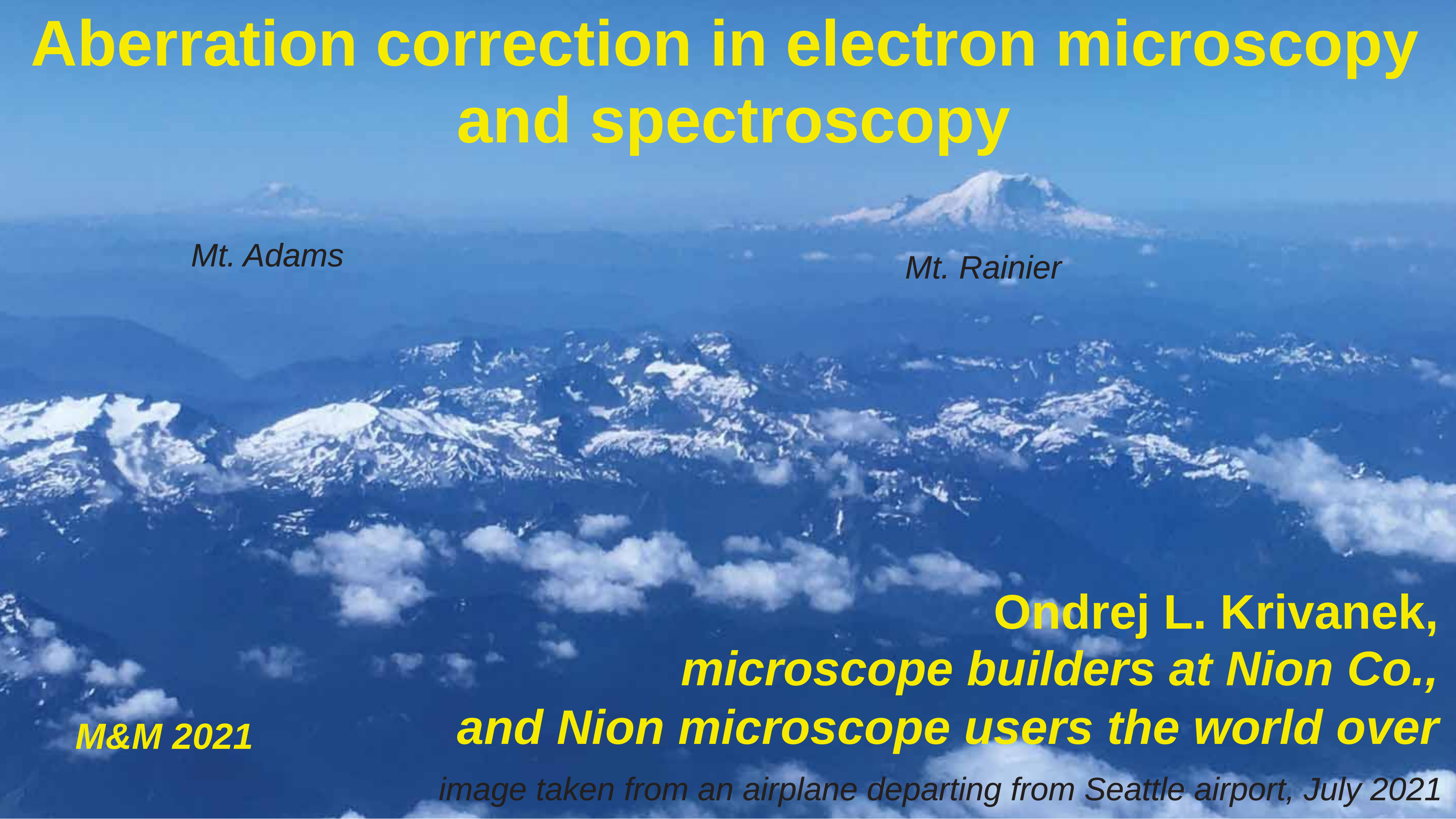
Aberration correction in electron microscopy and spectroscopy



Ondrej L. Krivanek,
microscope builders at Nion Co.,
and Nion microscope users the world over

M&M 2021

image taken from an airplane departing from Seattle airport, July 2021

Why is aberration correction important?

Hubble space telescope, **before repair.** Image is blurred by **spherical aberration (C_s)** of incorrectly made primary mirror.

After repair: spherical aberration of telescope's mirror is corrected by newly designed planetary camera optics.

Resolution became better, much fainter objects became visible.

In electron microcopy, spherical aberration was just as limiting as it was for the Hubble.

(S)TEM aberration correction: 50 years from first concepts to successful finish

1936: Scherzer's Theorem: round electron lenses have unavoidable spherical and chromatic aberration.

1947: Scherzer describes several approaches to aberration correction. The most promising: break cylindrical symmetry – use non-round optics to correct aberrations.

1953-1985: several proof-of principle correctors are built, but none of them reaches better spatial resolution than the uncorrected instrument.

1997 Haider, Rose et al. improve the resolution of a conventional TEM by C_s correction, in Heildeberg in Germany.

1997 Brown, Dellby, Krivanek et al. improve the resolution of a scanning transmission electron microscope (STEM) by C_s correction, in Cambridge UK.

2001-2003 Krivanek and Dellby mark II corrector reaches direct resolution <1 Å – better than any other microscope in the world at that time. Aberration correction takes off.

2020 Electron microscope aberration correction honored by the Kavli Prize in Nanoscience

(S)TEM aberration correction:
50 years from first concepts to successful finish

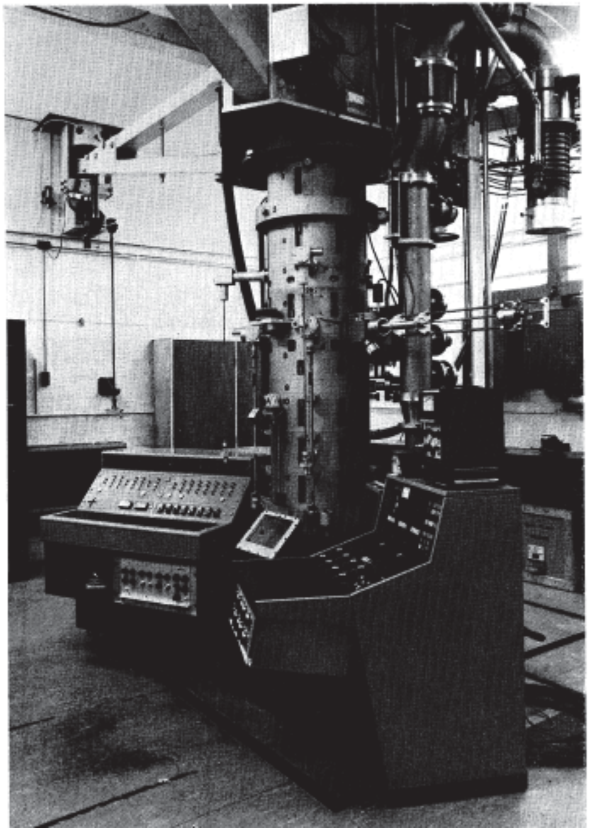
Max Haider Knut Urban Harald Rose Ondrej Krivanek

Kavli NanoScience Prize winners, 2020

"For sub-ångström resolution imaging and chemical analysis using electron beams."

…the Laureates constructed aberration corrected lenses and made sub-ångström imaging and chemical analysis in three dimensions a standard characterization method.

600 kV non-corrected electron microscope

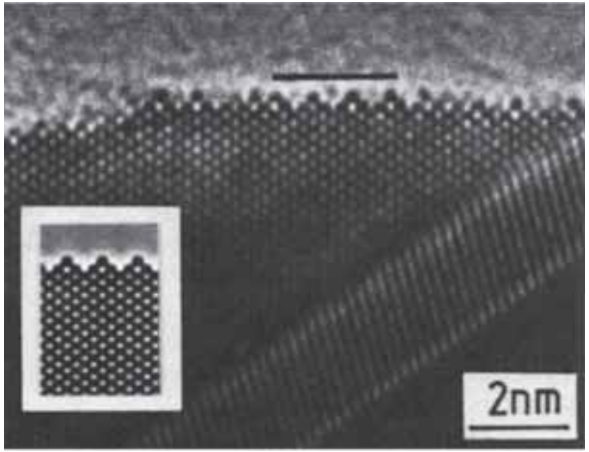


High resolution electron microscope (HREM) built in Cambridge UK ca 1980.

Weight ~ 10 tons, a building wing was needed to house it.

Resolution ~ 2Å at 600 kV.

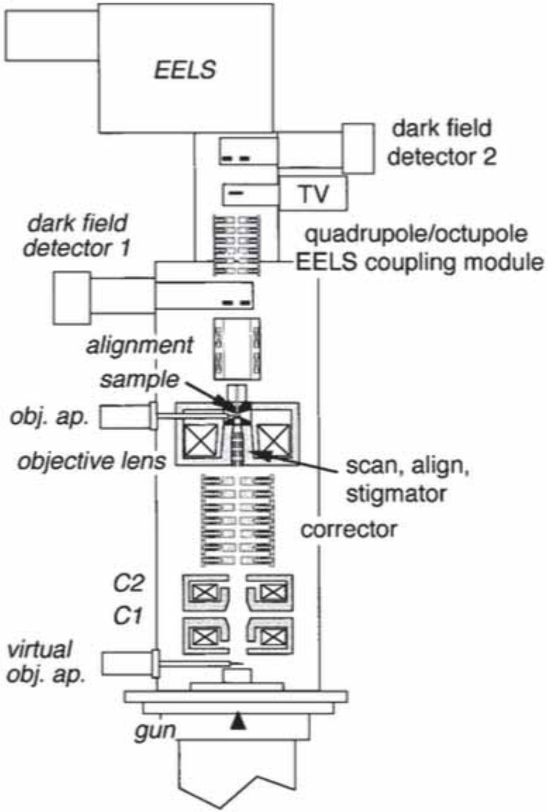
HREM at this resolution unlocked many “atomic secrets”.



Au surface
reconstruction
(Marks and Smith)

100 kV C_s-corrected STEM

Image of instrument at Nion



Instrument schematic

Aberration-corrected VG STEM built at Nion, 2000.

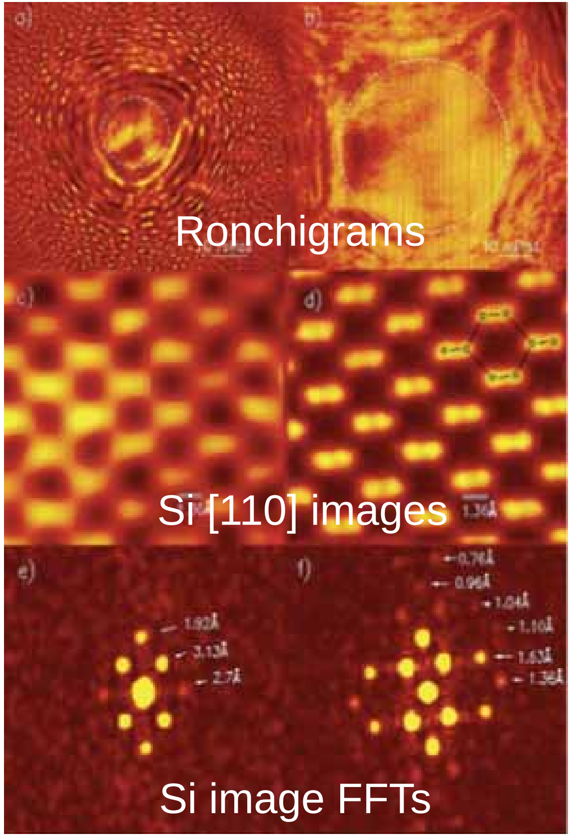
Weight ~ 1 ton, operated in a converted garage.

Resolution ~1Å at 100 kV. 0.78 Å at 300 kV.

The corrector and the microscope have since been improved substantially.

Updated versions reach 0.5 Å resolution at 200 kV.

