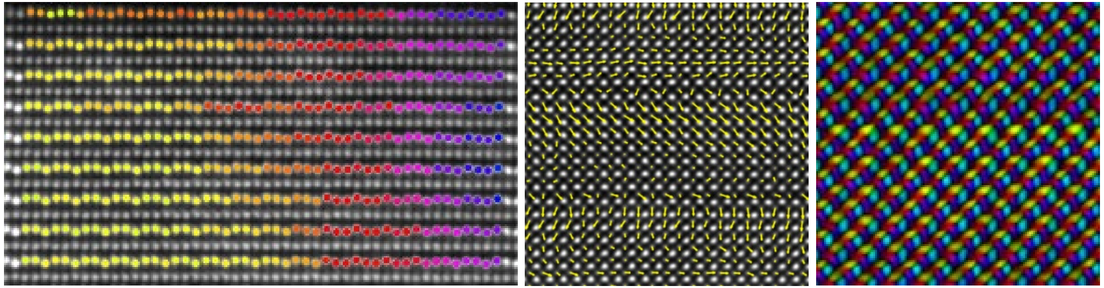
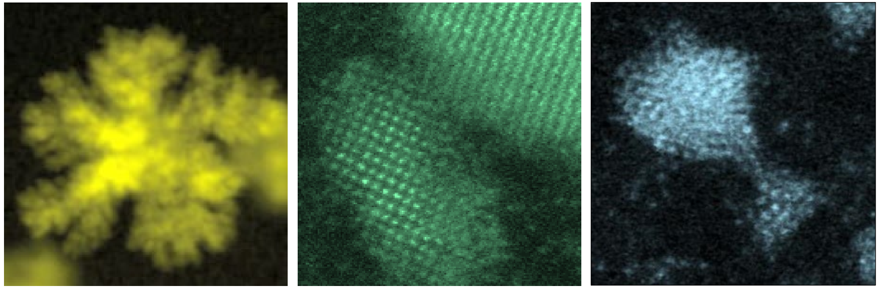


Applications of aberration-corrected STEM

Rolf Erni

Electron Microscopy Center
Empa, Swiss Federal Laboratories for Materials Science and Technology
Dübendorf, Switzerland

rolf.erni@empa.ch



MC2025, Karlsruhe, 31. August 2025

Scanning transmission electron microscopy methods

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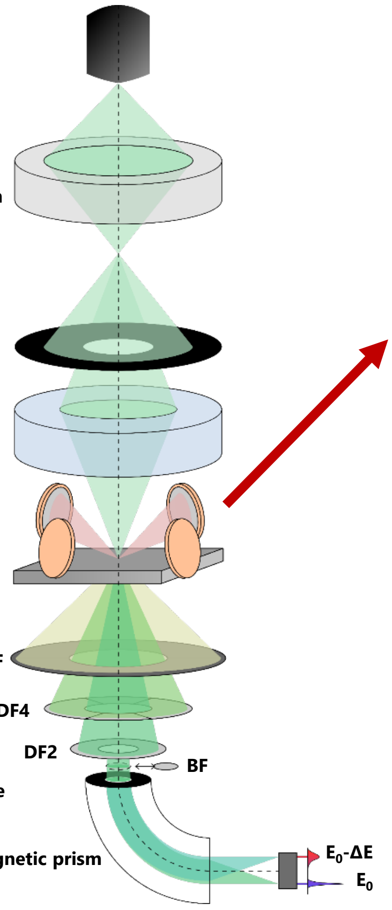
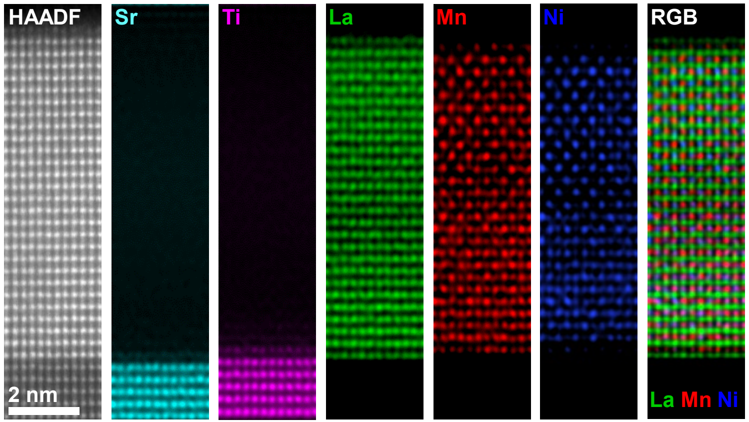


1. Energy dispersive X-ray spectroscopy (EDX)



La_2NiMnO_6 film on a $SrTiO_3$ substrate along the $[110]_{SrTiO_3}$ zone axis: HAADF image and EDX elemental maps of Sr, Ti, La, Mn and Ni.

