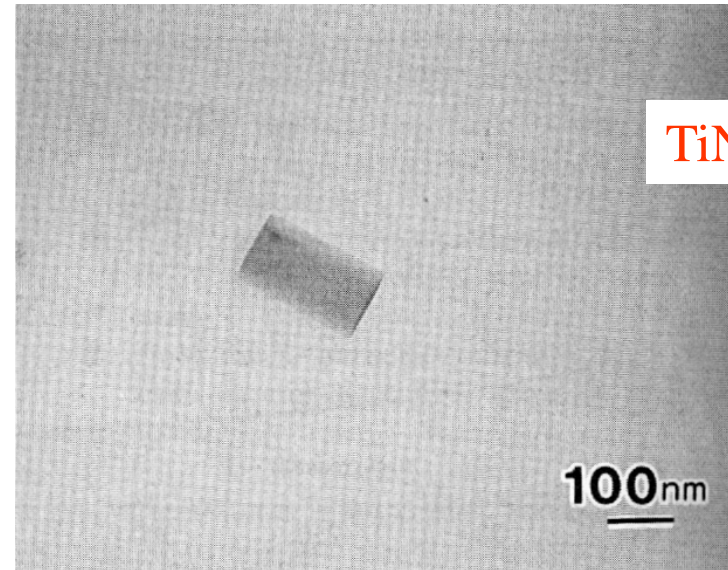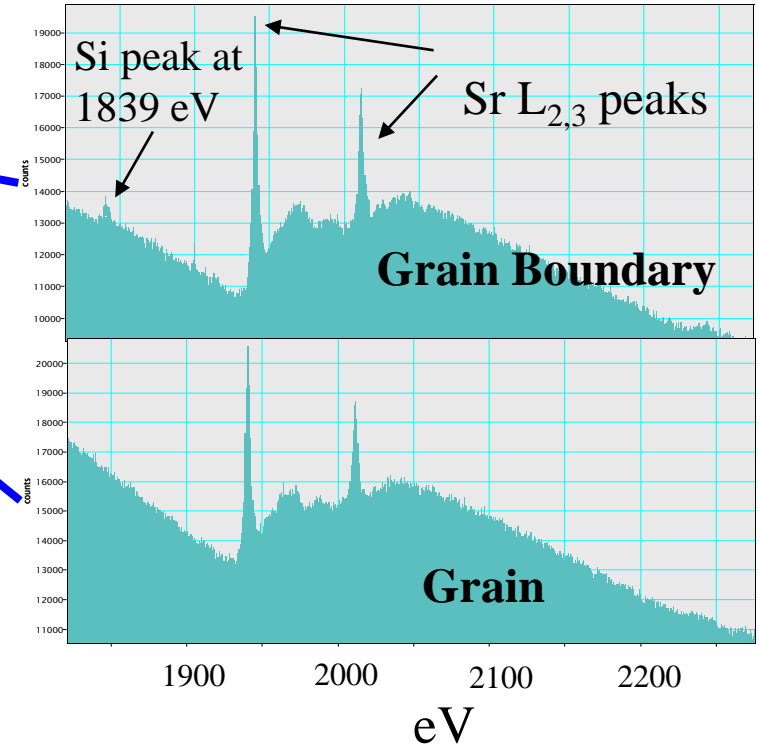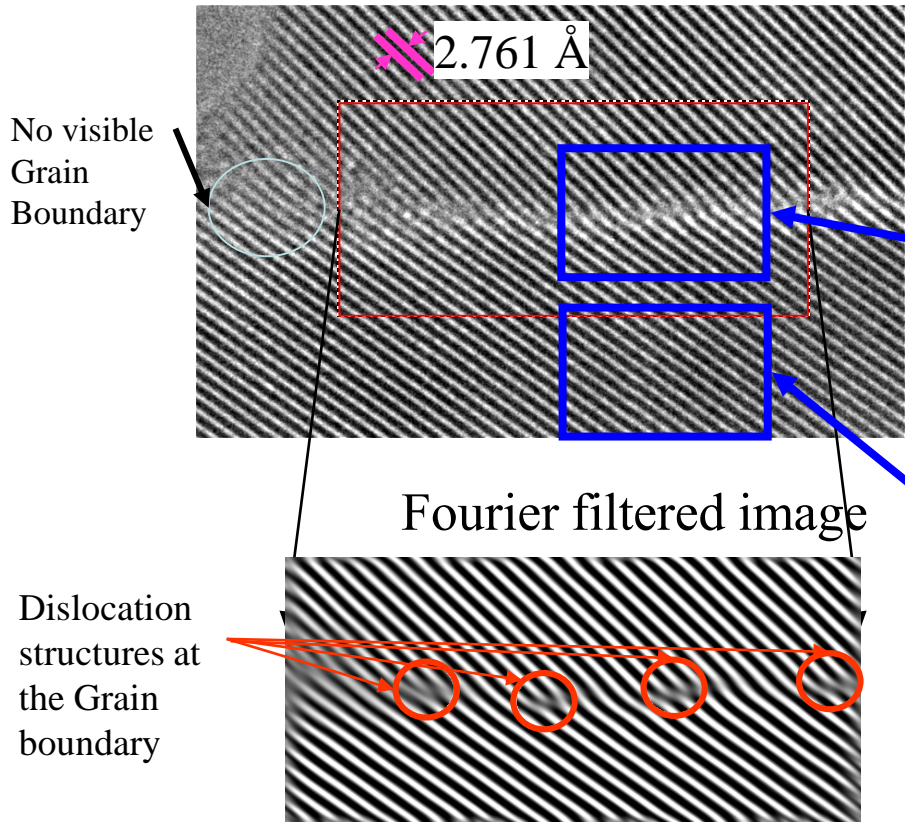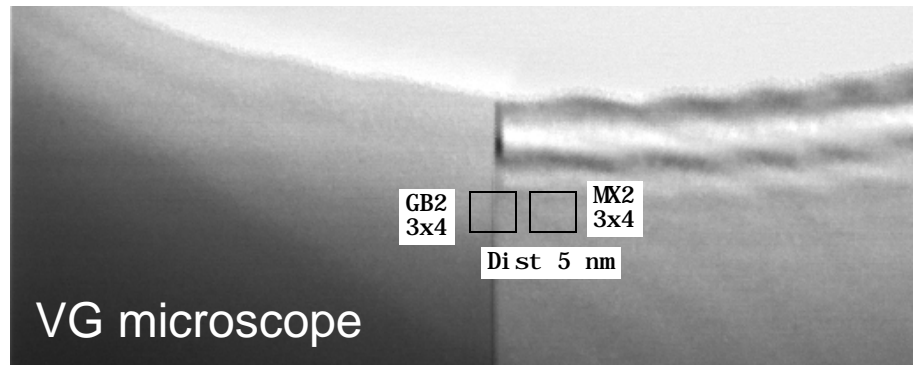
Examples

TiC

TiN

Stainless steel specimen

Transmission Electron Microscopy by David B. Williams and C. Barry Carter, Plenum Press, New York, 1996.

EELS

No visible Grain Boundary

2.761 Å

Si peak at 1839 eV

Sr $L_{2,3}$ peaks

Grain Boundary

Fourier filtered image

Dislocation structures at the Grain boundary

Grain

1900   2000   2100   2200

eV

~8° TILT BOUNDARY IN THE SrTiO$_3$ POLYCRYSTAL

GB2 3x4   MX2 3x4

Dist 5 nm

VG microscope

Single Ba$_x$Sr$_{1-x}$TiO nanocube EELS

7 nanocubes are detected as EELS, and the Ba/O=0.16-0.19
Ti/O=0.33-0.36, X average value is close is 0.5.

Relative quantification:

Elem.	Atomic ratio (/)
Ti	0.33 $\pm$ 0.046
O	1.00 $\pm$ 0.000
Ba	0.15 $\pm$ 0.022

Elemental mapping

Three-window method

- **W3 / (W1 +W2) = Elemental map**

Window 1

Window 2

Window 3

What is Spectrum Imaging?