Results from Nion-corrected VG STEMs

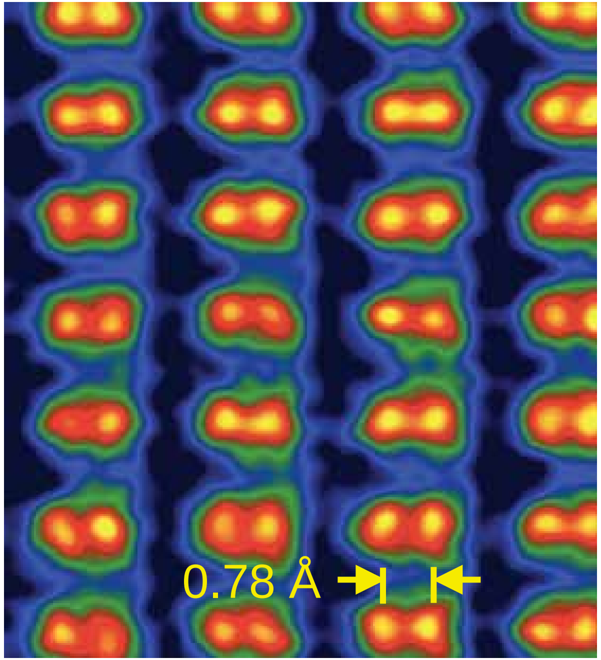


uncorrected corrected

Corrected VG HB501:

Si (110) HADF image showing spacings down to 0.76 Å in a diffractogram.

P.E. Batson et al., Nature **418** (2002) 617.



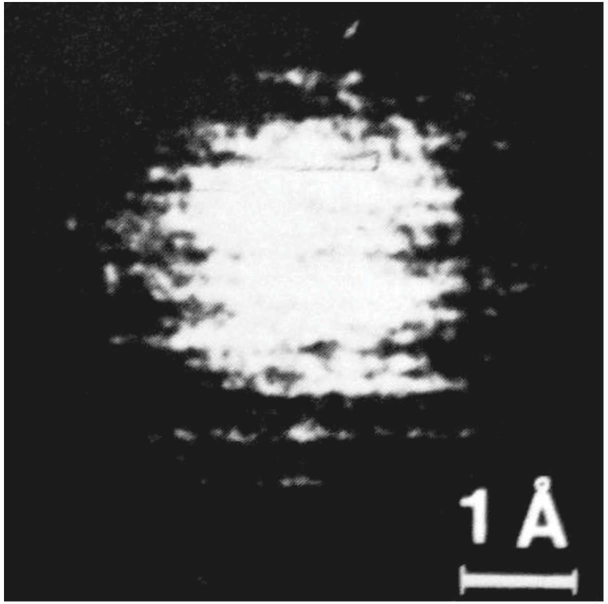
Corrected VG HB603:

Resolving 0.78 Å dumbbells in (210) Si.

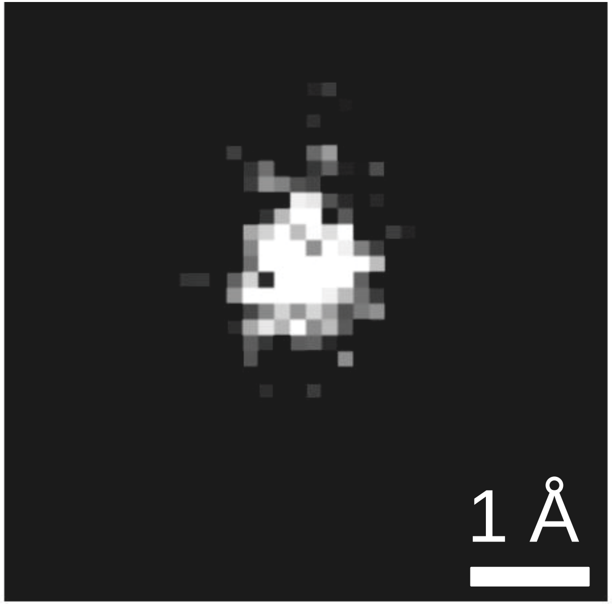
P.D. Nellist et al., Science **305** (2004) 1741.

First direct imaging of sub-Å structures *in any type of electron microscope.*

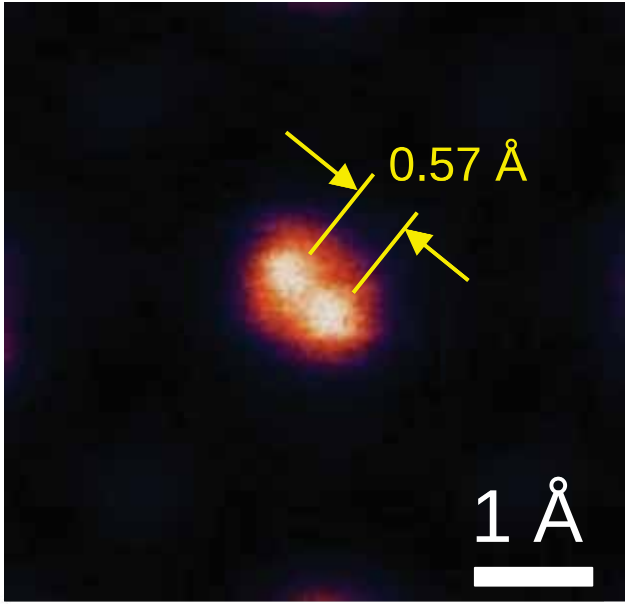
Progress in single atom imaging by ADF STEM



Chicago STEM ~1975
40 keV: 2.5 Å Au atom



Nion UltraSTEM 2007
100 keV: 1 Å Au atom

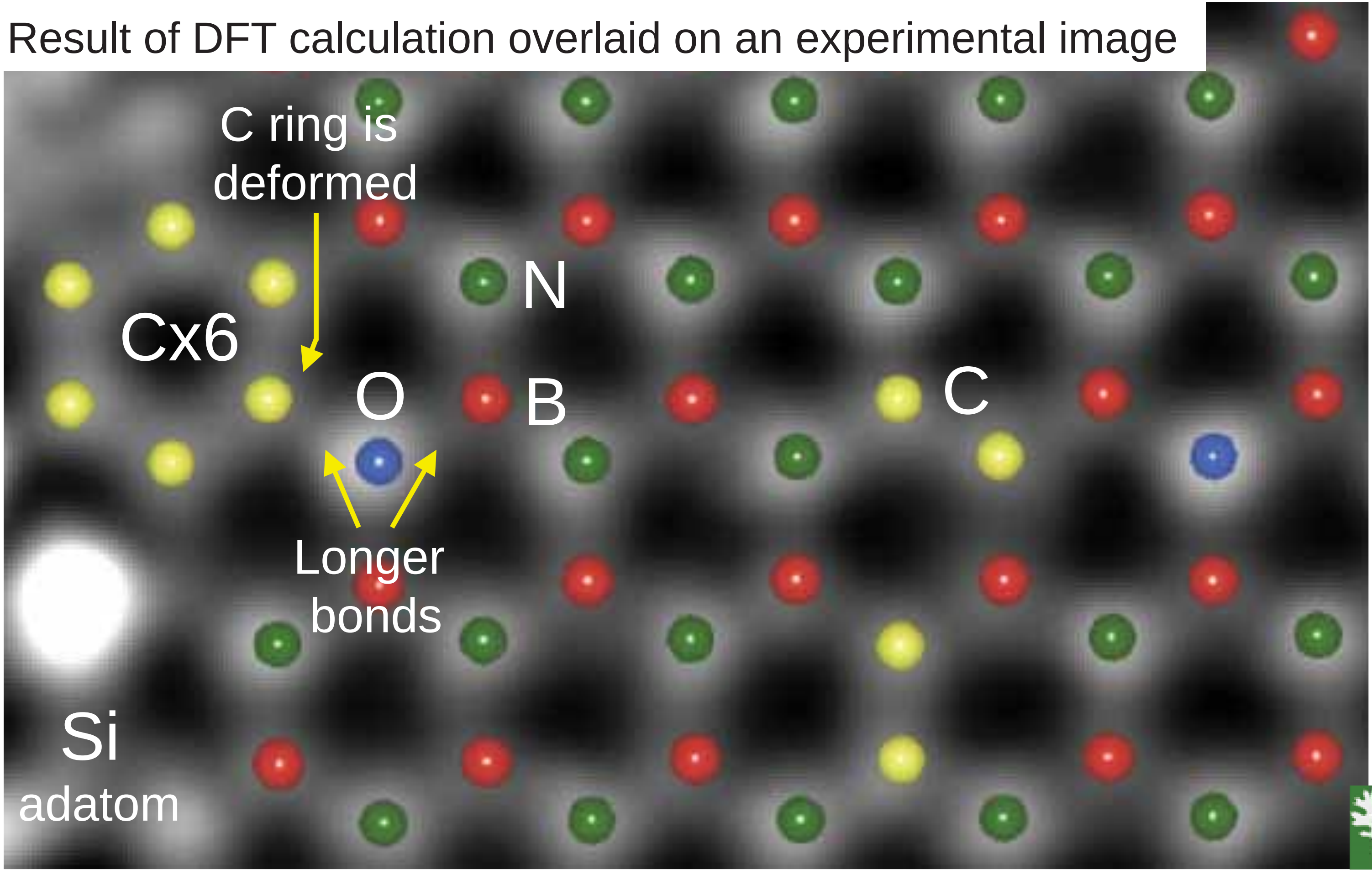


Nion UltraSTEM 2013
200 keV: two Y atomic columns
0.57 Å apart in $YAlO_3$

The resolution has improved, and so has the stability.

BN monolayer with impurities imaged by MAADF

Result of DFT calculation overlaid on an experimental image



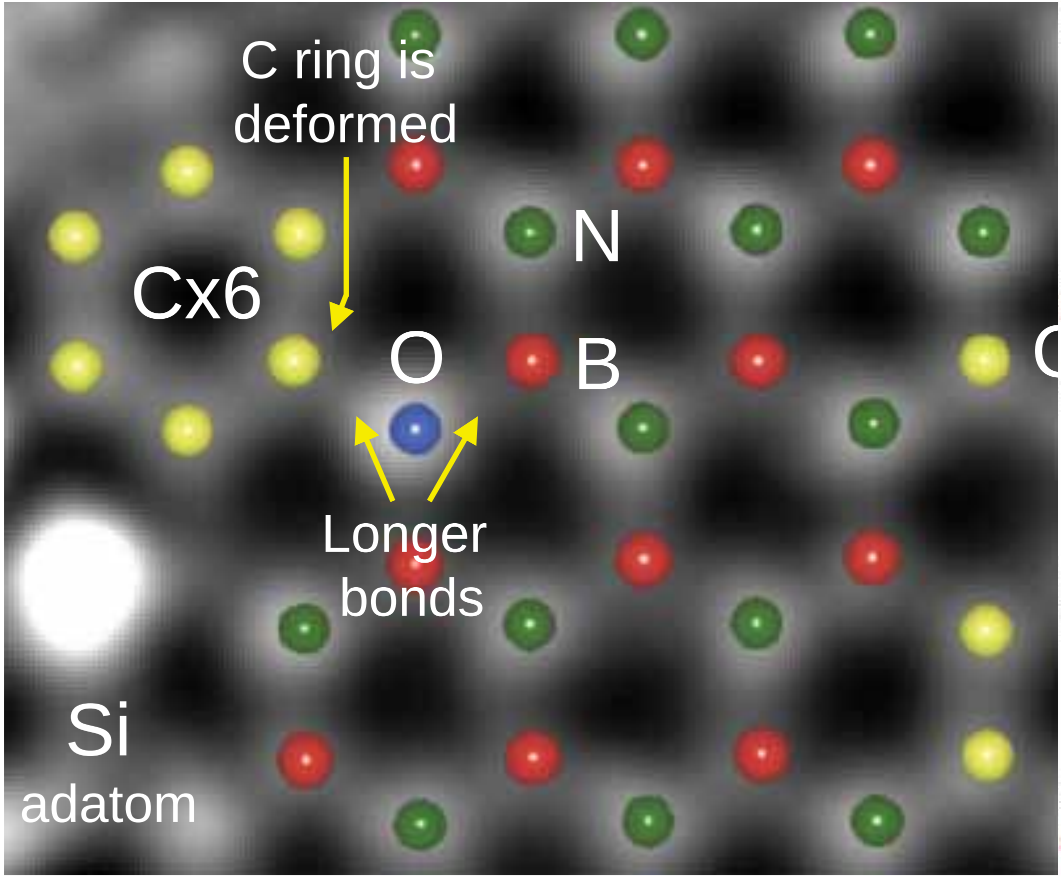
MAADF (medium -angle annular DF) image, 60 kV, courtesy Matt Chisholm, ORNL.