G. De Luca *et al.* Adv. Mater. (2022) 2203071.

Scanning transmission electron microscopy methods

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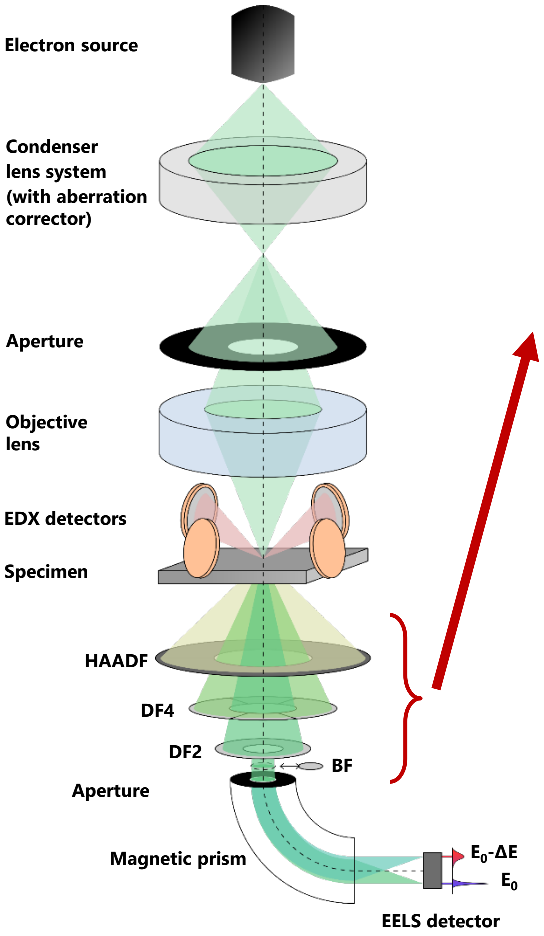
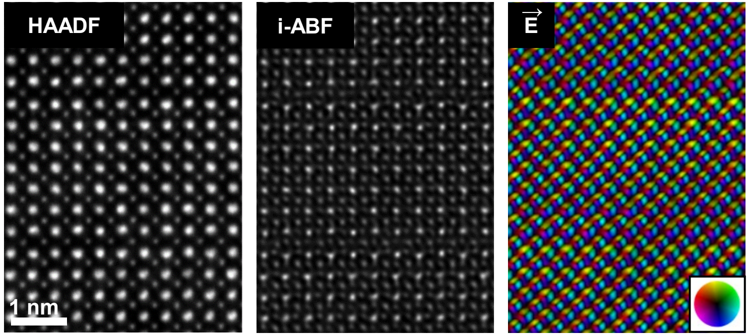


1. Energy dispersive X-ray spectroscopy (EDX)

2. Post-specimen detectors



$Bi_{0.8}Ca_{0.2}FeO_{3-\delta}$ thin film exhibiting periodic dopant fluctuations: HAADF image (left), inverted-ABF image (middle) and projected electric field vector colour map (right).

HAADF: high-angle annular dark-field
DPC: differential phase contrast (DF4)
ABF: annular bright-field (DF2 + DF4)
BF: bright-field

M. Campanini *et al.* Nano Lett. **18**, 717-717 (2018)

Scanning transmission electron microscopy methods

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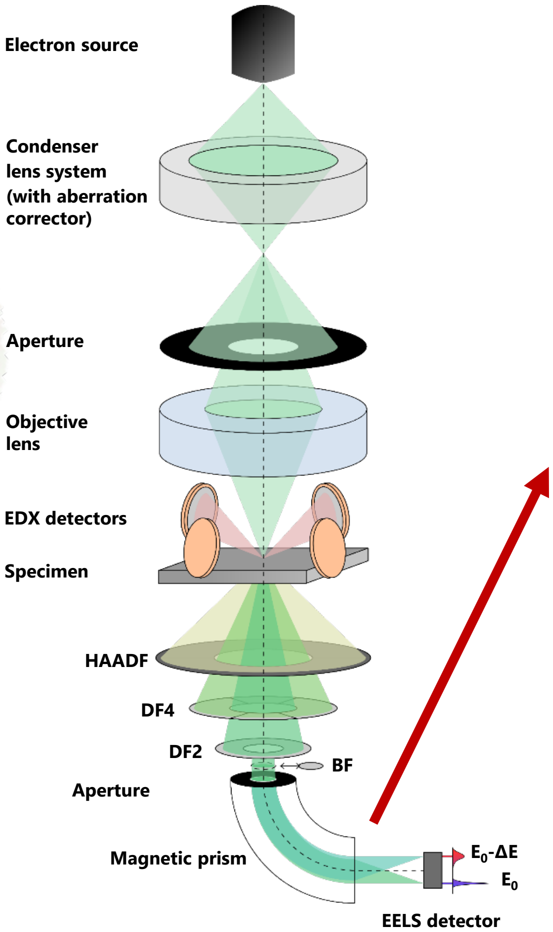
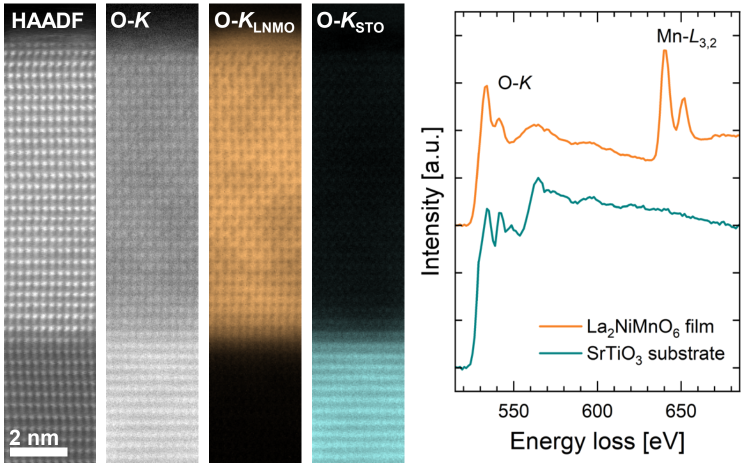
In-situ / operando STEM



1. Energy dispersive X-ray spectroscopy (EDX)

2. Post-specimen detectors

3. Electron energy loss spectroscopy (EELS)



La_2NiMnO_6 (LNMO) thin film on $SrTiO_3$ (STO): HAADF image and EELS maps of the O-*K* edges generated by fitting the components of the LNMO film (orange) and STO substrate (turquoise) using the multiple linear least square (MLLS) fitting method.