- Spectrum imaging is the technique of acquisition, storage, processing, and analysis of spectroscopic data at each pixel in a digital image
- Conventional image pixels contain one intensity value only
- Spectrum image pixels contain complete spectra
- Produces quantitative elemental maps and profiles

Spectrum image schematic:

Δx, Δy Spatial dimensions
ΔE Energy-loss dimension

Vertical columns are spectra

Horizontal planes are energy filtered images

Δx
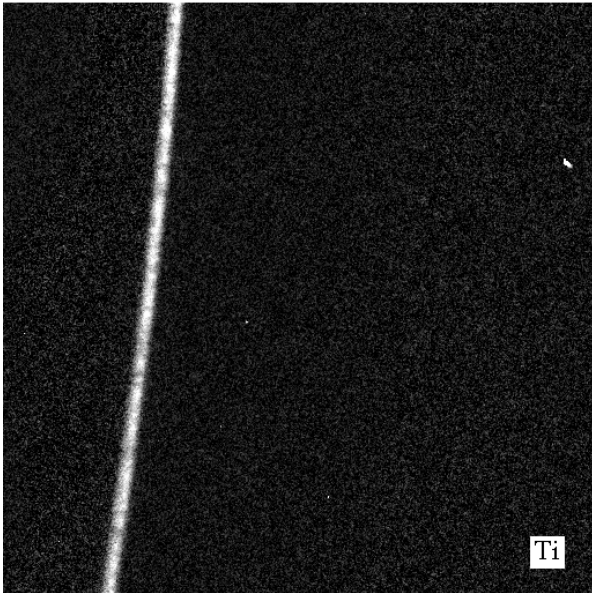
Δy

ΔE

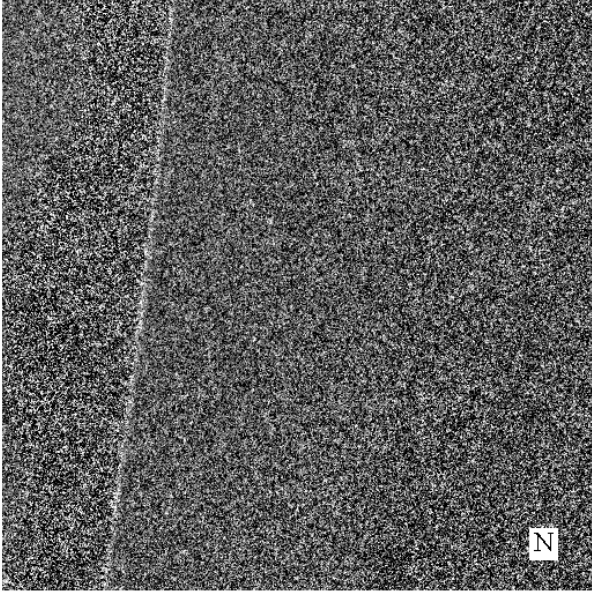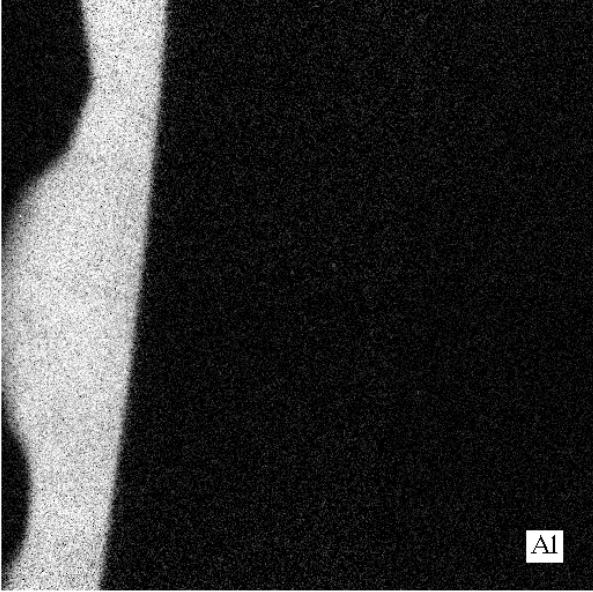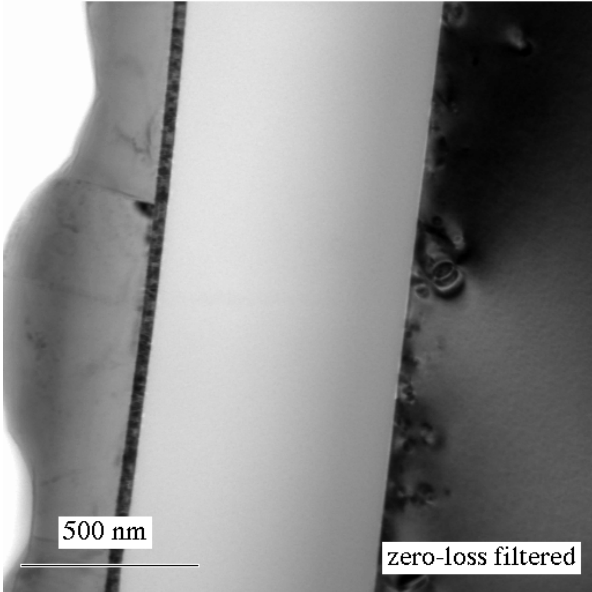spectrum at pixel Δx_i, Δy_i
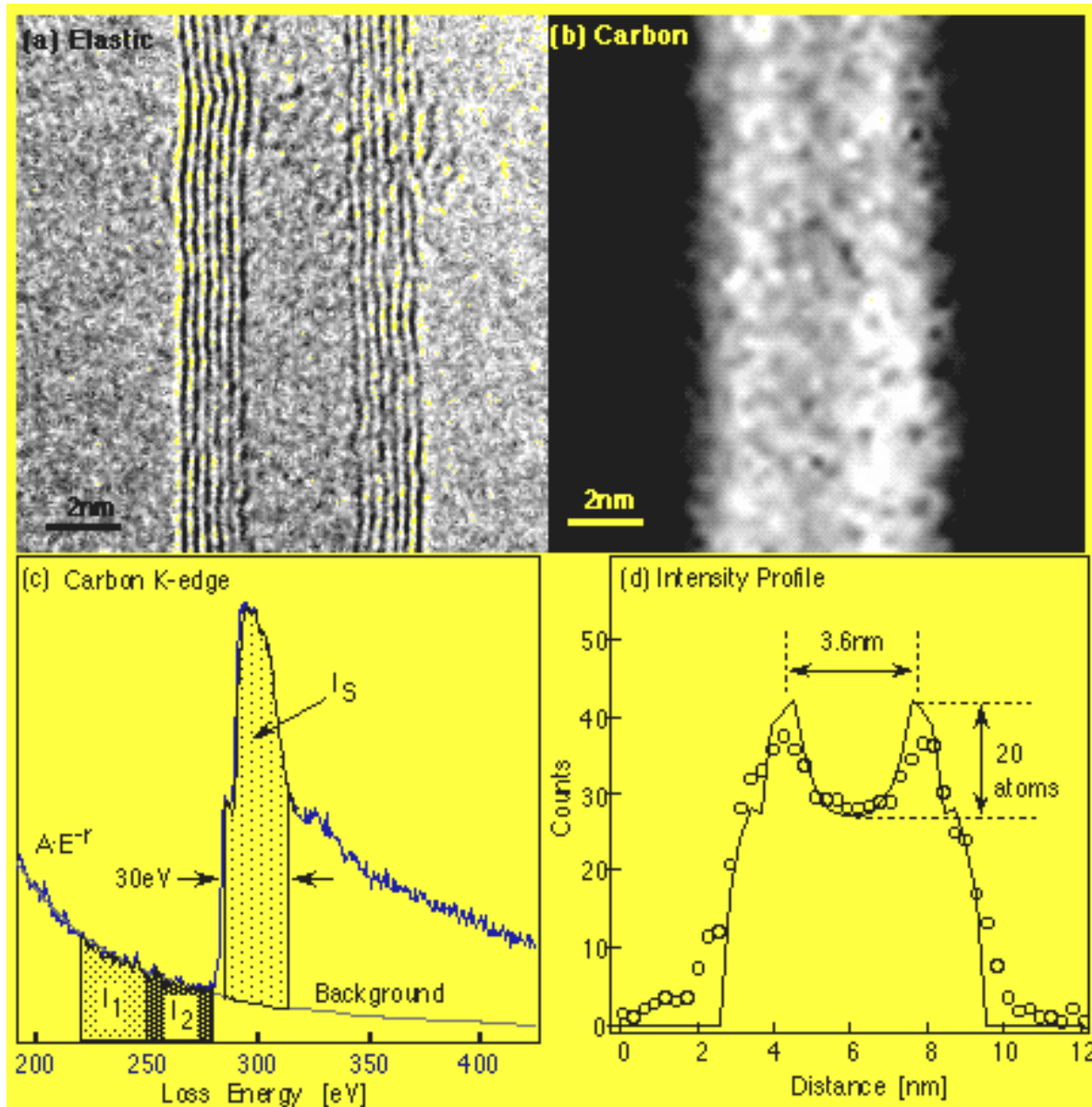
gatan

Acquisition of Spectrum Images

- A spectrum image is typically acquired in STEM mode by stepping a focused electron probe from one pixel to the next

- The spectrum image data cube is filled one spectrum column at a time

- In STEM it is possible to collect EELS, X-ray or both spectra simultaneously

- Use of the DF or SE signal during acquisition permits spatial drift correction and assurance that information is coming from the desired area
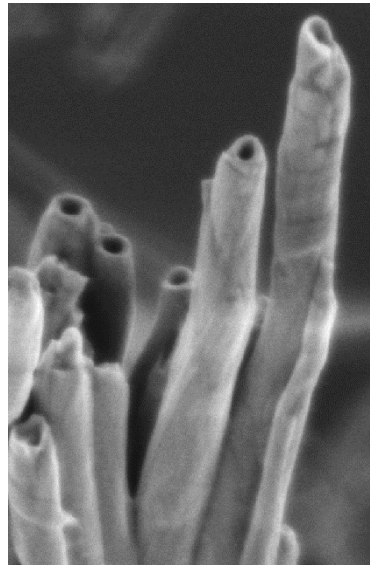
EDX