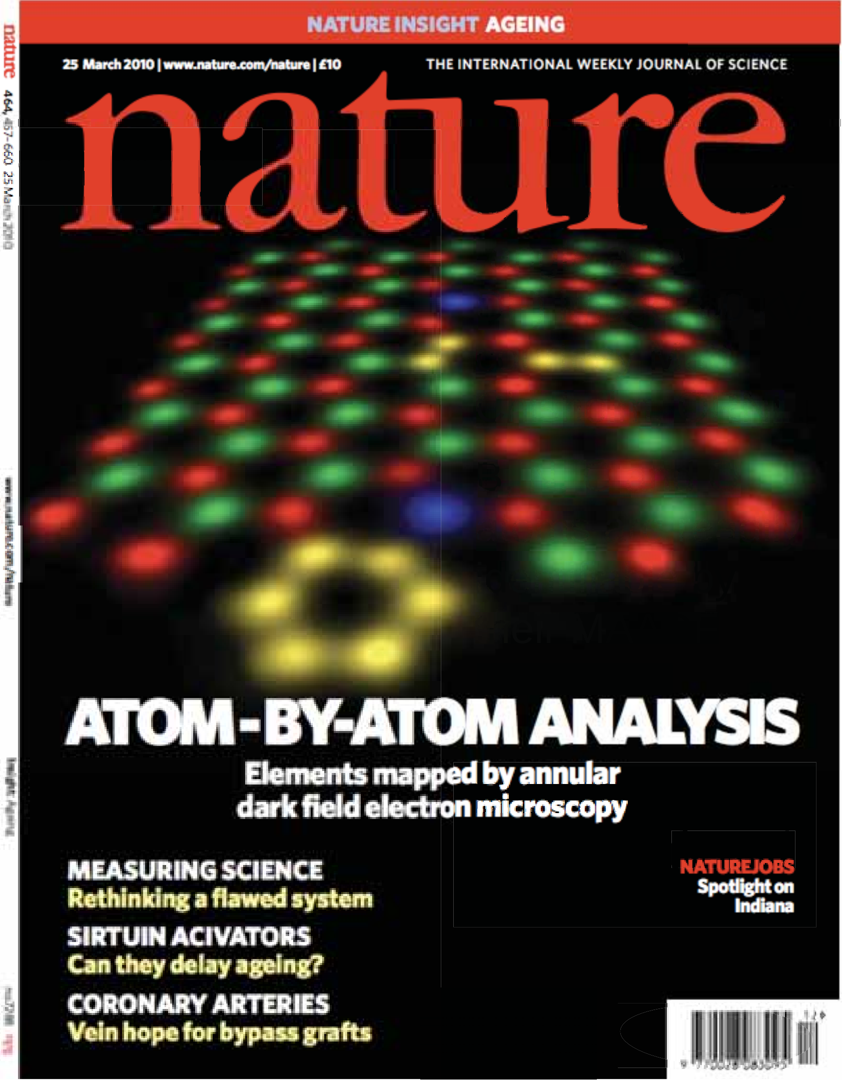
B, N, C and O atoms are readily identifiable by their MAADF intensities.

O.L. Krivanek et. al., Nature (2010) 571-574.

BN monolayer with impuritie

Result of DFT calculation overlaid on an experime




nature 464, 457–660 25 March 2010

NATURE INSIGHT AGEING

25 March 2010 | www.nature.com/nature | £10

THE INTERNATIONAL WEEKLY JOURNAL OF SCIENCE

nature

ATOM-BY-ATOM ANALYSIS

Elements mapped by annular dark field electron microscopy

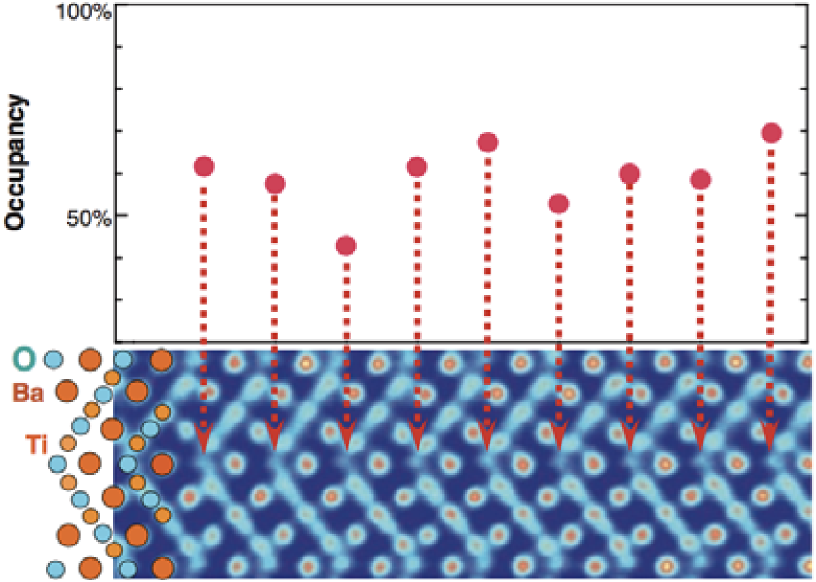
MEASURING SCIENCE
Rethinking a flawed system

SIRTUIN ACIVATORS
Can they delay ageing?

CORONARY ARTERIES
Vein hope for bypass grafts

NATUREJOBS
Spotlight on Indiana

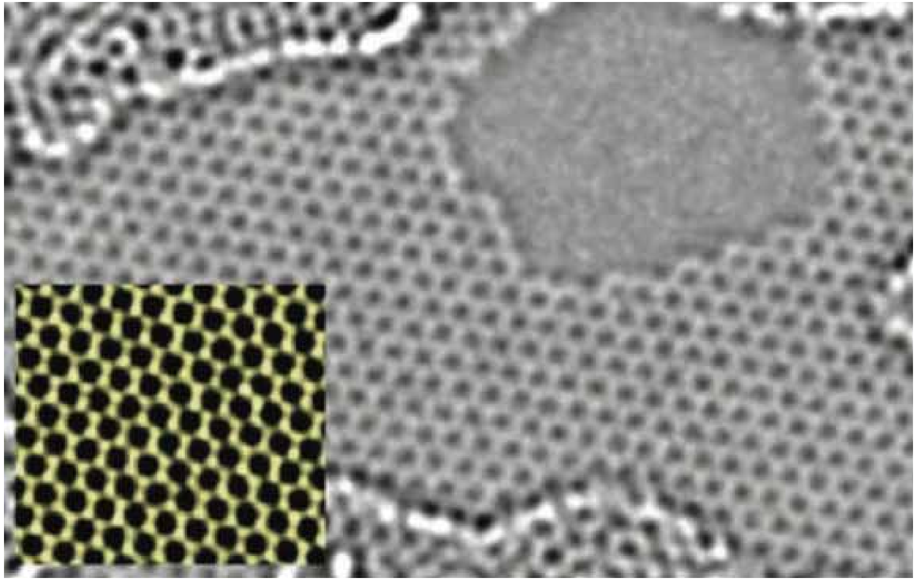
Results from CEOS-corrected FEI TEMs



Aberration-corrected TEM image of twin boundary in $BaTiO_3$. The local intensity values indicate that only 40 and 70% of the O column sites are occupied.

Jia and Urban, Science ***303*** *(2004) 2001.*

ER-C



Aberration-corrected TEM image of a hole in a single layer of graphene. Inset shows an averaged image with improved resolution.

Girit et al., Science ***323*** *(2009) 1706.*

CEOS
Corrected Electron Optical Systems GmbH

BERKELEY LAB

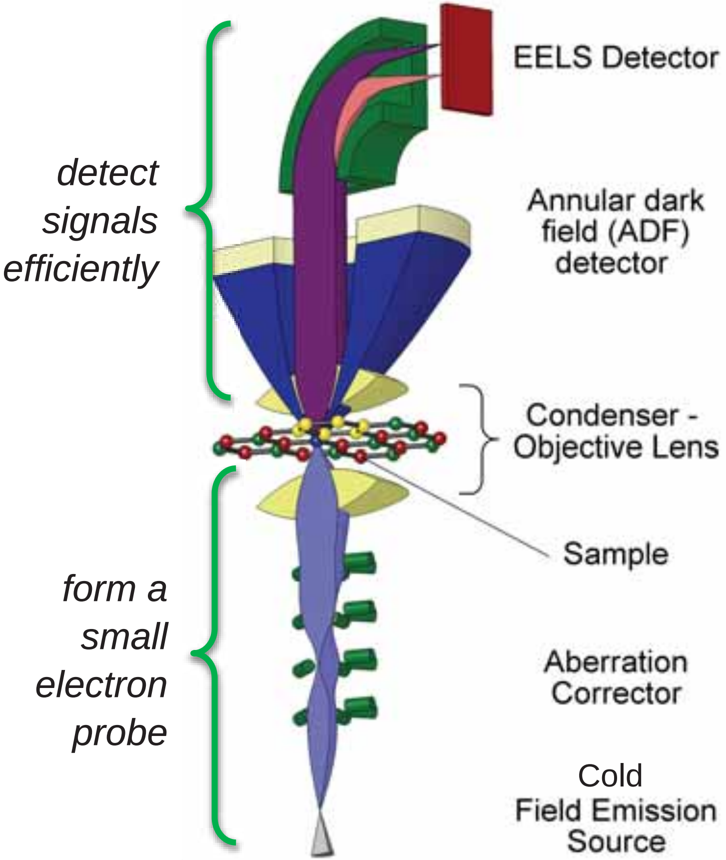
Primary analytical signals available in a STEM

In the scanning transmission electron microscope (STEM) an electron probe, with ~10^{10} fast e- per second and **smaller than one atom,** is scanned across the sample.

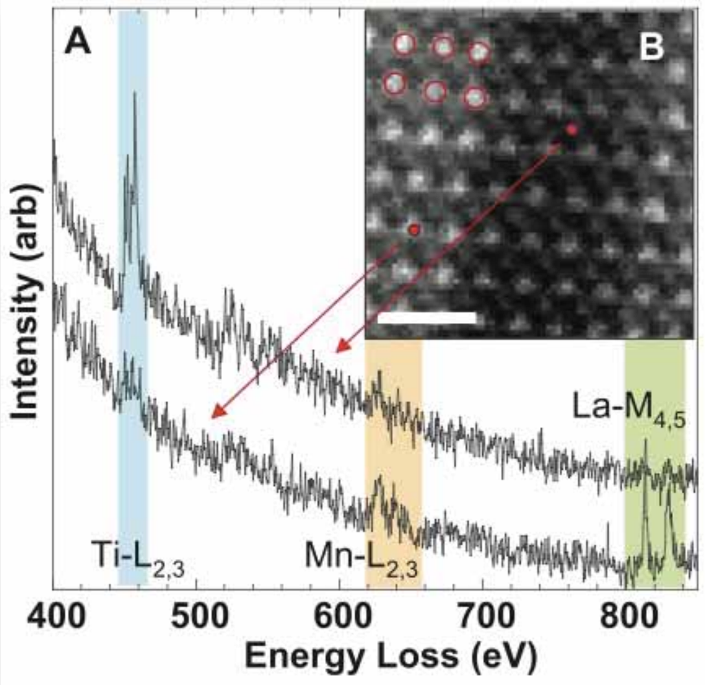
Many types of interactions of the fast electrons with the sample can be detected, typically in parallel.