A. Ruiz Caridad *et al.*, Micron **160** 103331 (2022)

Before aberration correction

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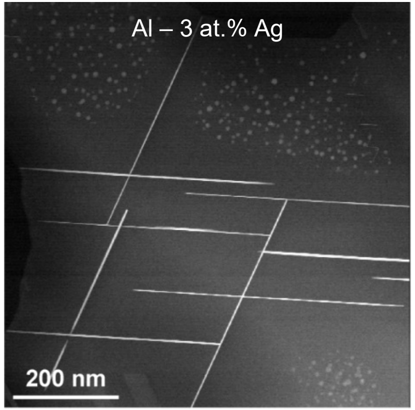
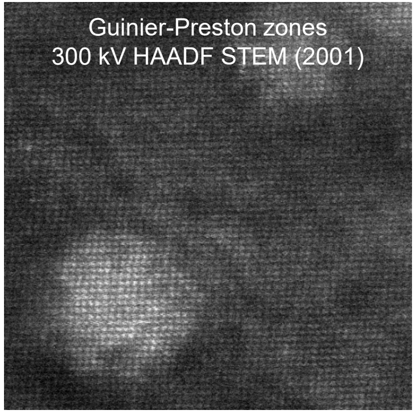
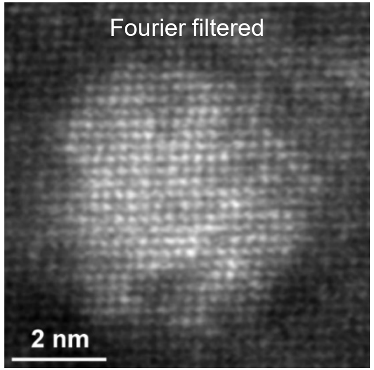
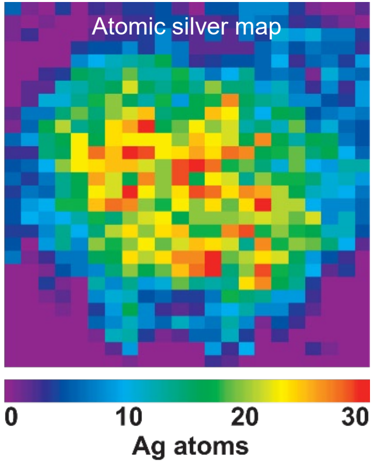
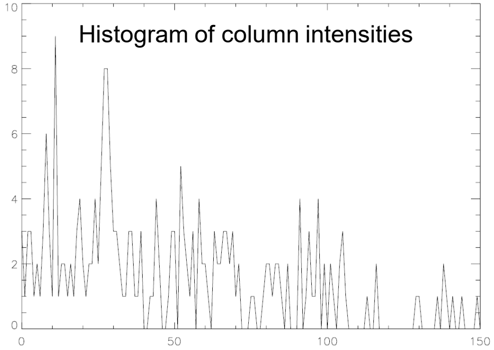








Idea: exchanging an Al atom with a Ag atom should give a discrete change of image intensity (incoherent imaging model): make a histogram of column intensities and get that discrete energy change = quantification!



Issues:

- Noisy data, limited resolution… limited reliability!
- Instrument and scan stability
- 300 keV electrons: possibility of radiation damage.
- Lots of manual work… human bias?

First HAADF-STEM image quantification: R. Erni, H. Heinrich, G. Kostorz, Ultramicroscopy **94** (2003) 125-133.

10 years later – with aberration correction

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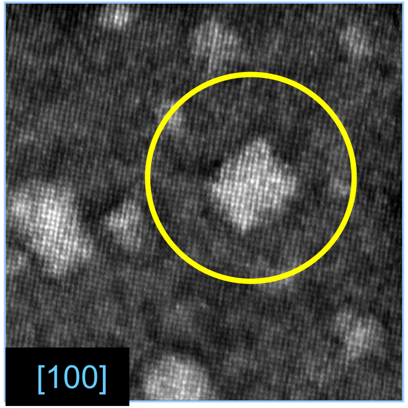
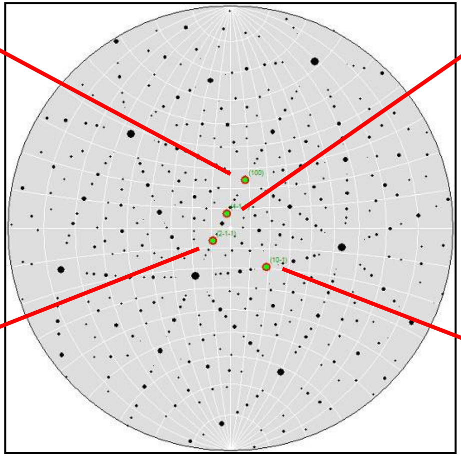
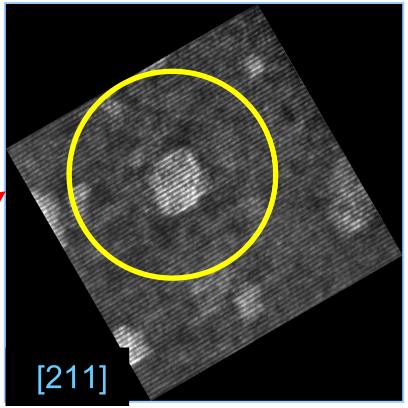
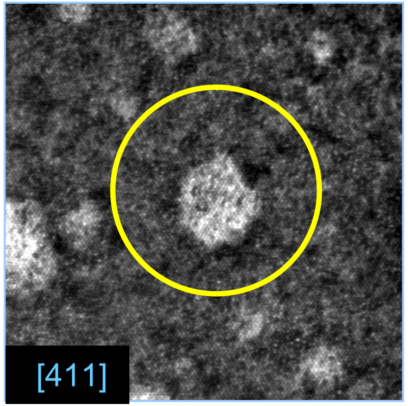