STEM

DF

EELS

gatan

Multilayer coating

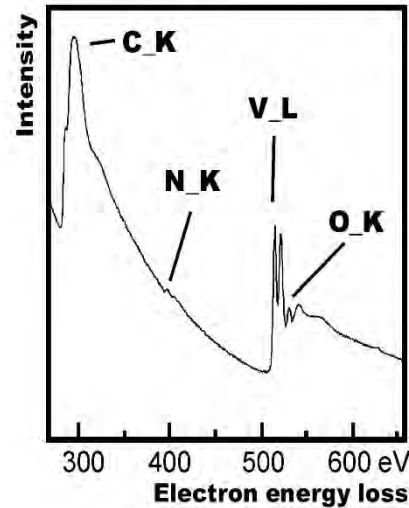500 nm

zero-loss filtered

Al
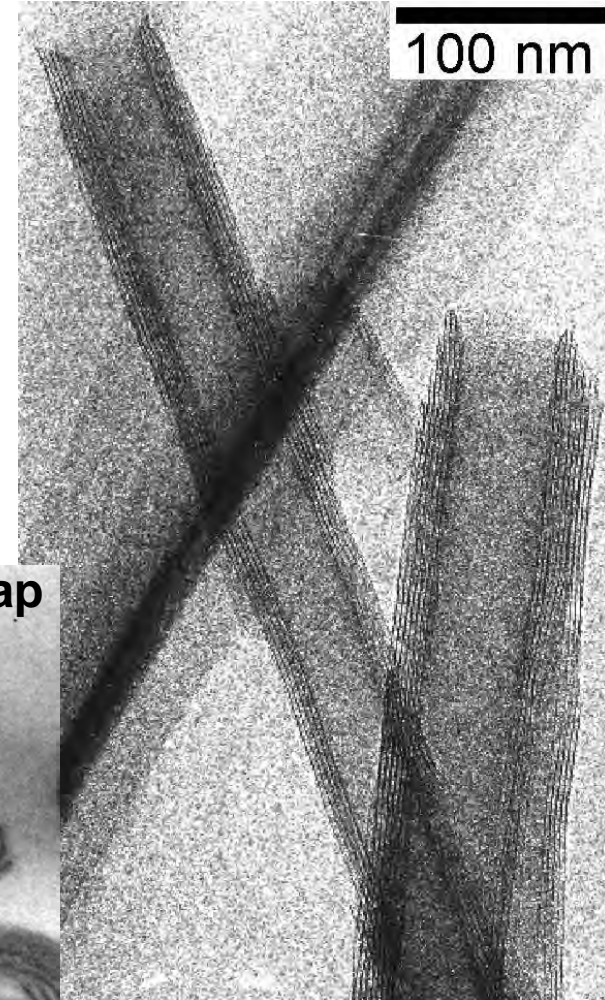
N

Ti

O

Si

Carbon Nanotube

Electron Microscopy Methods for the Characterization of Nanomaterials
(Example: Vanadium Oxide Nanotubes)
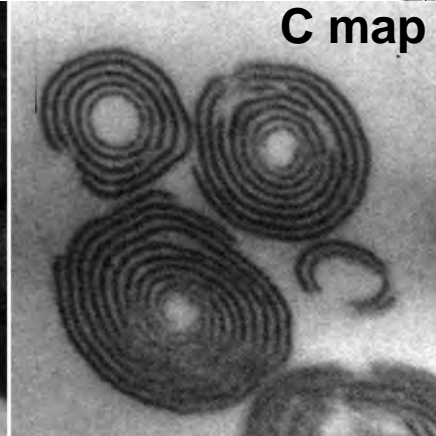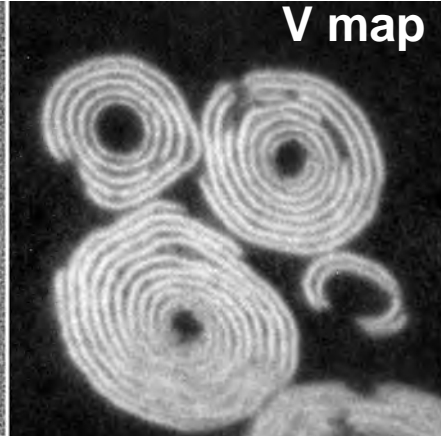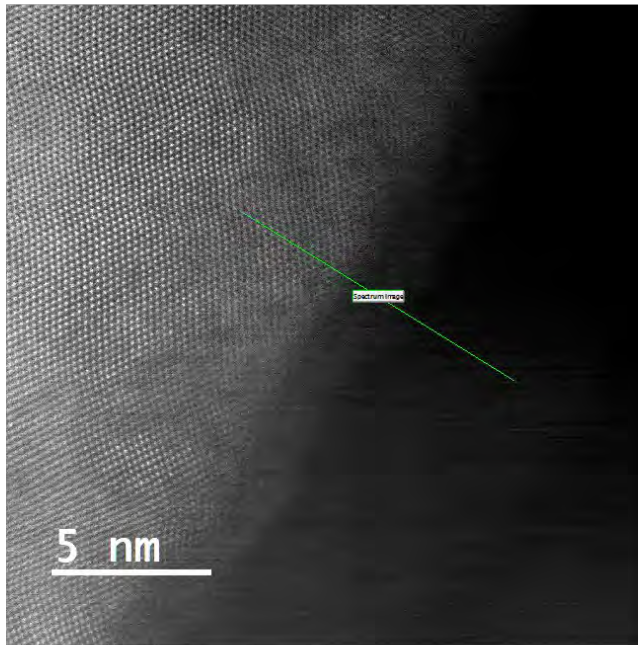

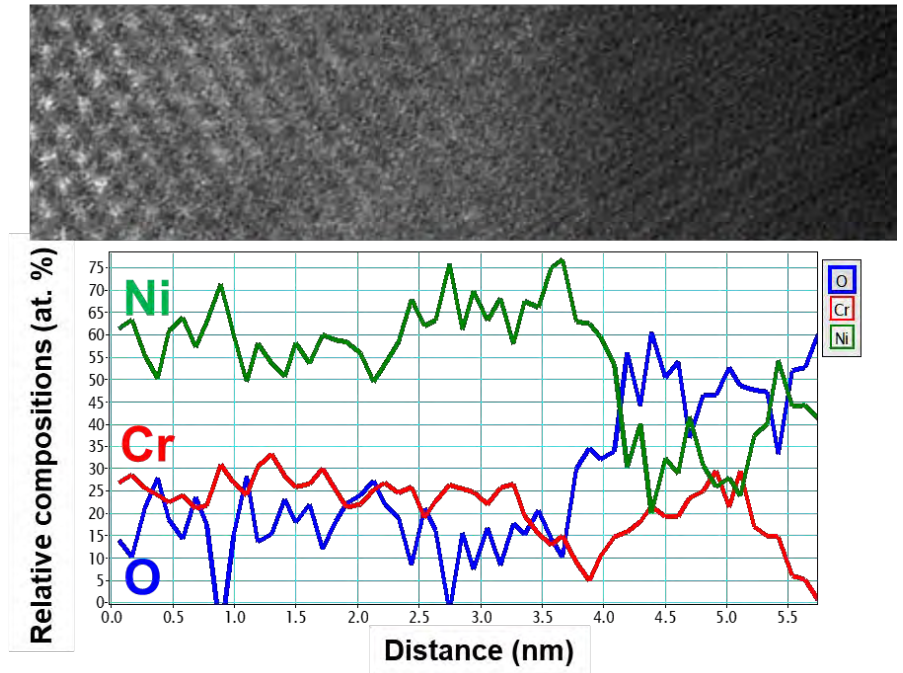SEM: characterization of tubular morphology

EELS: composition

V map

C map

100 nm

50 nm

Cross-sections of VO_x nanotubes: TEM and elemental maps obtained by electron spectroscopic imaging

TEM: characterization of the wall structure

NiCr Oxidation

Column-by-column EELS?