Key **primary** signals:

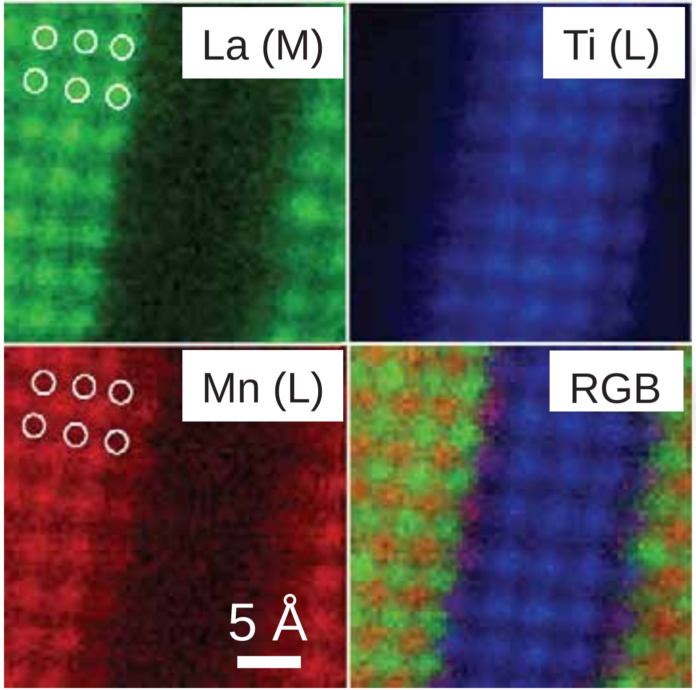
1) **Coherent electron scattering*:*** *BF imaging, holography, ptychography*
2) **Incoherent electron scattering** (from the atomic nucleus), i.e. Rutherford scattering: *HAADF imaging*
3) **Inelastic scattering** by sample's electrons: *regular electron energy loss spectroscopy (EELS)*
4) **Inelastic scattering exciting atomic vibrations:** *ultra-high energy resolution EELS*



Going further: atomic-resolution chemical mapping



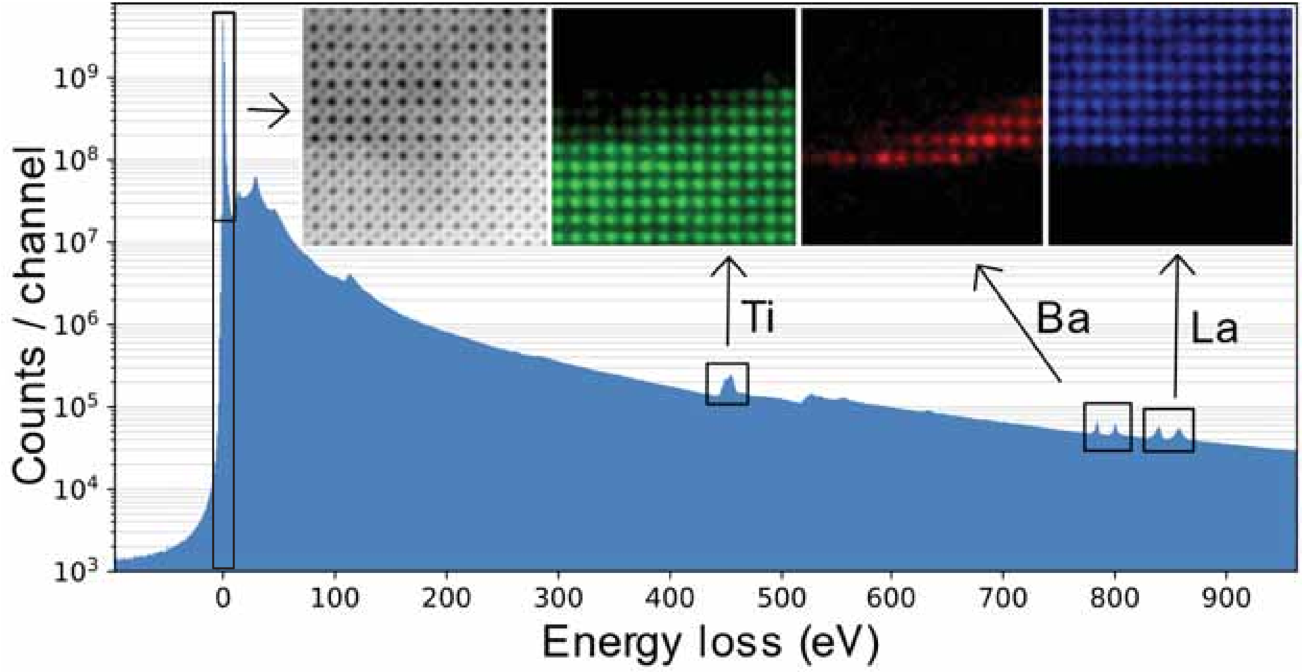
Electron energy loss spectra (**EELS**) of $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ multilayer structure. Nion UltraSTEM, 100 keV.

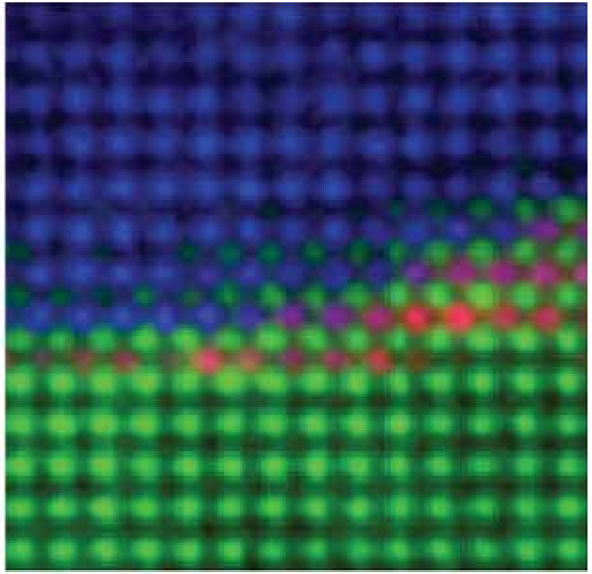


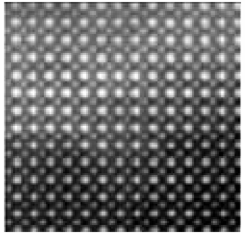
Elemental maps constructed by quantifying EELS spectra at every pixel

Muller et al., Science 319, (2008) 1073

Fast multi-pass chemical mapping






HAADF

128 x 128 spectrum image (SI) of an STO / BTO / LMSO multilayer,
acquired as 32 separate SIs of 8 s each, aligned and summed (4.3 min total).
Dectris ELA hybrid pixel detector, sample courtesy U.C. Irvine

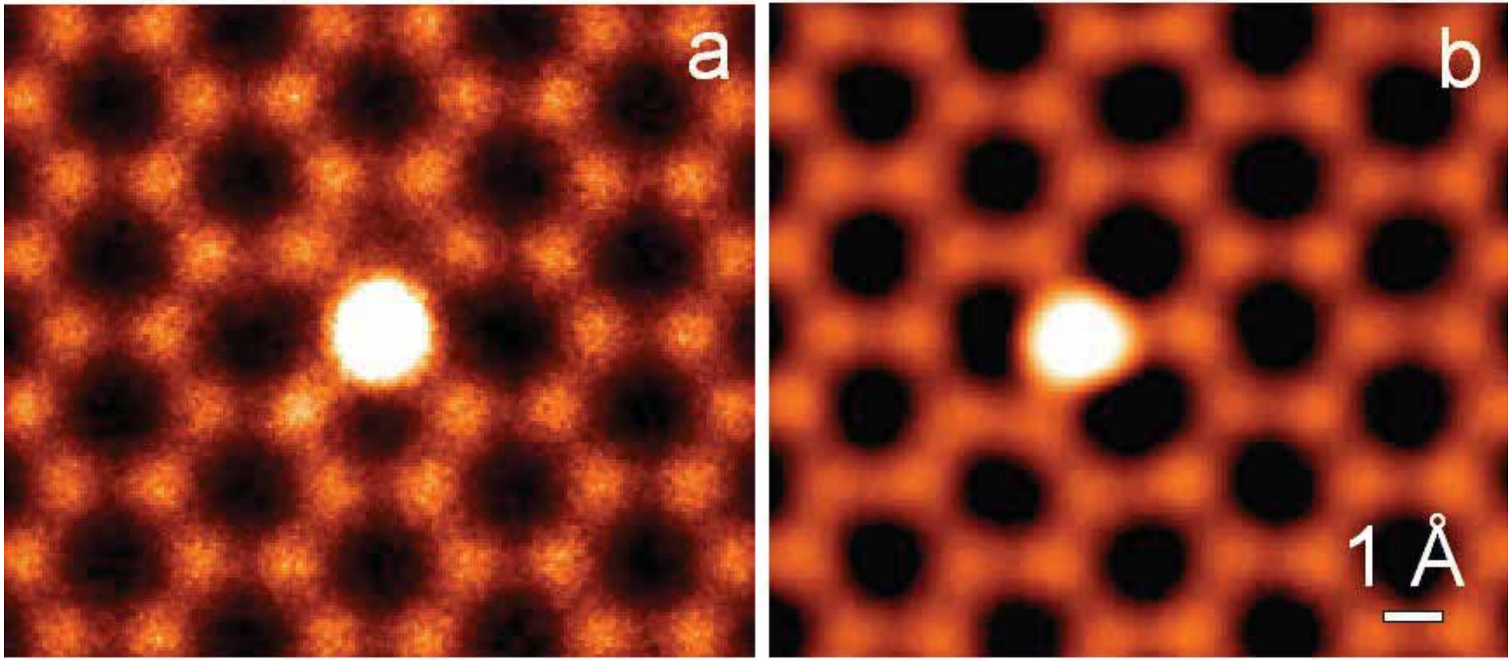
DECTRIS
detecting the future

Time-resolved and multi-pass chemical mapping is now possible.

nion

Imaging single Si atom impurities in graphene

Si atoms in graphene can occupy two different sites (UltraSTEM images, 60 kV, ca 2010).

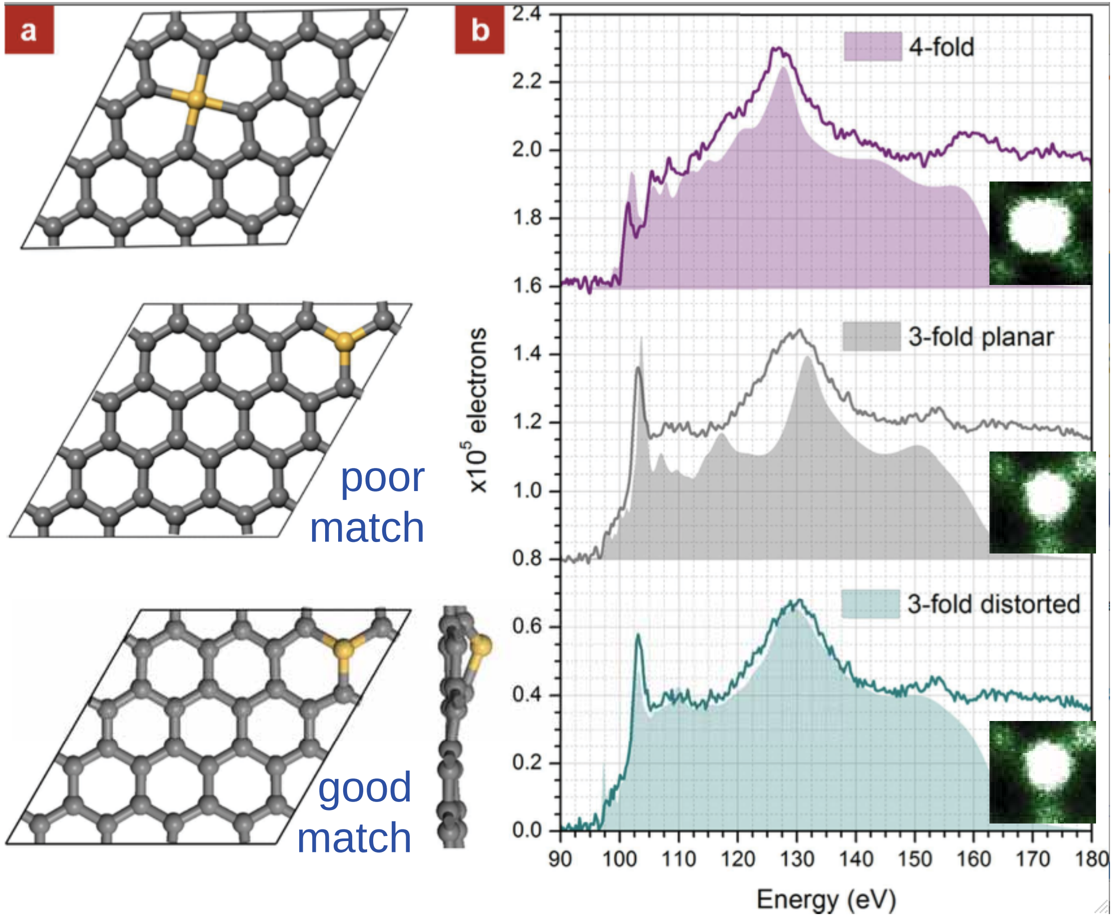


4-fold: Si substitutes for 2 C atoms
Courtesy Wu Zhou, ORNL

3-fold: Si substitutes for one C atom
Courtesy Matt Chisholm, ORNL

Can we determine the bonding environment of a single atom?