2009
Guinier Preston zones in Al-3 at.%
Ag aberration corrected, 80 kV

Wulff's net: fcc







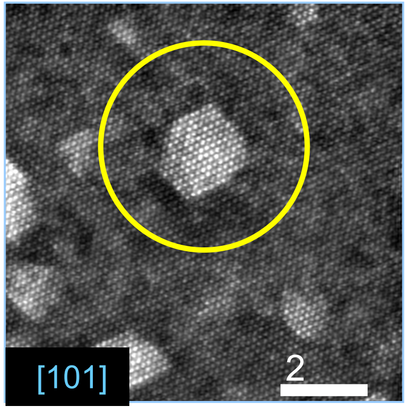
With aberration correction

HR-STEM at 80 kV: No radiation damage!

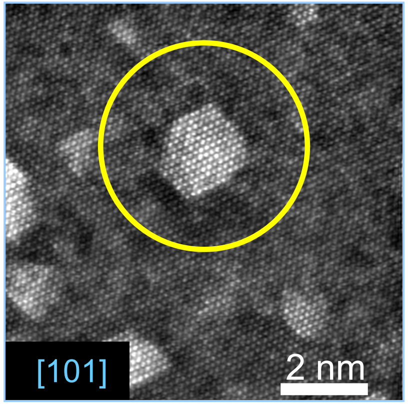
Signal-to-noise ratio: largely improved

Instrument and scan stability improved

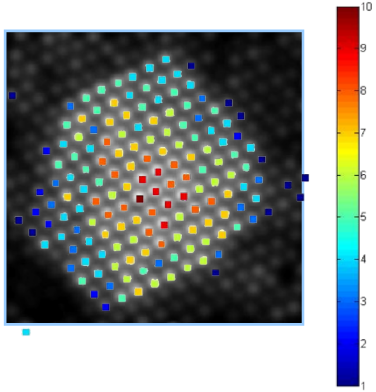
We can monitor a particle in different orientations in a controlled way at atomic resolution with no radiation damage!

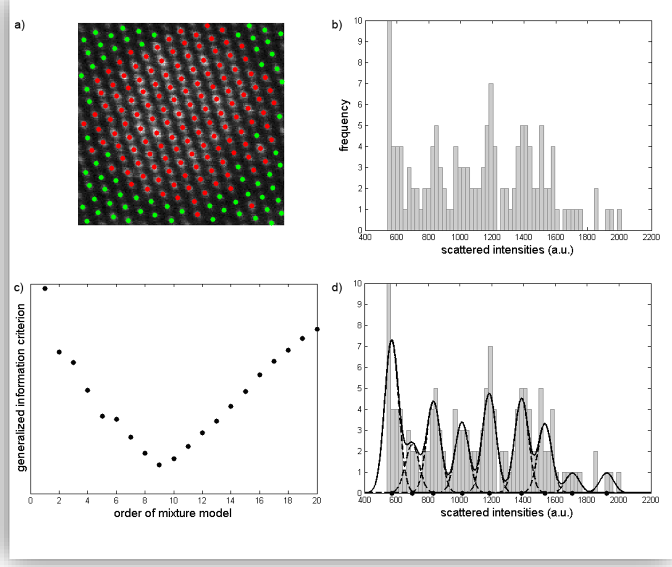


Towards quantification



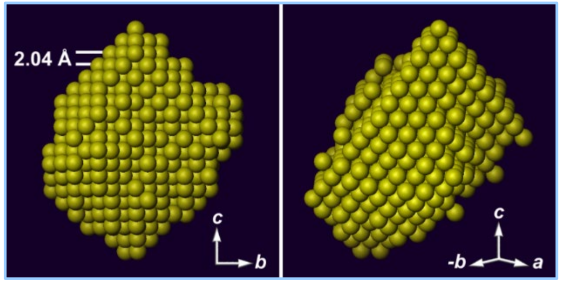
Model based image quantification: discrete intensity change, and histogram
(Sandra Van Aert, EMAT, Antwerp)

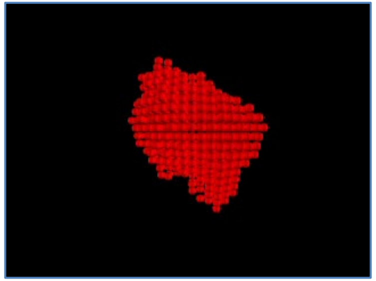




With aberration correction plus improved analysis method:

- Quantification becomes more reliable
- Human bias is reduced
- Improved data: quantification in different directions
- 3D reconstruction (Jost Batenburg, now Leiden University)





First atomic resolution electron tomography: S. Van Aert, K. J. Batenburg, M. D. Rossell, R. Erni, G. Van Tendeloo, Nature **470** (2011) 374-377.