Dynamical effects
Beam broadening
Localization
Interpretation

Scanned Incident Probe

Specimen

ADF

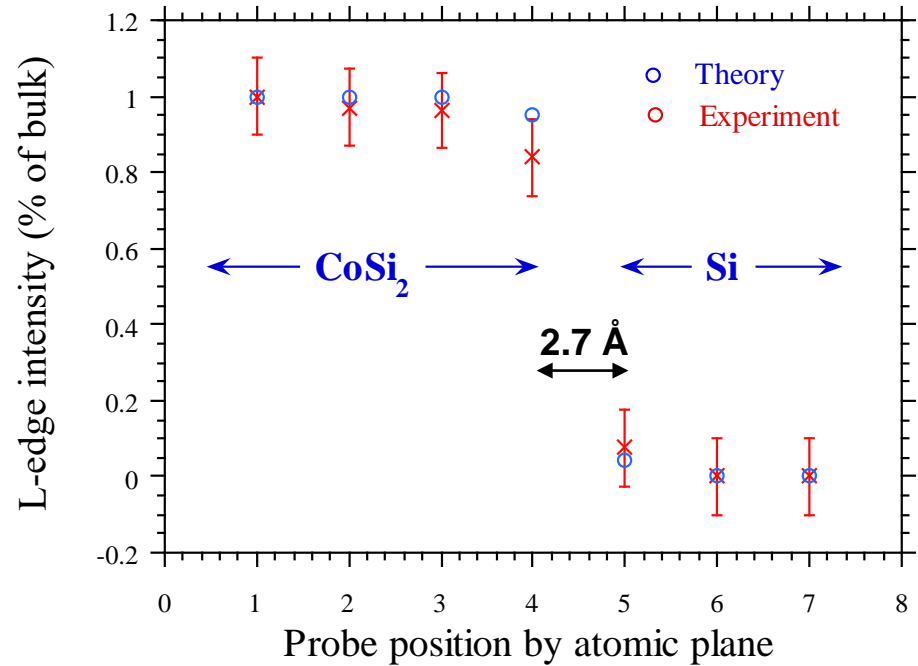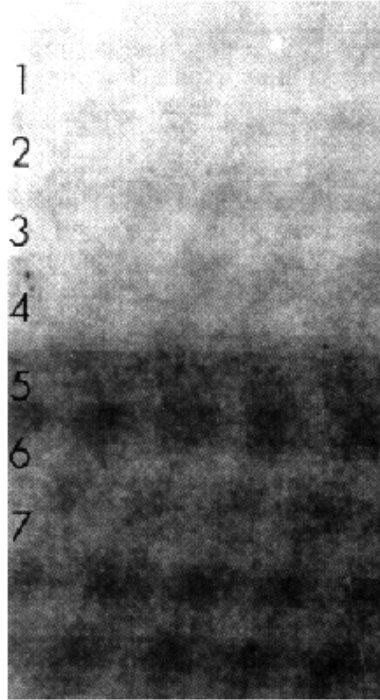Column by column image

IBF = 1-ADF

Prism

EELS

Column by column EELS?
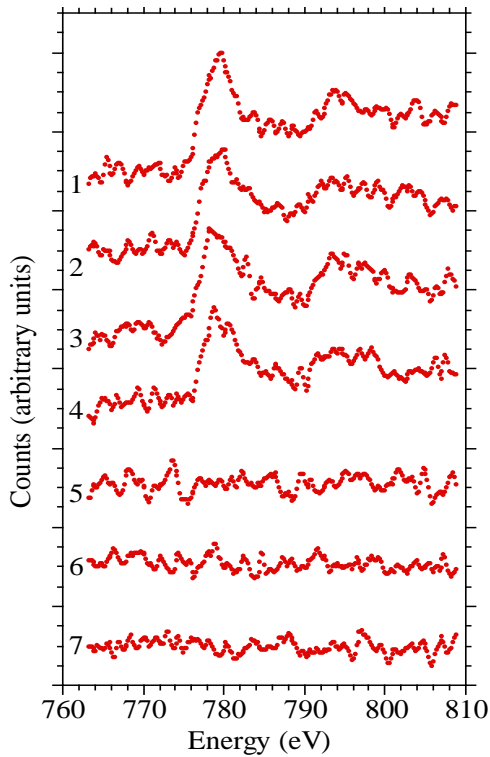
Atomic resolution chemical analysis

– **Edge resolution test on CoSi$_2$/Si(111) interface**

– **VG Microscopes HB501UX, 100 kV, ~ 2.2 Å probe**

Browning, Chisholm, Pennycook, Nature 1993

Single Atom Spectroscopy

Scanned Probe

M. Varela, et al., Phys. Rev. Lett. 92 (2004) 095502

La-doped $CaTiO_3$

Annular Detector

$I \propto Z^2$

EELS Spectrometer

5 Å

La $M_{4,5}$

Intensity

820   850   880

Energy (eV)

EELS ~ XAS with atomic resolution and sensitivity to 1 atom

~ STM but below the surface

An example

D. A. Muller, Nature 399, 58 (1999)

Chemical Imaging in 2D
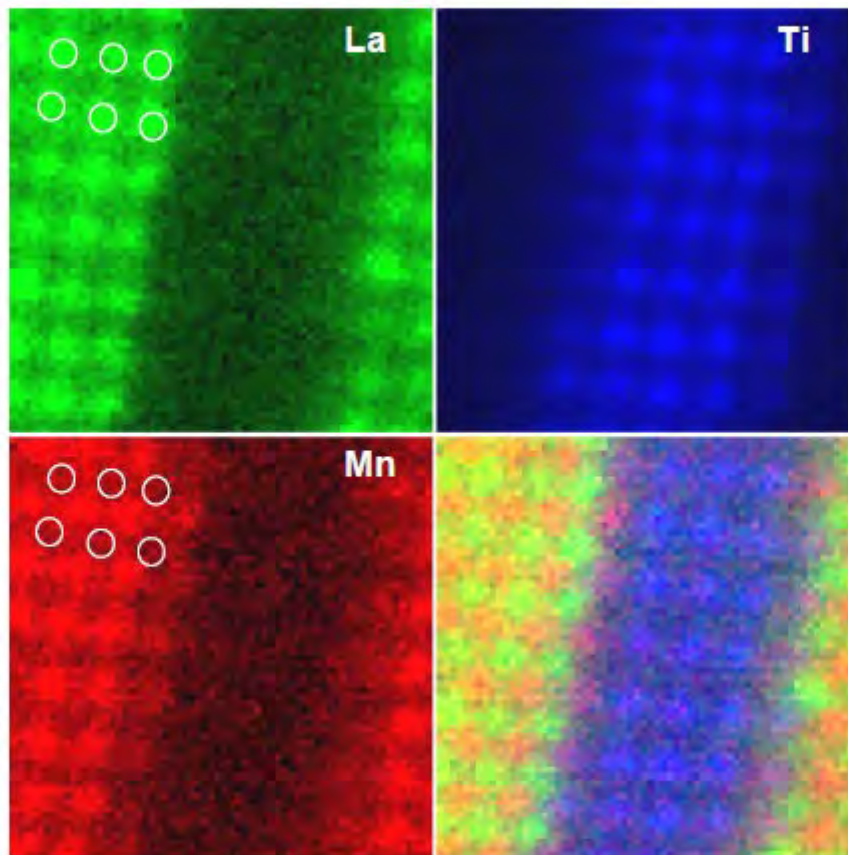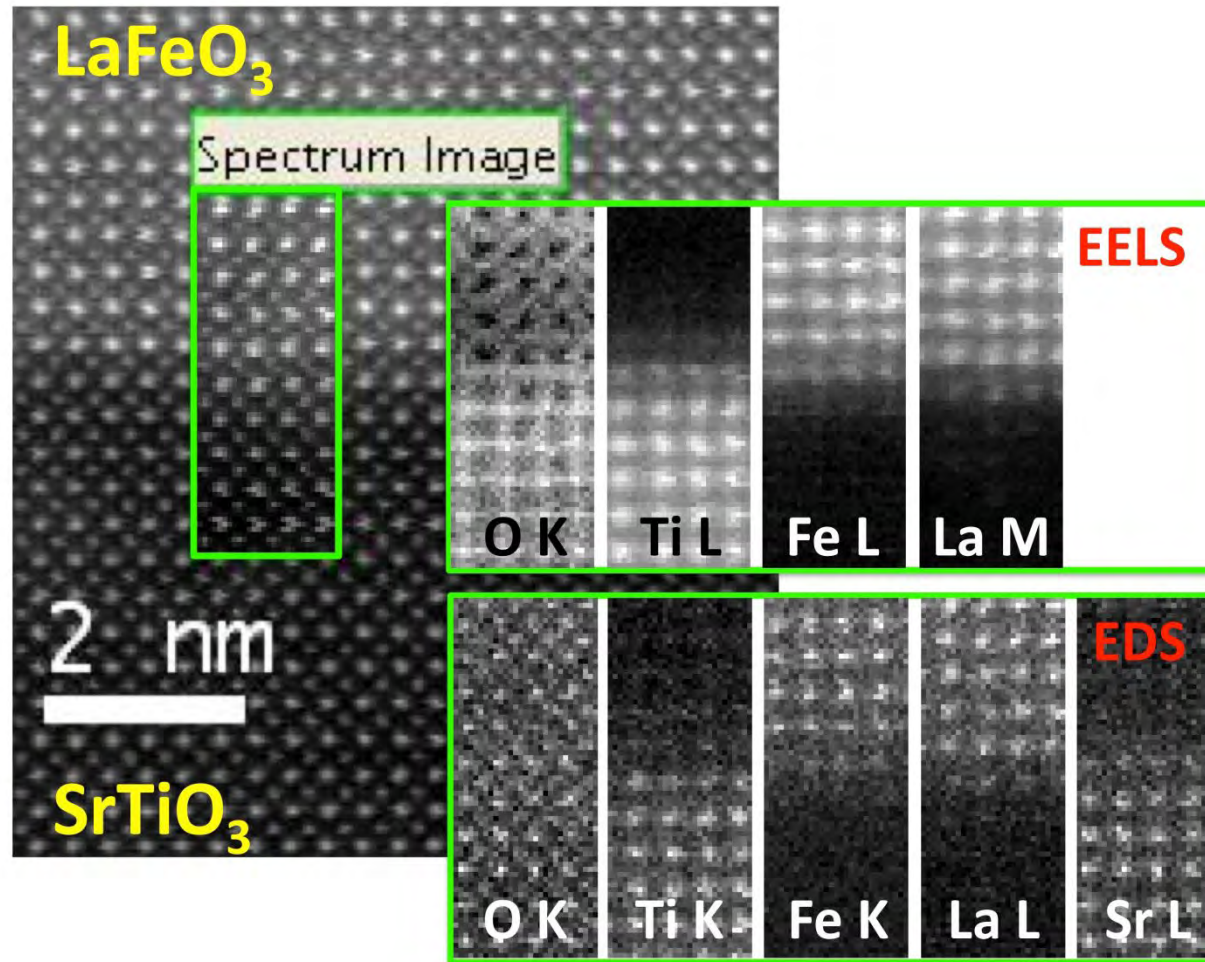
(Integrated counts above background)