Probing the bonding of individual atoms by EELS



Lines: experimental EELS spectra recorded in UltraSTEM100

Solid spectra: simulations.

Ramasse et al., Nano Letts (2013), DOI: 10.1021/nl304187e

Zhou et al., *Phys. Rev. Lett. (2012)109: 206803*

➔ ***atomic environment*** *of a* ***single atom*** *determined by EELS*

SuperSTEM DARESBURY

nion

Progress in EM spatial resolution

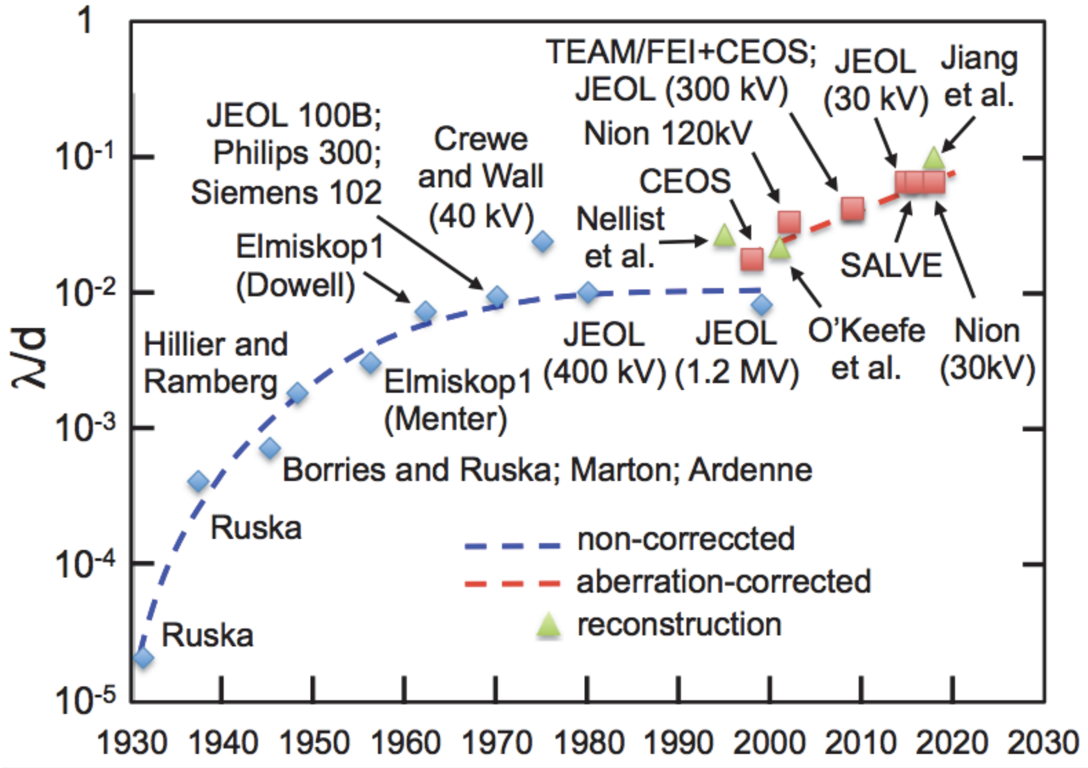


Figure of merit (FOM) for EM imaging resolution

FOM = λ/d

plotted vs time.

The best resolution performance is now ~0.3 Å,

obtained using aberration correction combined with ptychographic reconstruction:

Jiang et al. Nature ***559*** *(2018) 343.*

Denis Gabor (The Electron Microscope, 1948):
“Resolution [quest] will have to stop at 0.5 Å, due to lack of objects.”

Progress in EELS-in-the-EM energy resolution

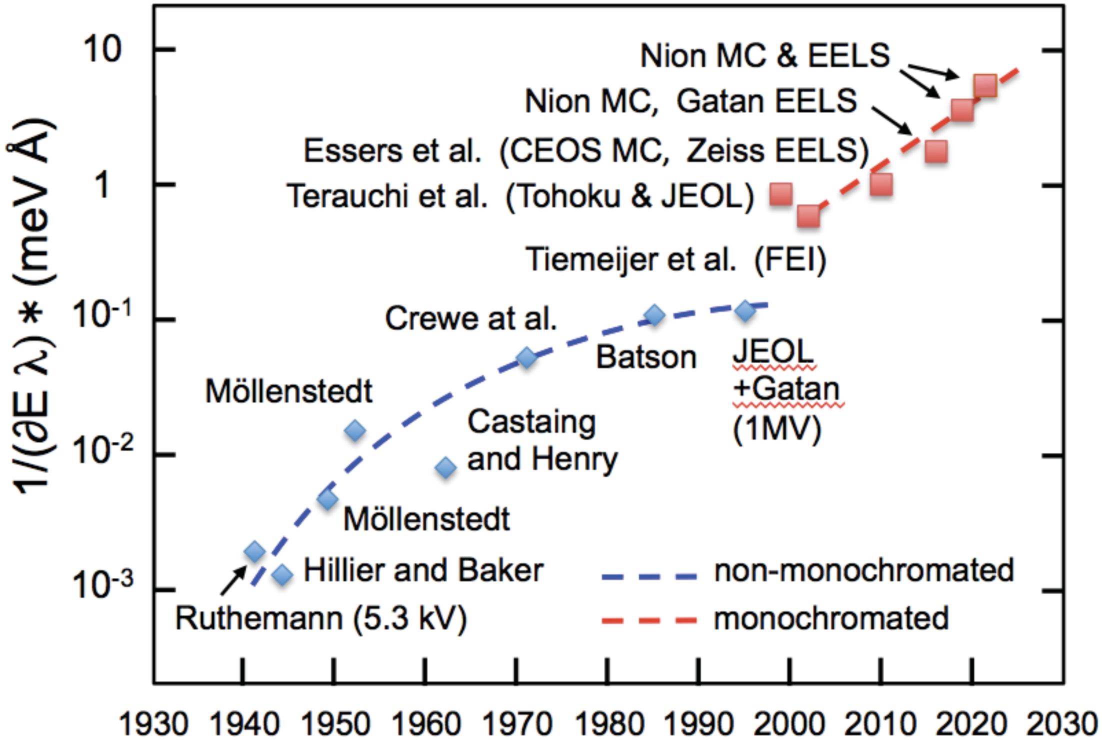


Figure of merit (FOM) for EELS energy resolution plotted vs. time.

FOM = 1/(∂E λ)

FOM α 1/(energy resolution x smallest possible illuminated sample area).

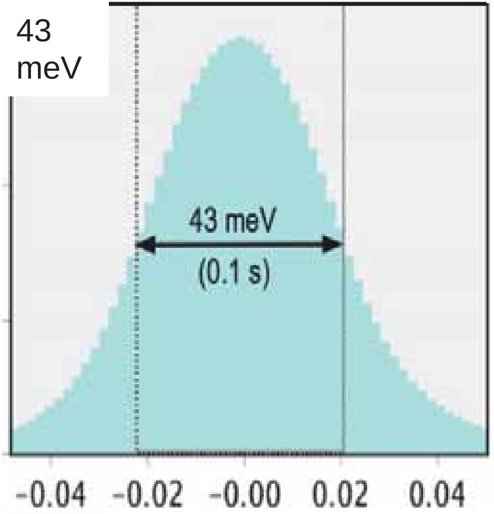
It gauges our ability to extract EELS information from very small (diffraction-limited) sample areas.

The best resolution energy resolution obtained in an electron microscope is now 2.7 meV at 30 kV

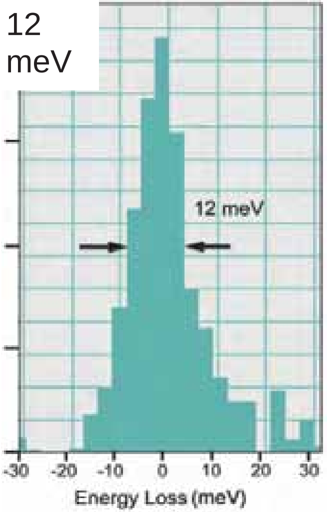
Dellby et al., unpublished (2021)

The quest for better energy resolution has not come up against any insurmountable obstacles yet, and further progress is very likely.

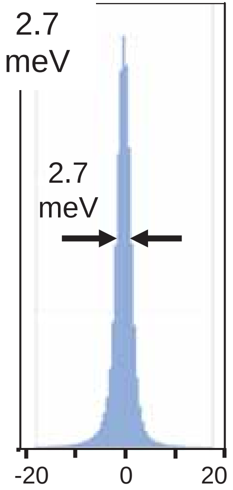
Recent progress in STEM-EELS energy resolution



2010: Zeiss SESAM, CEOS Ω MC,
Zeiss Mandoline EELS, 200 kV,
100 ms



2013: Nion HERMES, Gatan
EELS, 60 kV, 2 ms
(16 meV FWHM ZLP in 55 msec)



2021: Nion HERMES,
Nion Iris EELS, 30 kV,
300 x 3 ms (aligned)

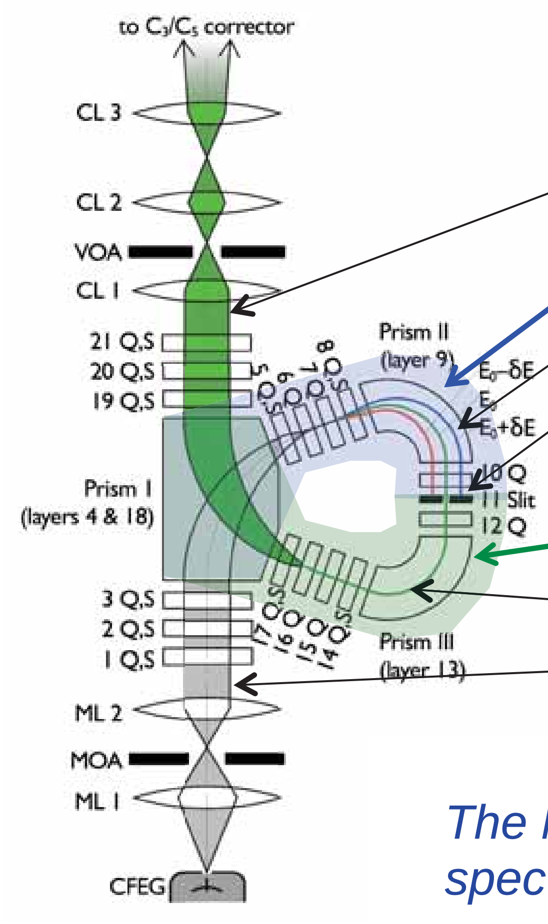
All spectra plotted on the same horizontal scale.

Note also the differences in the extent of the ZLP "tail".

EELS energy resolution in the EM has improved ~16x in one decade.

Nion ultra-high resolution monochromator

Full description in: Krivanek et al., Phil. Trans. R. Soc. **A 367** (2009) 3683 and US Patent #8,373,137



un-dispersed outgoing beam

EELS 1

energy-dispersed beam

energy-selecting slit is at ground potential

➔ when the STEM’s high voltage changes, the selected energy stays the same.

EELS 2

monochromated outgoing beam

incoming beam

The Nion monochromator is equivalent to 2 parallel EEL spectrometers arranged back-to-back.