Catalytic Pt clusters on CeO_2 - Reducing human bias

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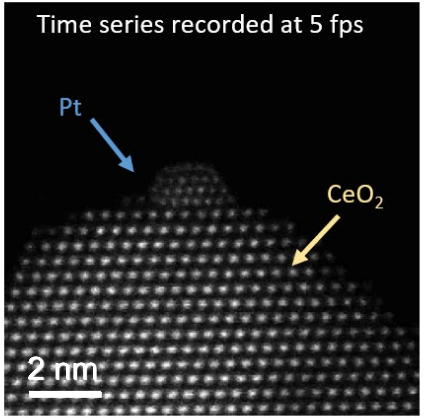
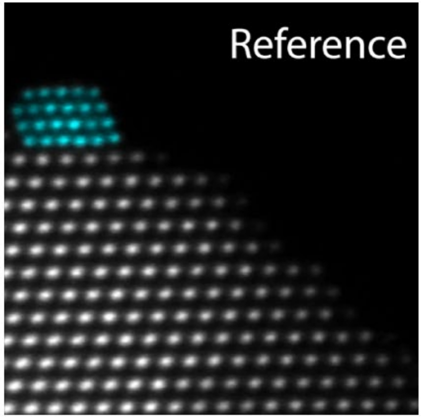
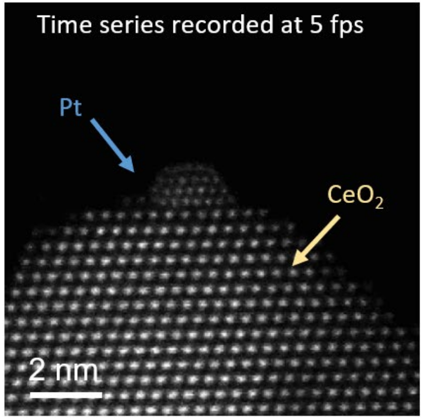


Henrik Eliasson, Y. Niu, R. Palmer, H. Grönbeck, R. Erni, Nanoscale 15 (2023) 19091.

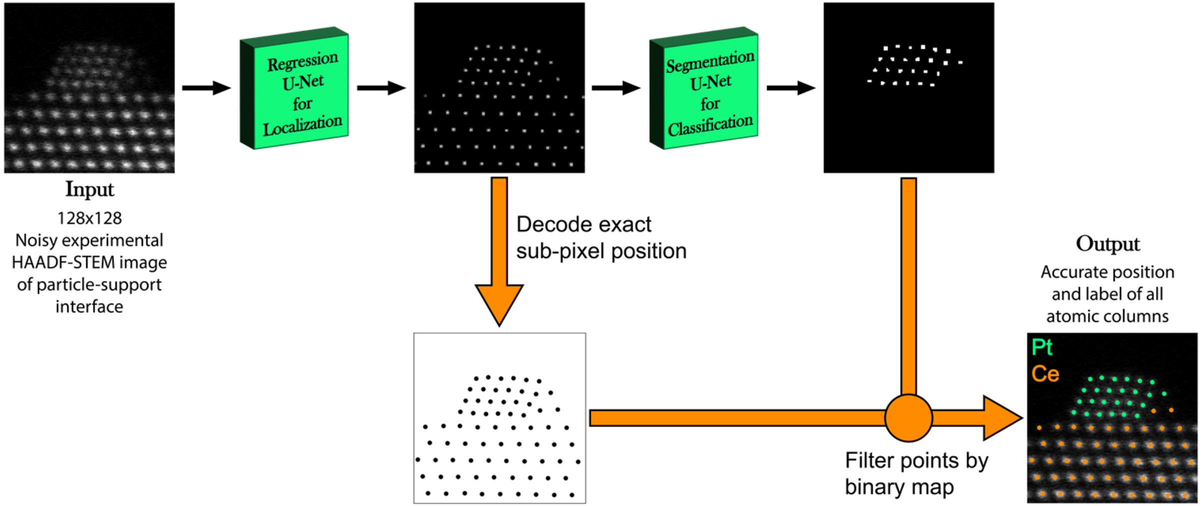


- Increased beam current of an aberration-corrected probe: temporal resolution!
- Remove human bias in data analysis & speed up analysis (time series)
- Use machine learning: identify and accurately locate atomic columns
- Ultimately: each micrograph should provide an atomic 3D model

Catalytic Pt clusters on CeO_2 - Reducing human bias



Henrik Eliasson, Y. Niu, R. Palmer, H. Grönbeck, R. Erni, Nanoscale 15 (2023) 19091.



- Increased beam current of an aberration-corrected probe: temporal resolution!
- Remove human bias in data analysis & speed up analysis (time series)
- Use machine learning: identify and accurately locate atomic columns
- Ultimately: each micrograph should provide an atomic 3D model

Daily routines – some tips

- Choice of beam current
  - Aberration-corrected optics provides flexibility. With little penalty on resolution, a significantly larger beam current can be set, simplifying analytics (EDX, EELS).

- A look at the electron probe or at the Ronchigram is useful before employing the tuning software.