EELS map
Of $LaMnO_3/SrTiO_3$
recorded
on the Nion SuperSTEM

28 seconds live time
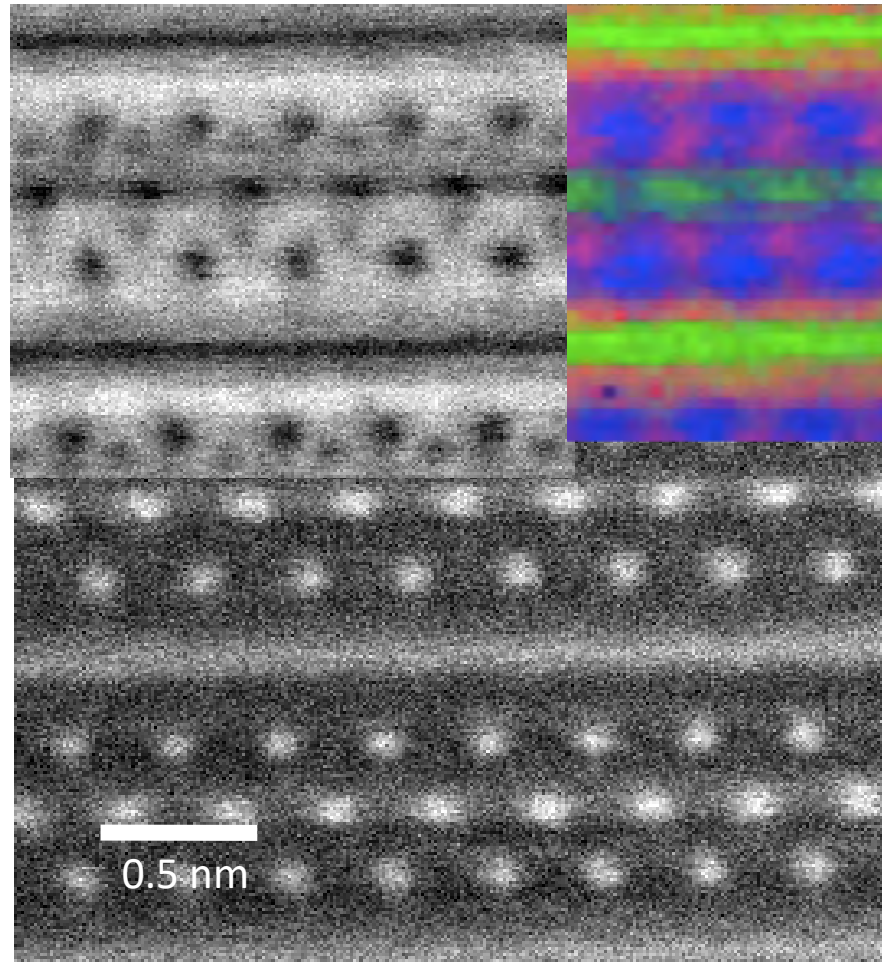(10 seconds overhead)

David Muller 2006

30

Atomic resolution EELS and EDX

Simultaneously acquired EELS and EDS maps from a LaFeO3/SrTiO3 interface. Principal component analysis was used to remove random noise. Data acquired in aJEOL JEM-ARM200F at 200 kV, courtesy of E. Okunishi (JEOL) and M. Varela (ORNL). Sample courtesy of Jacobo Santamaria's group (Complutense University, Spain).

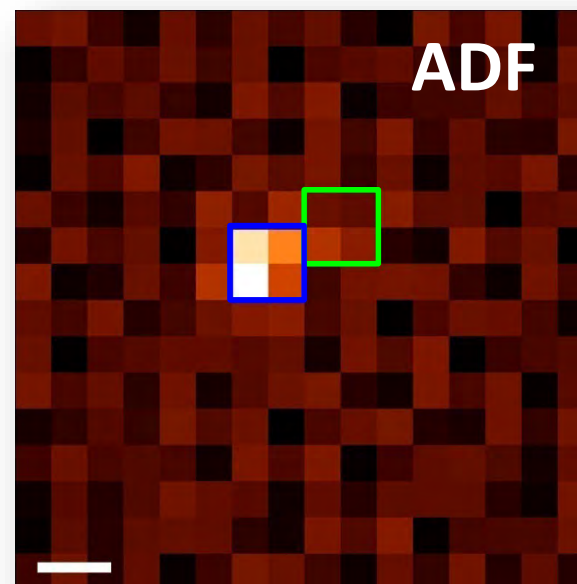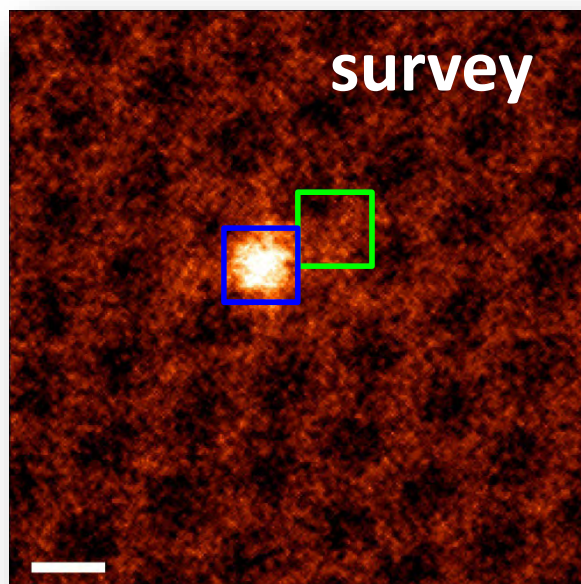# Atomic resolution Imaging and EELS map with High Energy Resolution

$Ca_3Co_4O_9$ (110)

Annular Bright Field (ABF)

HAADF

EELS SI

- Ca (blue)
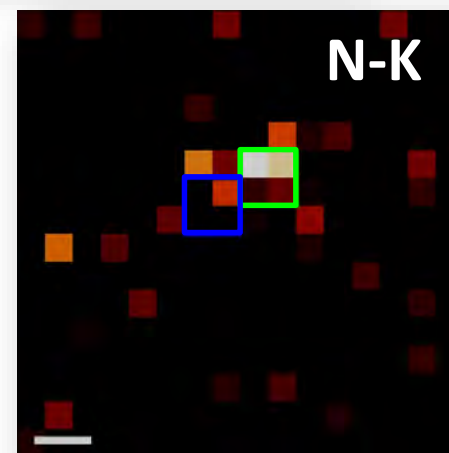- Co (green)
- O (red)

0.5 nm

Data courtesy of Dr. Robert Klie, University of Illinois at Chicago

Atom by atom spectroscopy

Zhou, W., Lee, J., Nanda, J., Pantelides, S. T., Pennycook, S. J., & Idrobo, J.-C. (2012). Atomically localized plasmon enhancement in monolayer graphene. *Nature nanotechnology*, *7*(3), 161–165.

Materials Science and
Engineering and Scientific
User Facilities Divisions

Bonding of single Si atoms in the graphene lattice

Some 3*d* states in Si-C$_4$ structure are missing!

Monochromator / Energy-Filter Performance

No Monochromator @ 200KV

FWHM=
600 meV

FWHM=
81 meV

FWHM=
62 meV

Monochromator 1um Slit @ 200KV

Monochromator 1um Slit @ 80KV

Schematic of the Nion high resolution monochromator

Full description in: Krivanek et al., Phil. Trans. R. Soc. **A 367** (2009) 3683.

un-dispersed outgoing beam

EELS 1

energy-dispersed beam

Energy dispersion at slit is variable from ~ 2 μm/eV to ~ 200 μm/eV

EELS 2

monochromated beam

incoming beam

The Nion monochromator is equivalent to 2 parallel EEL spectrometers arranged back-to back, with an energy-selecting slit in the mid-plane, plus (next slide):

More recent zero loss peaks

Two zero losses 500 meV apart

Nion UltraSTEM100™ with monochromator
Gatan Enfinium EELS
60 keV, 0.2 sec acquisition time
3 meV/channel EELS energy dispersion
500 meV square wave on EELS drift tube

31 meV

ZLP, UltraSTEM100™ MC
2 msec acq. time

19 meV

MC in final position, stabilization schemes not yet connected up.

Stabilization scheme 1 connected, but not making much difference: short exposure time is needed to avoid broadening the ZLP.

The instability is due to elements outside the stabilization scheme, e.g. the quadrupoles of the MC or the quads of the EELS. The probe on the sample does not jitter, and this points to the EELS as the source of the problem.

nion

Vibrational EELS.

nature

STEM Imaging and EELS spectra of MgO cubes

nature

Phonons due to a *single Si atom* in graphene

EELS aperture

EELS collection schematic

Si atom (HAADF image)

theory (graphene spectrum in grey)

experiment

*Hage et al., Science **367** (2020) 1124–1127*

Phonon spectrum of a single Si atom has been recorded.