Nion U-HERMES™* STEM and Iris EELS

*****U****ltra-****H****igh* ***E****nergy*
R*esolution*
M*onochromated*
E*ELS-****S****TEM*

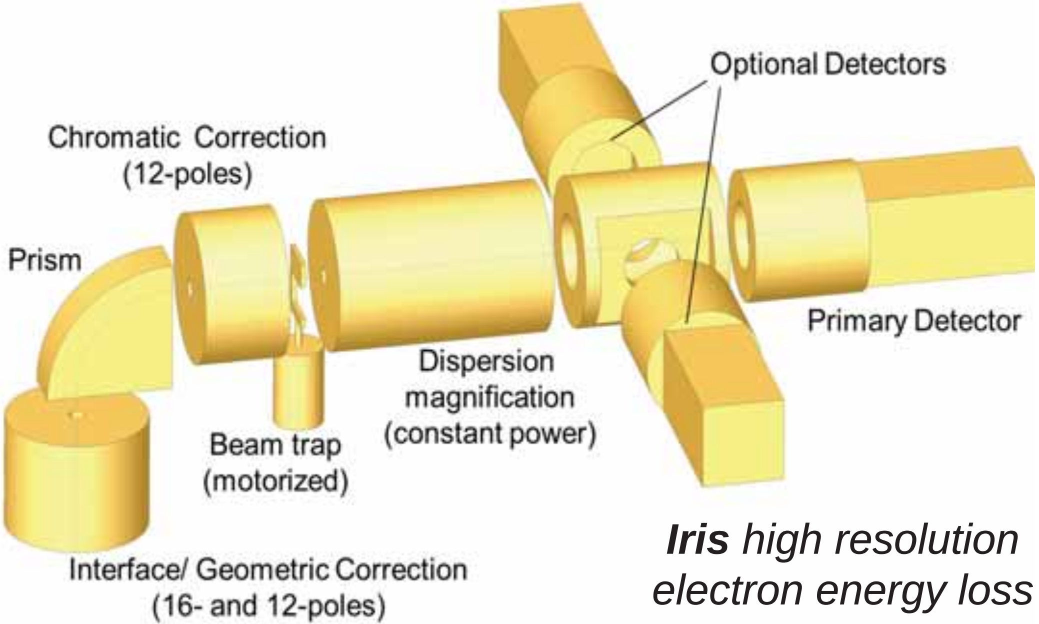
Iris spectro-meter

Side-entry stage with liquid N2 cooling

C3-C5 aberration corrector

Nion monochromator

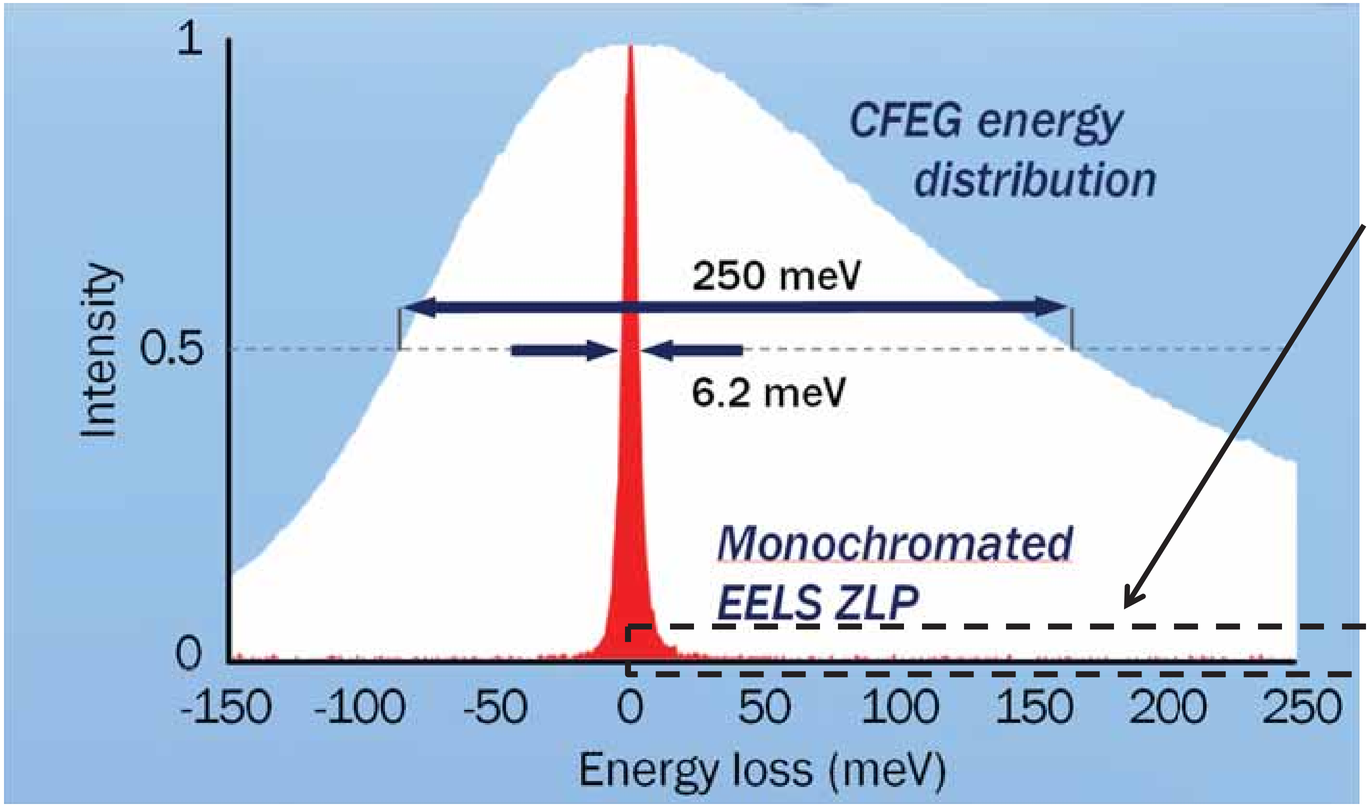
100 or 200 kV CFEG



Iris *high resolution electron energy loss (and gain) spectrometer*

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

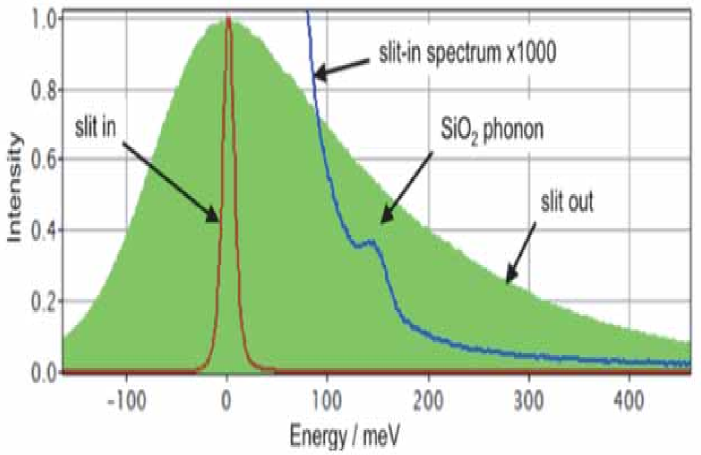
Comparison with non-monochromated EELS



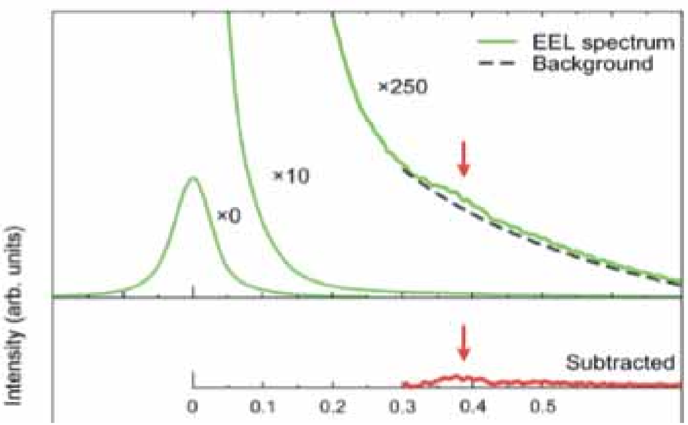
The 0-500 meV spectrum region contains vibrational (phonon) losses and is of great interest.

Before high-energy-resolution monochromated EELS, this region was hidden by the tail of the ZLP.

First glimpses of phonons in the STEM (2014)

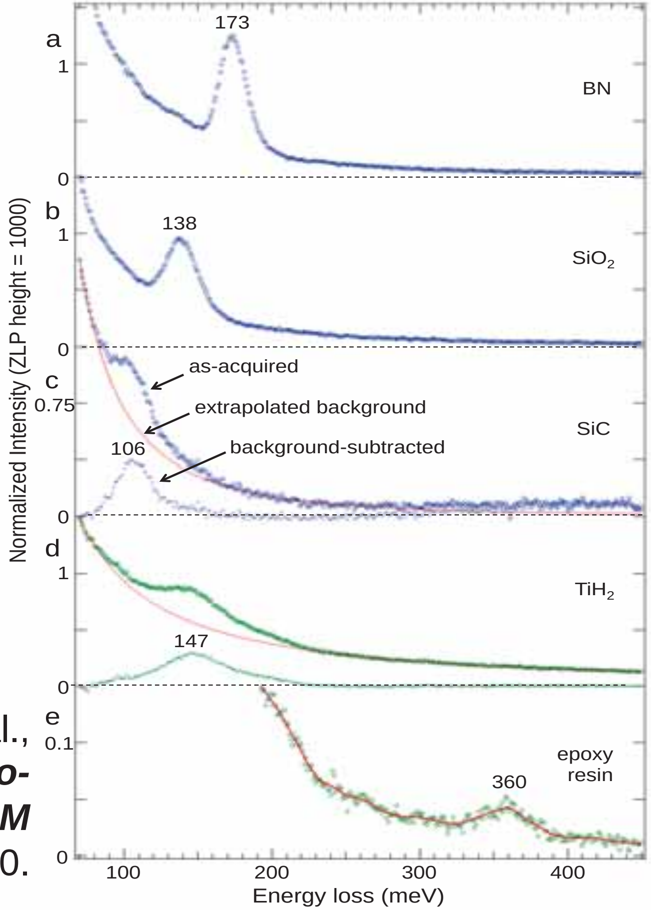


Krivanek et al., ***Exploring phonon signals*** Microsc. Microanal. **20** (Suppl. 3, 2014) 66.



Mizoguchi, Mukai et al., …***vibrational spectrum of [ionic] liquid …*** Microscopy **63** (2014) 377.

Krivanek et al., ***Vibrational spectro-scopy in the EM*** Nature **514** (2014) 20.

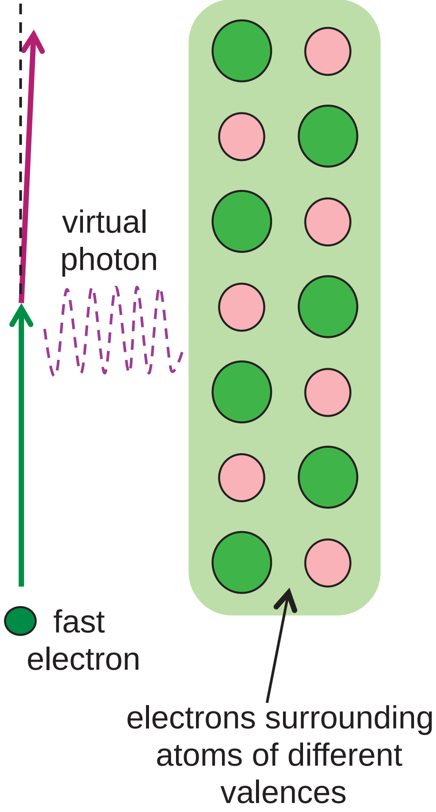


Two types of phonon (vibrational) scattering

A) Dipole scattering:
the fast electron interacts with the whole charge distribution in a ***polar material***.
The scattering angle is small, and the interaction distance is large.

It is similar to the way infrared photons interact with matter.