- Using the full dynamic range of the detector for aberration measurements can increase reliability.

- If the alignment is far off, tuning with a higher beam current than normal can be of help. This increases the reliability of the measurement and speeds up the iteration process.

- Once the desired alignment state is achieved, recording another tilt tableau provides confidence.

- A slightly smaller probe convergence angle increases the stability of the alignment, with little penalty on resolution.

Diffraction limit: $d = 0.61 \frac{\lambda}{\alpha}$

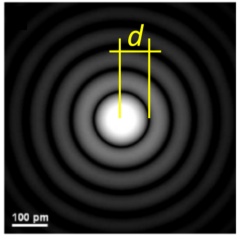
300 kV:

$\alpha = 25 \text{ mrad}: \; d = 49 \text{ pm}$

$\alpha = 18 \text{ mrad}: \; d = 68 \text{ pm}$

Microscope high tension – electron energy

Diffraction limit: $d = 0.61 \dfrac{\lambda}{\alpha_{\mathrm{corr}}}$



Airy pattern

- The angle corrected by the optical system α_{corr} is rather insensitive to the electron energy.
- The achievable resolution thus linearly depends on the electron wavelength.

Reducing the electron energy

- Penalty in resolution (often acceptable)
- Less knock-on damage
- Chromatic aberration gains in importance

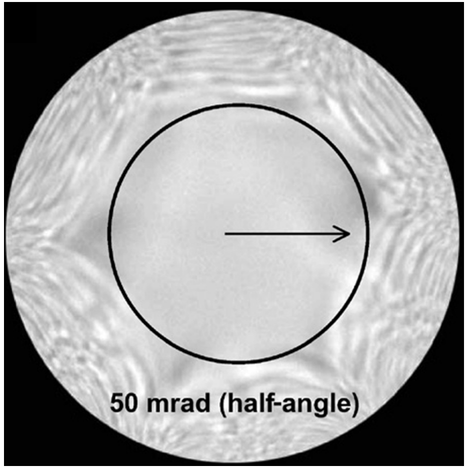
Microscope	Optimum C_1	Optimum C_3	Optimum C_5	Optimum α	Resolution
C_3-limited*	$C_1 = -\sqrt{\lambda C_3}$	fixed, positive	n/a	$\sqrt[4]{4\frac{\lambda}{C_3}}$	$0.43\sqrt[4]{\lambda^3 C_3}$
C_5-limited**	$-1.56\sqrt[3]{\lambda^2 C_5}$	$-2.88\sqrt[3]{\lambda C_5^2}$	fixed, positive	$\sqrt[6]{12\frac{\lambda}{C_5}}$	$0.40\sqrt[6]{\lambda^5 C_5}$
C_7-limited**	$2.38\sqrt[4]{\lambda^3 C_7}$	$7.07\sqrt[4]{\lambda^2 C_7^2}$	$-5.05\sqrt[4]{\lambda C_7^3}$	$\sqrt[8]{64\frac{\lambda}{C_7}}$	$0.36\sqrt[8]{\lambda^7 C_7}$
C_C-limited**	n/a	n/a	n/a	$1.2\sqrt{\lambda\frac{E_0}{\ell_C}}$	$0.51\sqrt{\lambda\frac{\ell_C}{E_0}}$

$\ell_C = C_C\,\Delta E$

Scherzer, J. Appl. Phys. (1949)

Crewe & Salzman, Ultramicrosc. (1982)

Itaraprasonk et al., Ultramicrosc. (2008)



Sawada et al., Ultramicroscopy (2008)

R. Erni, Aberr.-corr. imag. in TEM, Imp. Coll. Press (2015)

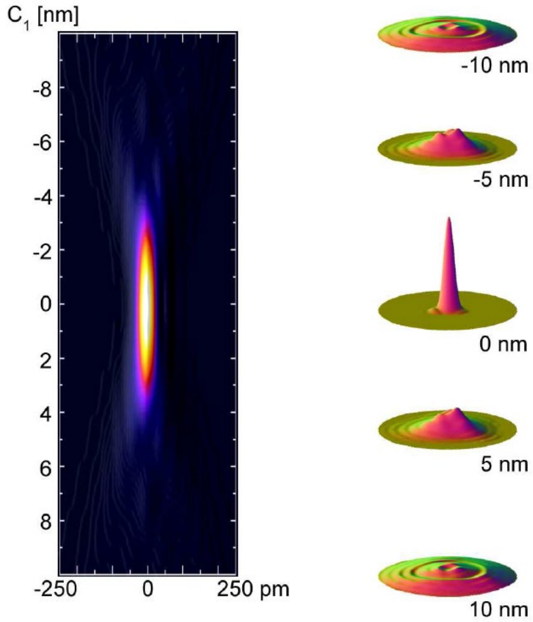
STEM probe: depth of field

The larger the convergence angle, the smaller the depth of field ΔC_1!

$$\Delta C_1 \approx \frac{\lambda}{\alpha^2}$$

300 kV:

$\alpha = 10 \text{ mrad}: \Delta C_1 \approx 20.0 \text{ nm}$
$\alpha = 18 \text{ mrad}: \Delta C_1 \approx 6.2 \text{ nm}$
$\alpha = 25 \text{ mrad}: \Delta C_1 \approx 3.2 \text{ nm}$