EELS Theory

In the first Born approximation, the partial cross section for the inelastic scattering of an electron wave packet (with initial group velocity v), undergoing a momentum transfer $\vec{q}$ and losing energy E,[58–60] is given by

$$\frac{d^2\sigma(E,q)}{dEdq} = \frac{8\pi e^4}{\hbar^2 v^2}\frac{1}{q}\sum_{i,f}|\hat{\epsilon}_q \cdot \langle f|\vec{r}|i\rangle|^2 \delta(E - E_f + E_i) + \cdots$$
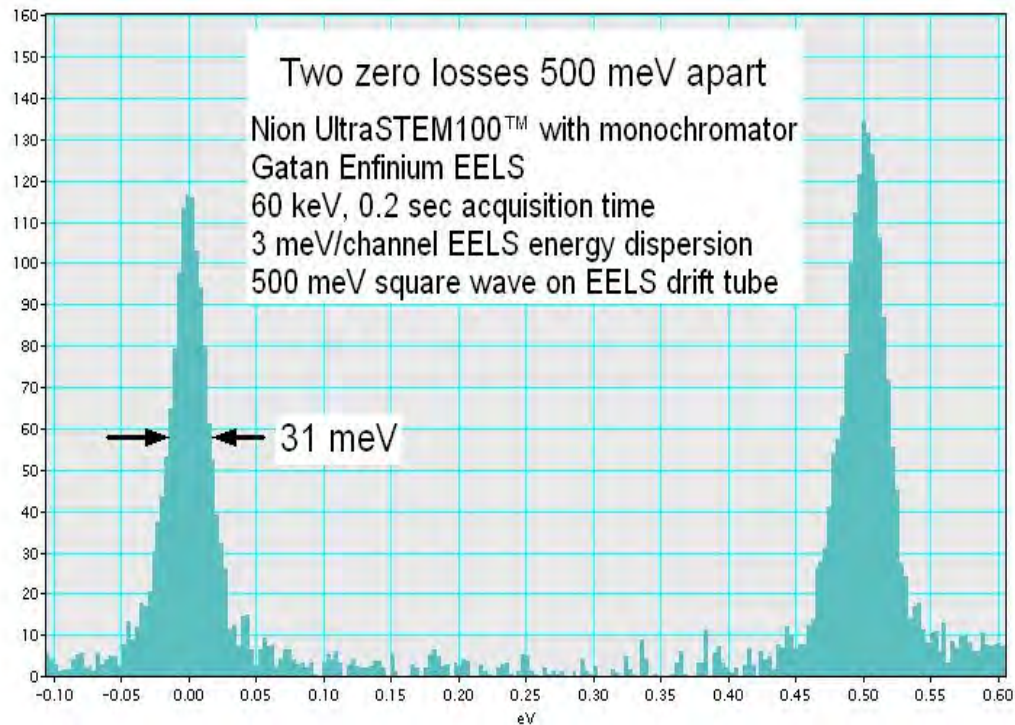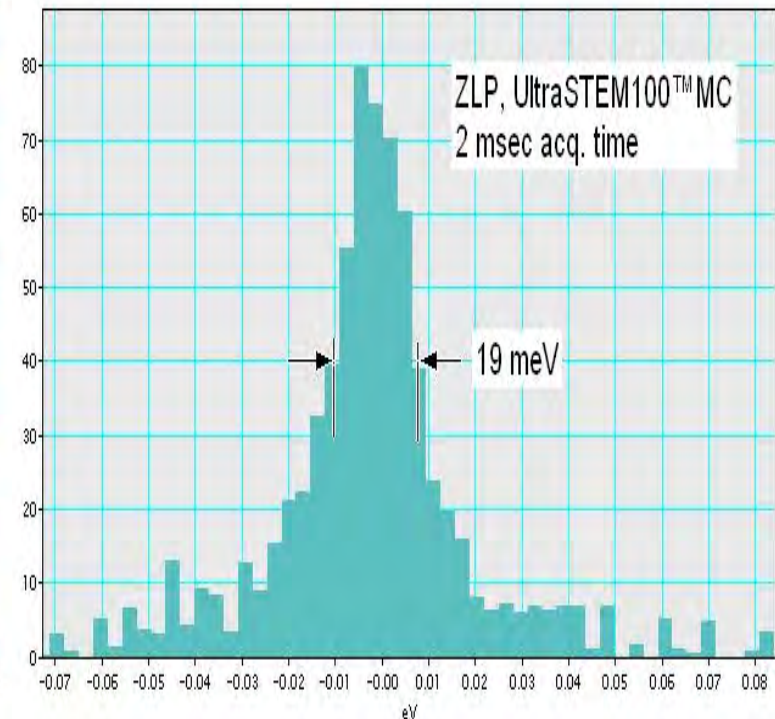