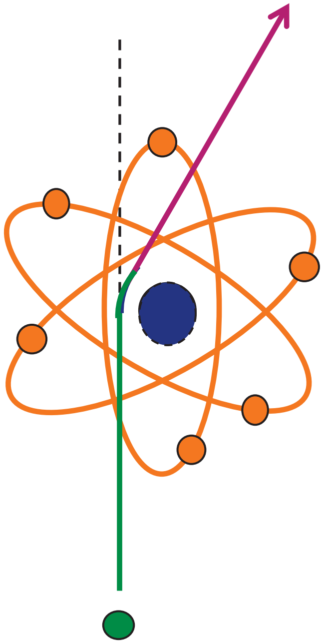
Dipole scattering can be selected by placing a small beam away from the sample (aloof spectroscopy) and emphasized by selecting small angles with an aperture.



B) Impact scattering:
the fast electron passes close to an individual atomic nucleus, transfers a small amount of energy to it, and is scattered by a large angle*.*

It is similar to the way neutrons scatter from matter.

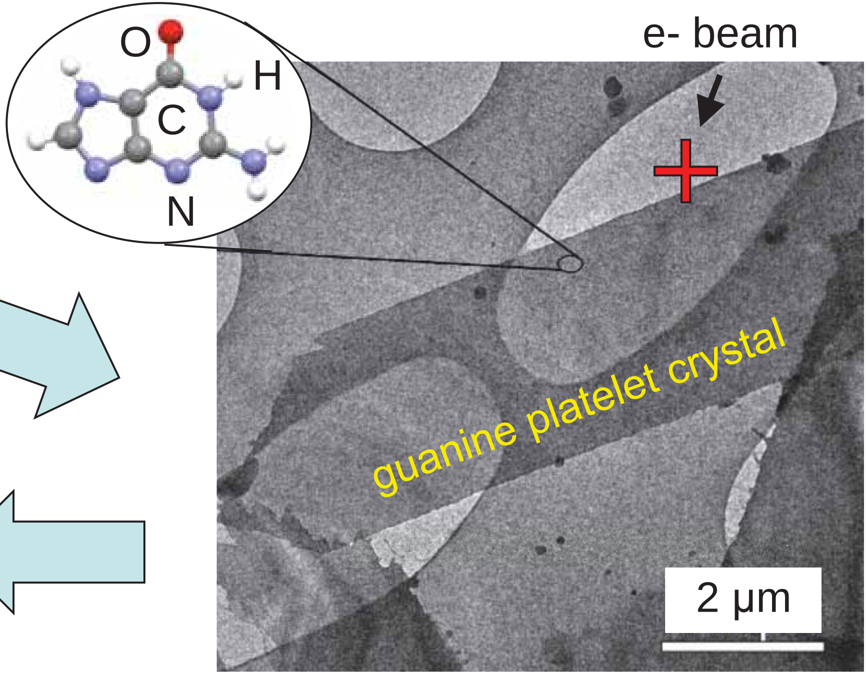
Impact scattering can be selected by an aperture placed at finite angles in the diffraction plane, and emphasized by placing a small beam close to an atomic nucleus.

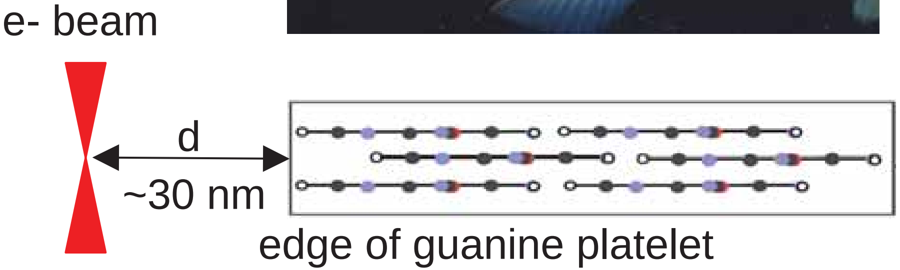


Using dipole scattering to analyze hydrogen bonding

Guanine crystals from Koi fish scales, examined by aloof beam spectroscopy

Japanese
Koi fish





edge of guanine platelet

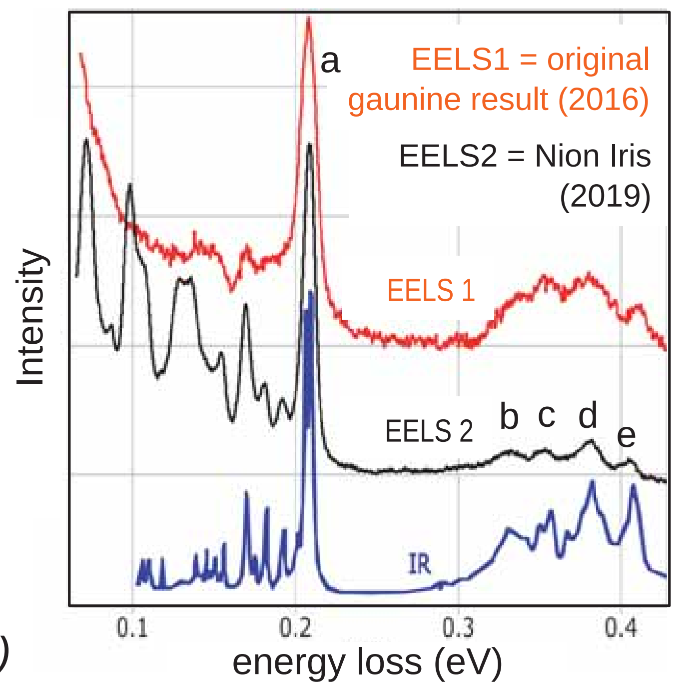
With the beam 30 nm outside the sample, there is essentially no radiation damage.

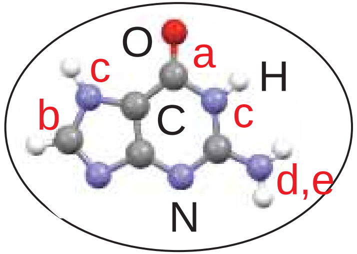
Sample courtesy Dwir Gur, Sharon Wolf & Hagai Cohen
(Weizmann Institute, Israel)

Anhydrous guanine: aloof EELS-FTIR comparison

EEL spectrum recorded in “aloof” mode, with ~ 2 nm Ø probe ~30 nm in vacuum (to minimize radiation damage), compared to a Fourier Transform IR (FTIR) spectrum.

Peak	**Energy (meV)**	**Frequency (cm^{-1})**	**Assignment**
a	209	1666	C=O stretch
b	334	2663	C-H stretch
c	357	2846	N-H stretch
d	386	3078	Symmetric NH_2
e	411	3277	Antisymmetric NH_2



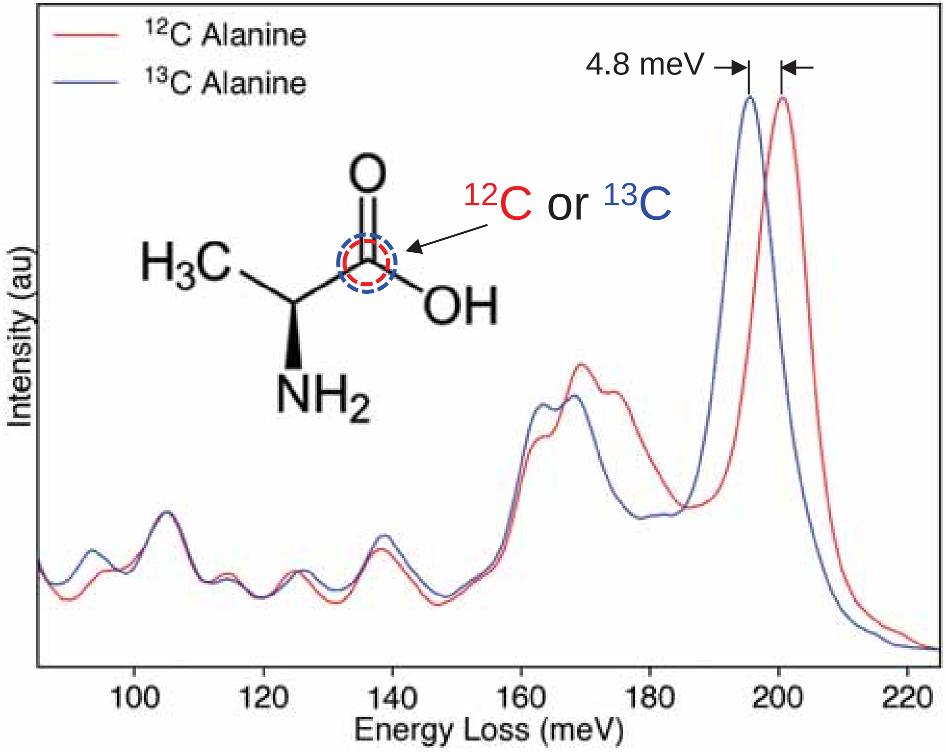


Peter Rez et al., Nature Coms (2016)

DOI: 10.1038/ncomms10945

Biological samples can be analyzed in a damage-free way.

Detecting isotopic substitution in L-alanine



Substituting ^{13}C for ^{12}C at indicated site lowers the C=O bond stretch vibration by 4.8 meV and is readily detectable.

The distributions of the two species can be mapped at ~30 nm resolution.

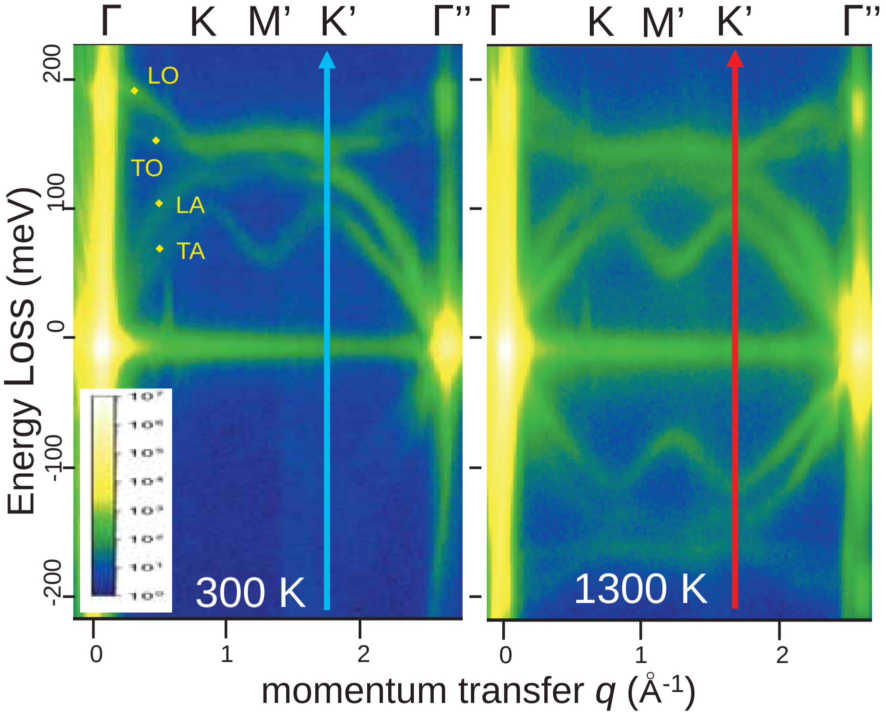
J. Hachtel et al.

Science ***363*** *(2019) 525–528*

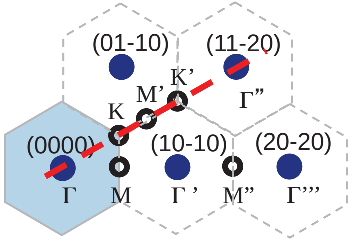
Isotopic substitution can be used to study metabolic pathways in cells and whole organisms.