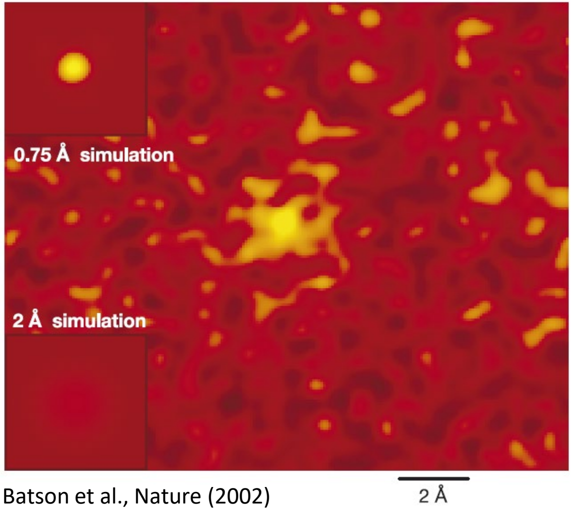


- Tomography might not benefit from a sub-Ångström beam: depth of field is limited, and complicates proper focusing

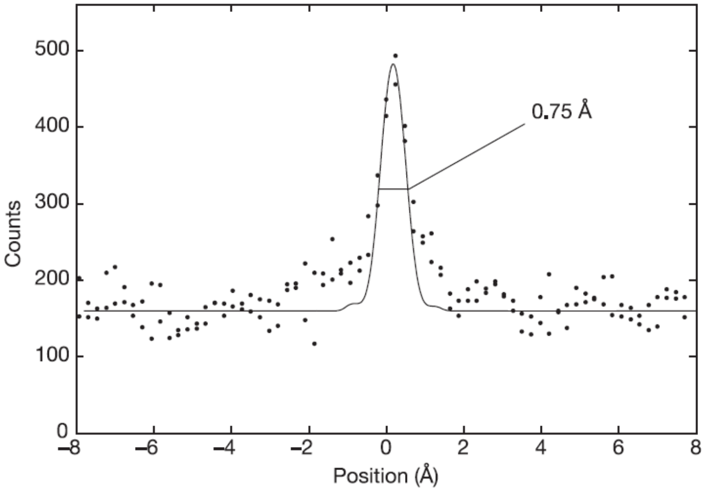
- If sample thickness significantly exceeds the depth of field, contrast might degrade (not resolution). A smaller convergence angle might be beneficial (e.g. 18 v. 25 mrad).

Assessing resolution with a point-like object – not trivial

- HAADF STEM: image is a convolution between object and electron probe
- Make an image of an atom
- Assess probe size from the image: assuming the atom is small or comparison with simulation



Batson et al., Nature (2002)



- The atom might move, making the measurable resolution smaller or larger
- What´s the optimal focus? Highest contrast or smallest feature size?

Assessing resolution using a crystal – not trivial

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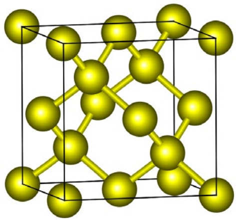
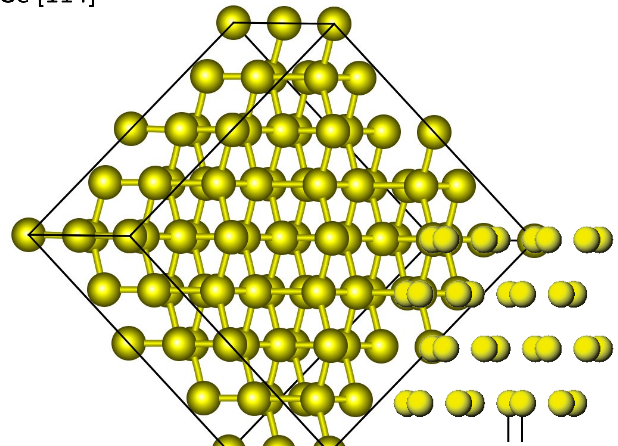
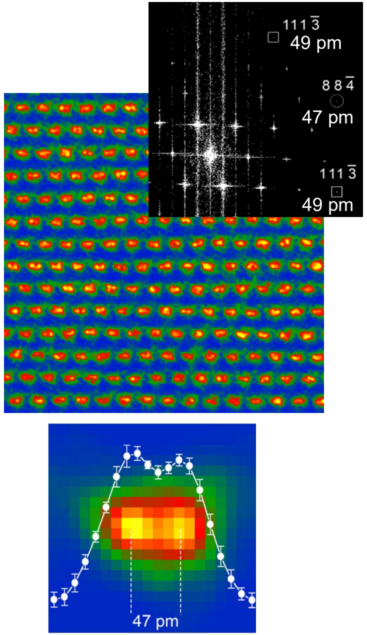
- Find a simple compound
- Find a suitable spacing
- Choose a large enough convergence angle (diffraction limit)
- Do imaging and confirm expected resolution

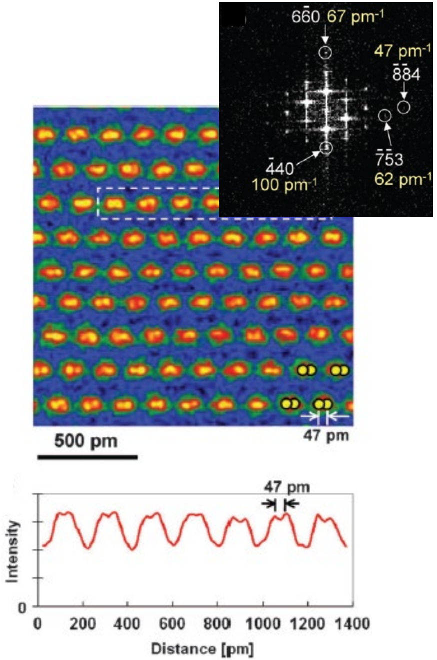


Ge [114]