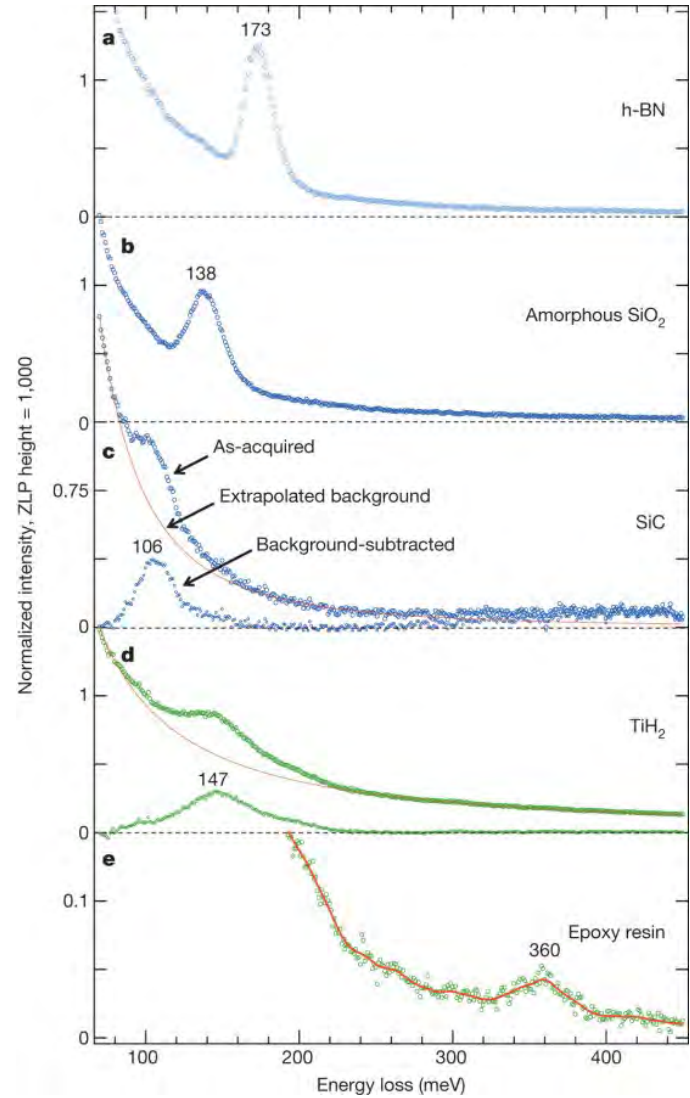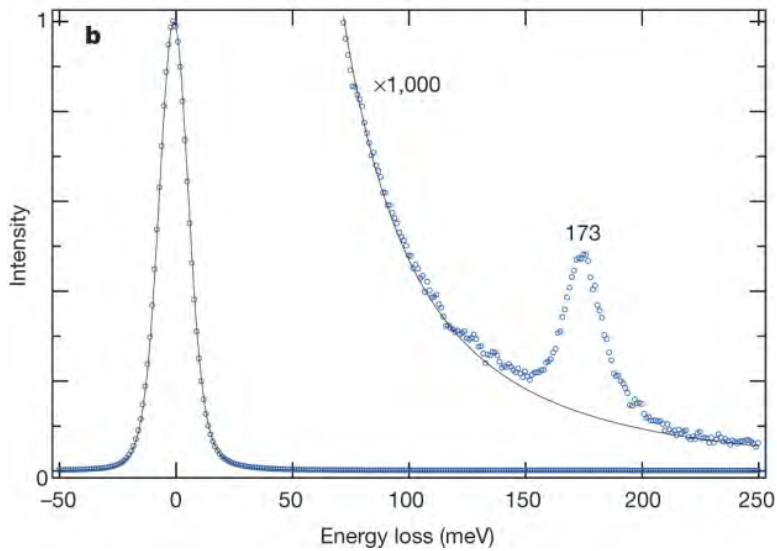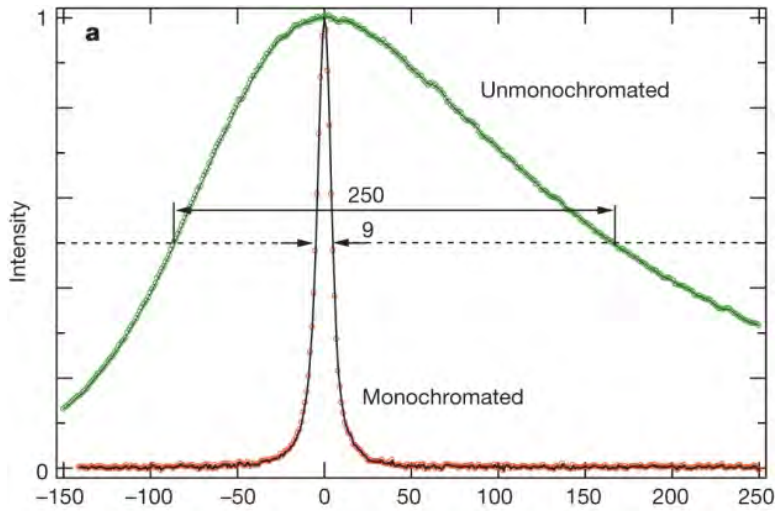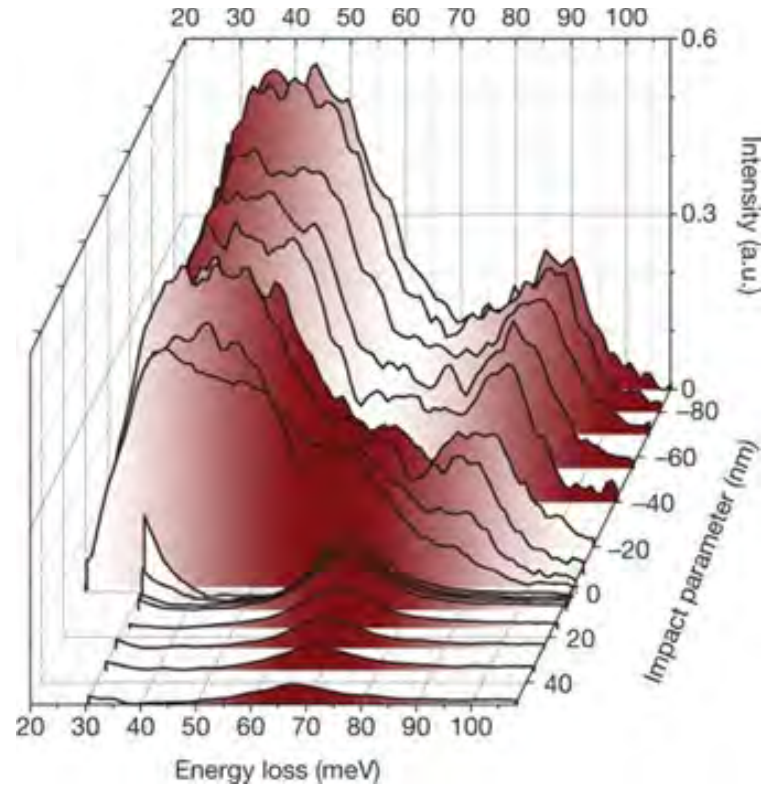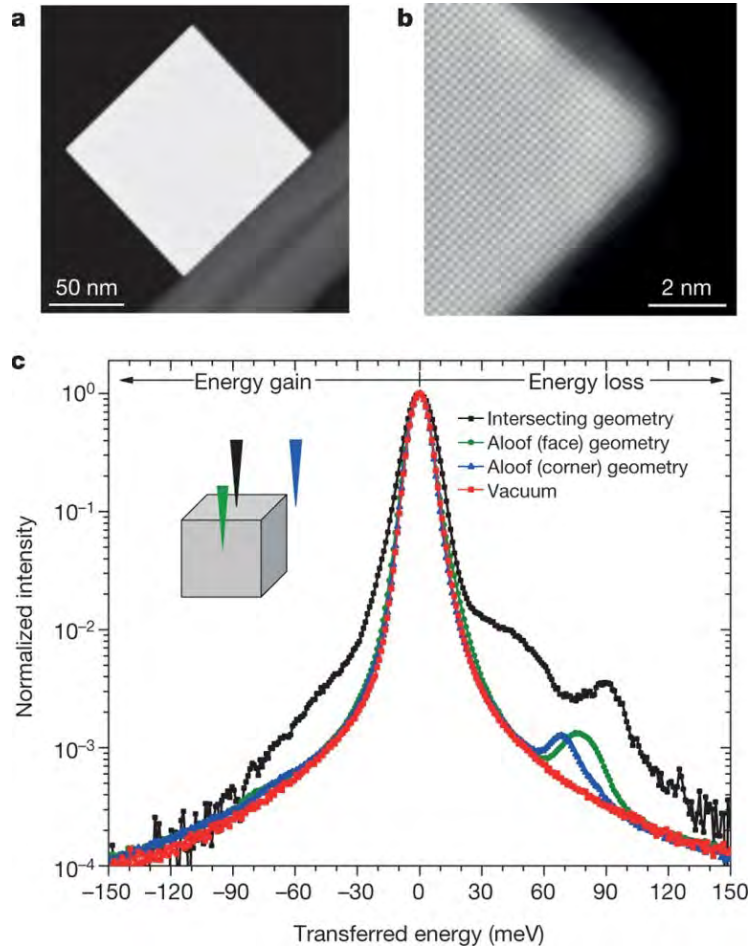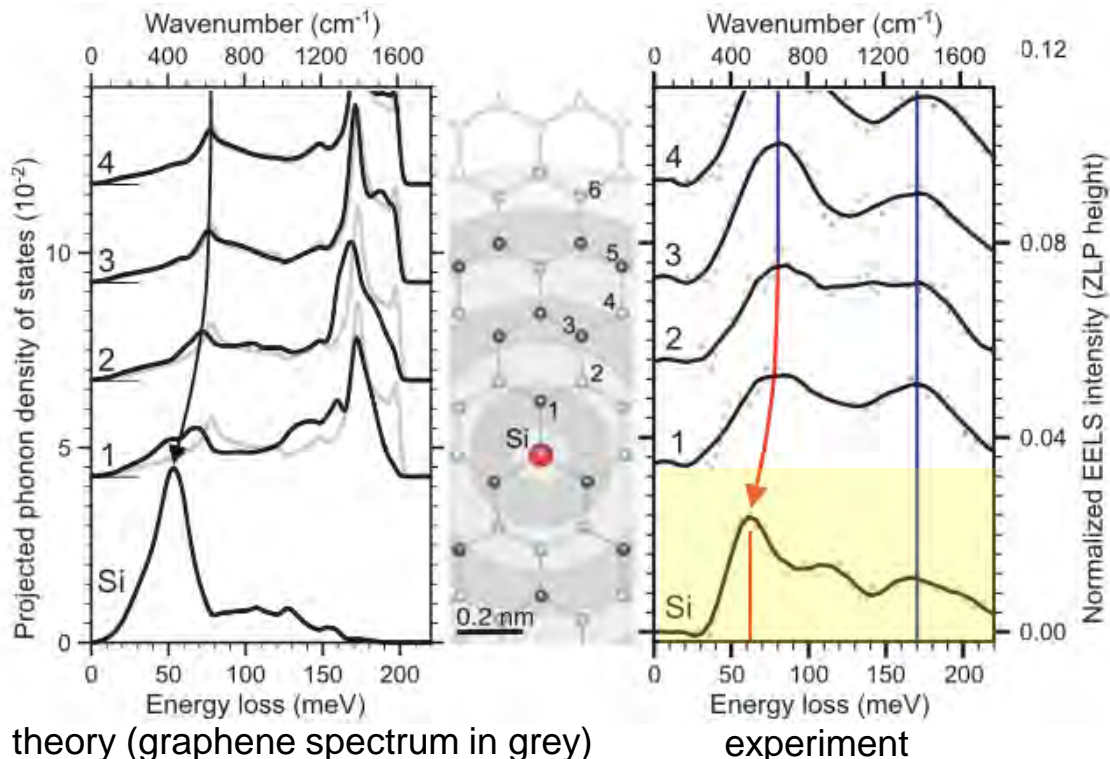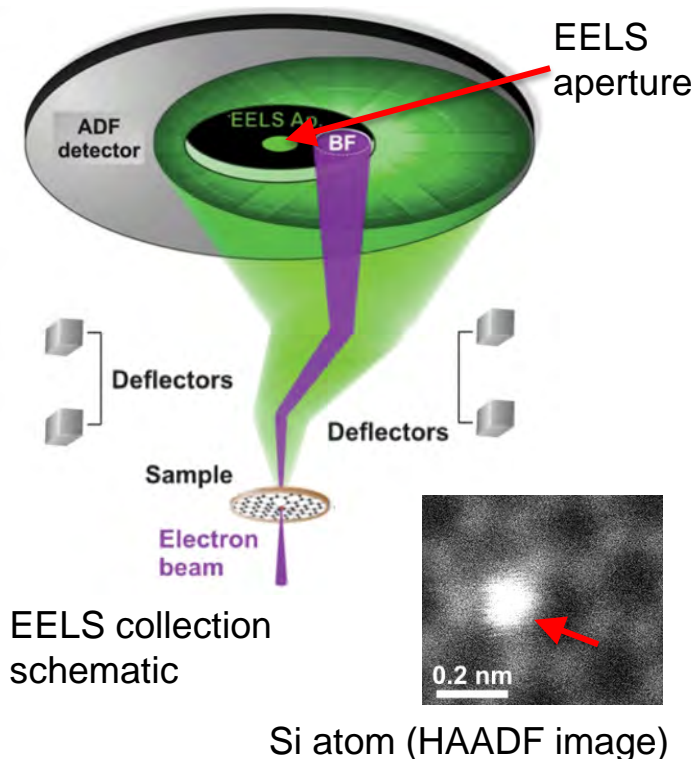
*Some subtleties as to which density of states is measured see Muller, Singh and Silcox, Phys Rev **B57**, 8181 (1998)*

This is very important if you want to measure charge transfers (you don't – there is no unique definition).