Momentum-Energy-Temperature exploration in the EM

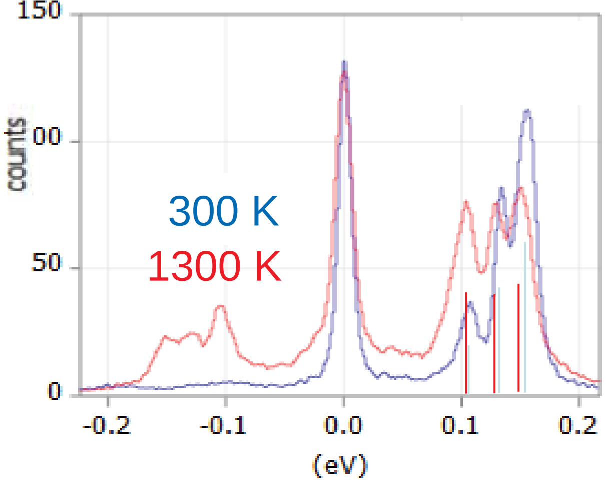
S(q, ω) diagram of hexagonal BN (parallel acquisition)



EELS entrance slit placement



Energy profiles at K’ point



- Peaks are red-shifted at high temperature
- Opposite effect expected from thermal expansion of lattice
- Origin is phonon-phonon scattering

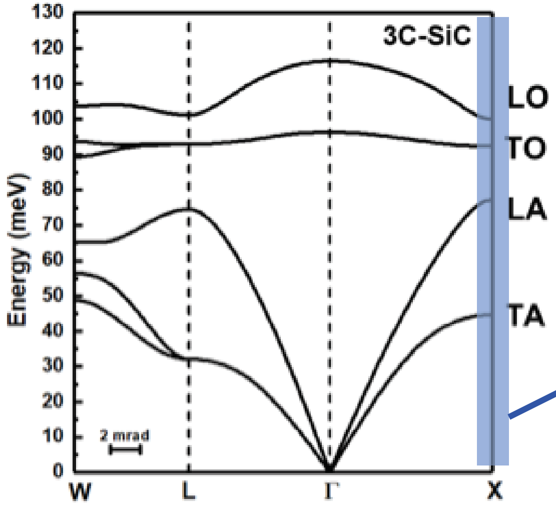
Lovejoy et al. (2021) unpublished

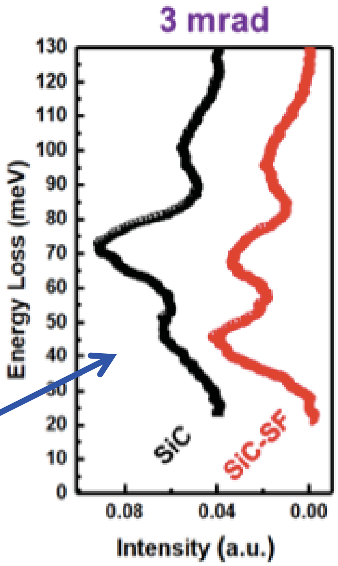
Temperature dependence of phonon interactions in a nanoscale sample revealed.

Detecting vibrational changes at a single stacking fault

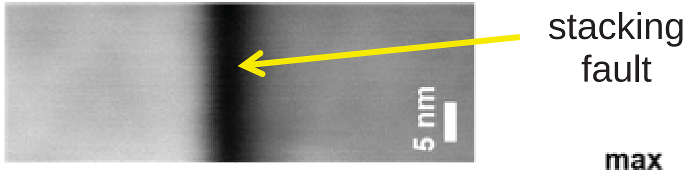
Optical phonon do not change at a stacking fault in cubic SiC. But acoustic phonons do change!

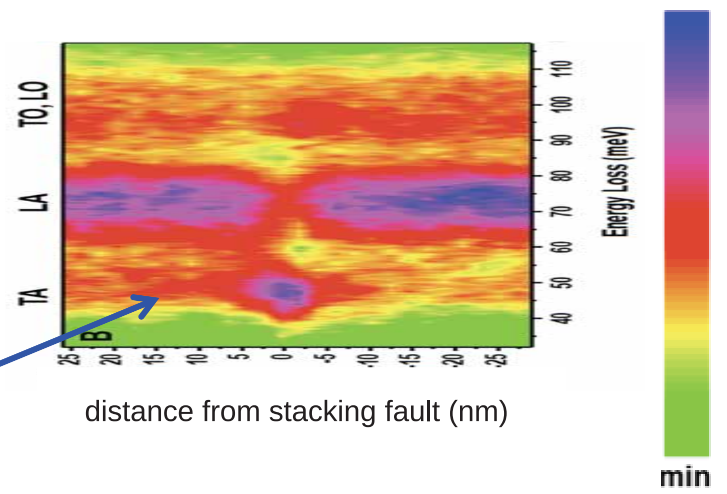
- ➔ Step 1: select q>>0, show the changes at stacking fault





- ➔ Step 2: map the signal in real space

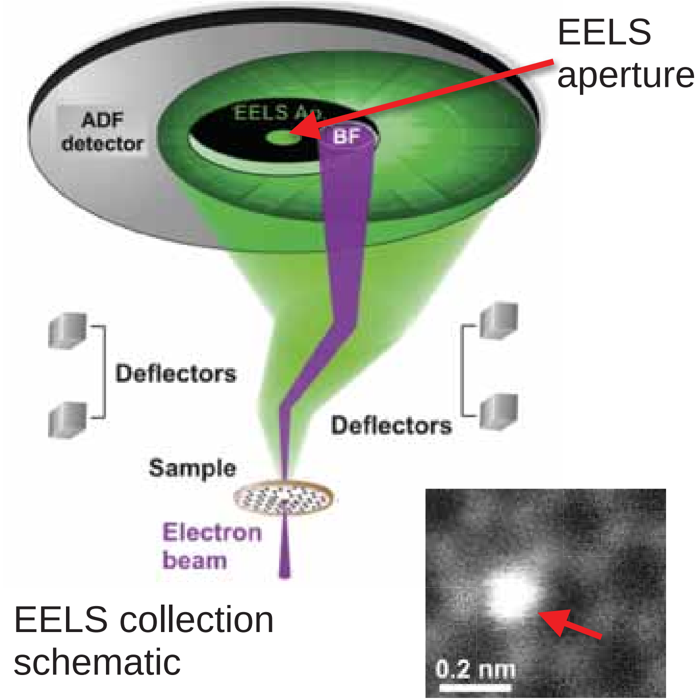




Phonon changes at individual defects detected.

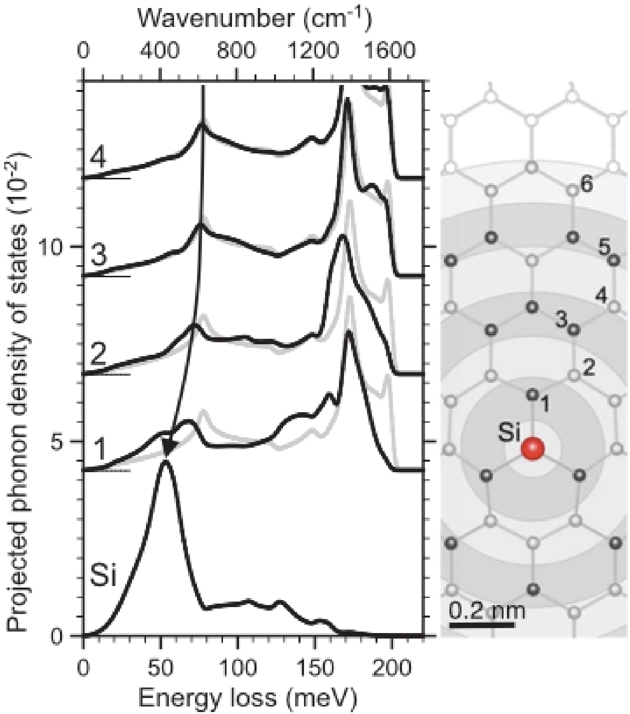
X. Yan et al., Nature ***589*** *(2021) 65-69*

Phonons due to a *single Si atom* in graphene

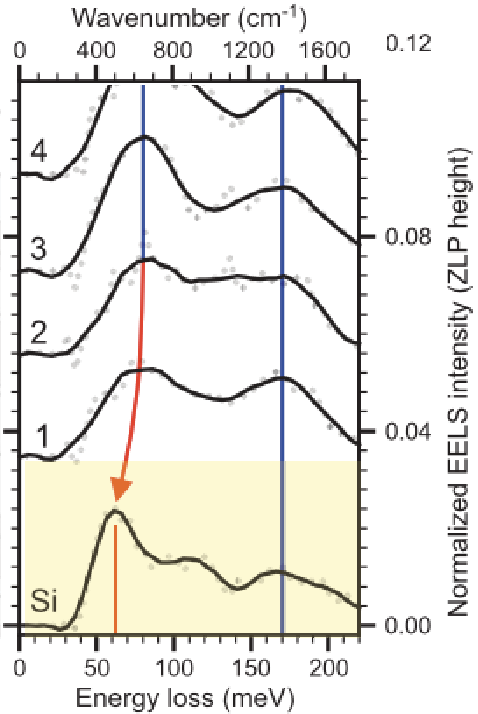


EELS collection schematic

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.

SuperSTEM DARESBURY

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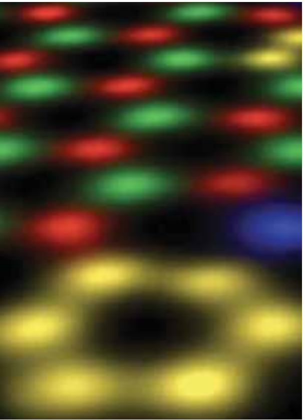
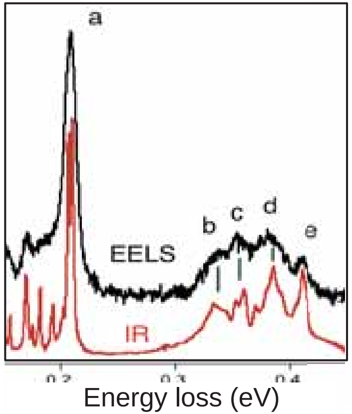
Summary

- Aberration-corrected (S)TEM and ultra-high energy resolution EELS have progressed remarkably since the 1990s.
- There have been major developments in both instrumentation and in theory.
- Many new capabilities are now available, leading to major new results.

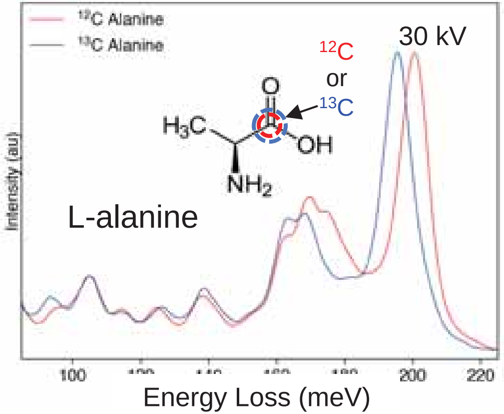
Low-kV atom. res. STEM (2010)



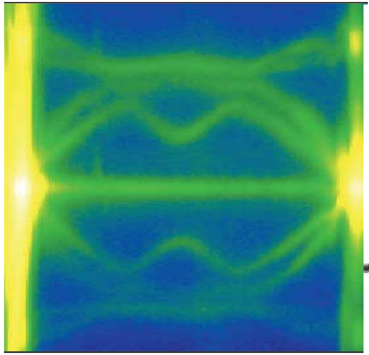
Damage-free EELS (2016)



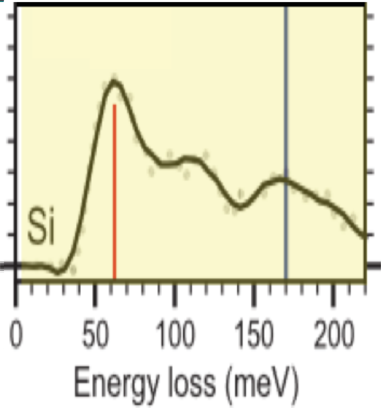
Isotopic substitution in biological molecules (2019)



Efficient q-Ω analysis (2019)



Phonon spectrum of a single atom (2020)



Conclusion: new instruments do open up new worlds!

Galileo Galilei and two of his telescopes

Members of the Orsay group and Nion's Niklas Dellby with Orsay's new 200 kV UltraSTEM. from left: Niklas Dellby, Christian Colliex, Odile Stephan, Katia March, Marcel Tence

Niklas Dellby (Nion co-founder), Christian Colliex, Odile Stephan, Katia March, Marcel Tence and the first complete aberration-corrected EM Nion built, for CNRS Orsay

Galileo’s telescope changed our view of the world. Aberration-corrected electron microscopes and spectrometers are changing our view of the nanoworld.

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