Dipole selection rules: $\Delta l = \pm 1, \ \Delta j = 0, \pm 1$

K-edge: $1s \to p$ L-edge: $L_1 : 2s \to p$; $L_{2,3} : 2p \to d, s$;

Calculation of the Final States

- *Cluster Methods: good for defects & clusters, often easier to run*
  - *Muffin-Tin Potential (OK for Metals, bad for semiconductors)*
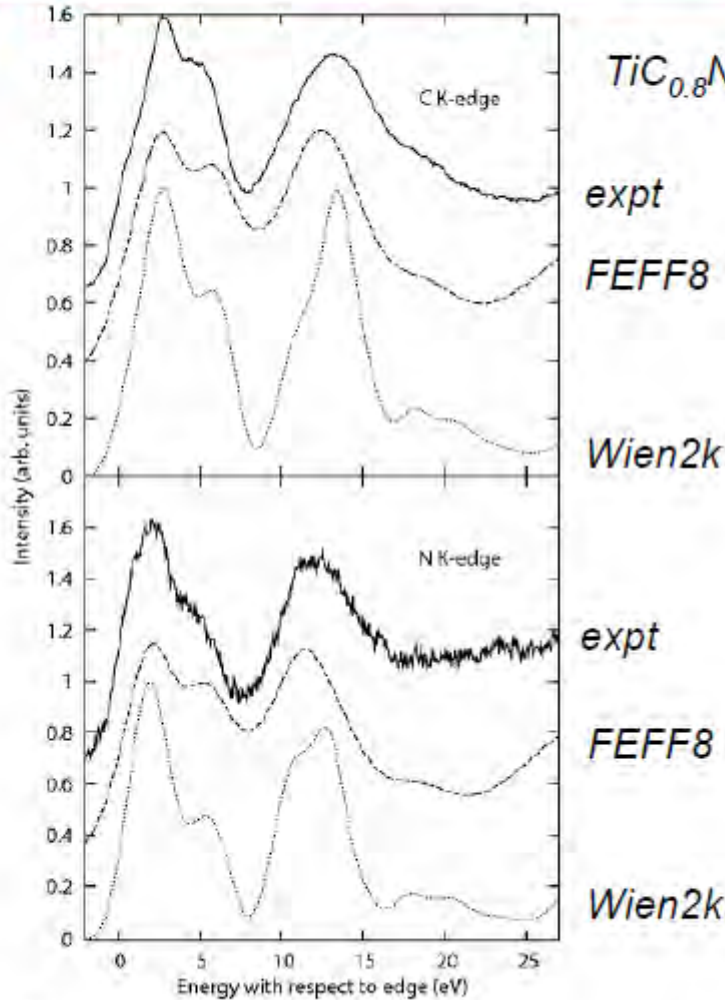   - *FEFF7 – no self-consistency: must guess charge transfers*
    - *FEFF8 – self –consistent: good for metals*
  - *Full Potential*
    - *FDMNES – no self-consistency, but it can input potentials from Wlen2k*

- *Bandstructure methods: (3D periodic structures or supercells)*
  - *Almost all bandstructure codes are self-consistent now*
  - *Muffin-Tin Potential*
    - *LMTO – good for close-packed structures, esp. metals*
  - *Full Potential*
    - *FP-LAPW*
      - *Wien2k – easy to calculate matrix elements & core hole effects*
    - *Plane-wave codes (faster and less prone to artifacts than APW codes*
      - *ABINIT (free, open-source and downloadable from abinit.org)*
      - *VASP   (commercial)*
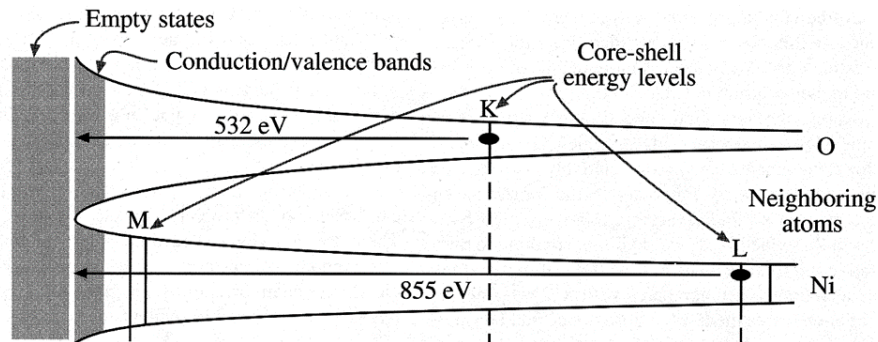   - *CASTEP (commercial, fancy user interface)*

Wien2k vs FEFF8

$TiC_{0.8}N_{0.2}$

C K-edge

expt

FEFF8

Wien2k

N K-edge

expt

FEFF8

Wien2k

Intensity (arb. units)

Energy with respect to edge (eV)

David Muller 2006

Core Hole Problem

+ve potential of departing core electron changes energy levels

- **No core hole (ground state)**
  - usually not a good approximation (maybe in metals ?)
- **Z+1 approximation (eg., replace C by N)**
  - also not very good
- **Core-hole (supercell) calculations**:
  - remove 1 core electron on ONE atom in the supercell, add 1 electron to conduction band
  - remove 1 core electron, add 1 electron as uniform background charge, considers statically screened e-h coulomb correlation
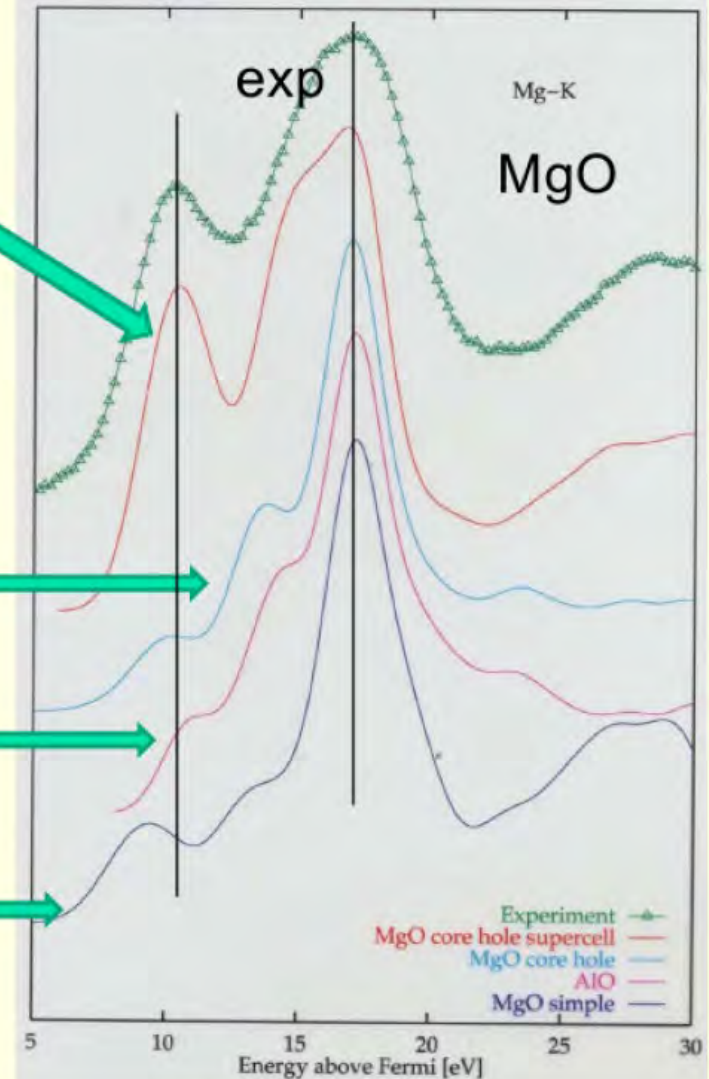 - fractional core hole (Slater ½ method)

Comparison

2x2x2 supercell calculation, with core hole in one of the Mg atoms. This allows the conduction state to relax (adjust to the larger effective nuclear charge), but also to have static screening from the environment.

core hole, no supercell:

Z+1 (AlO)

groundstate

exp

Mg–K

MgO

Experiment
MgO core hole supercell
MgO core hole
AlO
MgO simple

5   10   15   20   25   30
Energy above Fermi [eV]

Summary

- EELS can give chemical information, more interesting (IMHO) is electronic

- Simulations are becoming decent

- Significant recent instrument improvements

- ***But***, dynamical diffraction is ignored
  - OK if off a zone axis
  - Incorrect in general
  - I will return to this…