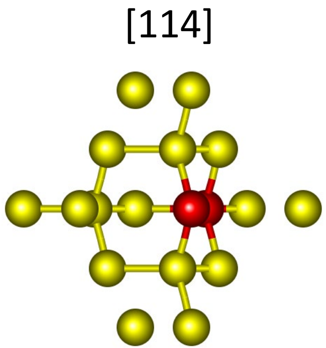
Erni et al., PRL (2009)

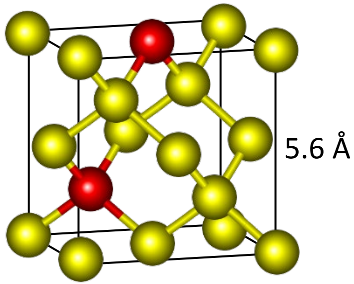


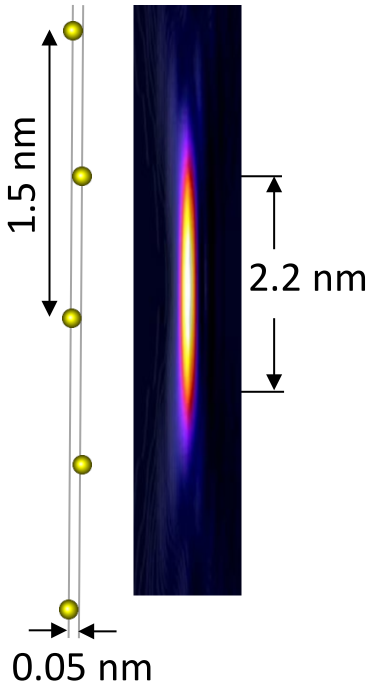
Sawada et al., JEM (2009)

What are the limiting factors?

The intrinsic sample problem of resolution tests







Spacing between [114]-projected Ge atoms: 0.47 Å
Spacing between Ge atoms: 7.5 Å

What makes the probe channel down one of the paired atomic columns and stay on it?

Thermal vibrations, stage stability, residual sample tilt etc.

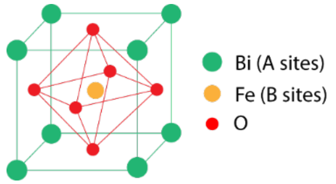
It is amazing that a splitting is observed at all!

Versatility of aberration corrected STEM – case study

Ca-doped $BiFeO_3$: a ferroelectric ferromagnet: Ca should improve magnetic properties

Ca: prevention of cycloidal spin modulation which deteriorates magnetic properties in BFO

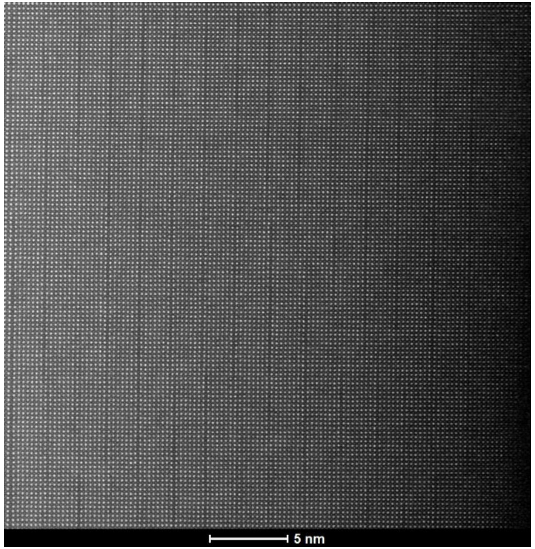
Donor doping (e.g. Ca^{2+} substituting Bi^{3+}): O vacancies?



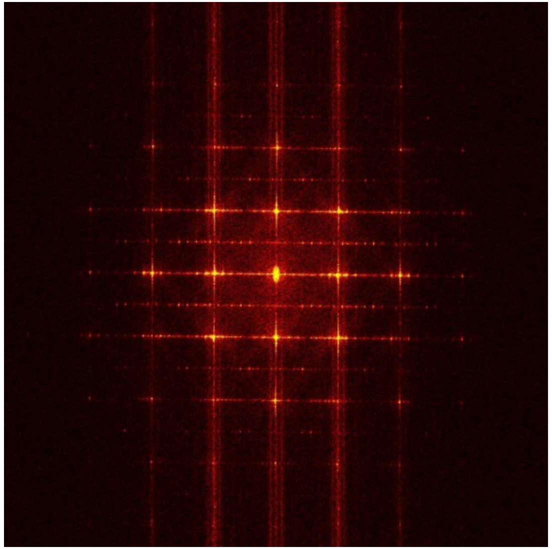
> Detailed atomic configuration still missing:
> Ordering of O vacancies? Ordering of Bi/Ca cations?

20% Ca: $Bi_{1-x}Ca_xFeO_{3-\delta}$
(x = 0.2, δ=x/2)

HAADF-STEM



Fourier transform



Long-range distribution of Ca in $BiFeO_3$: HAADF-STEM

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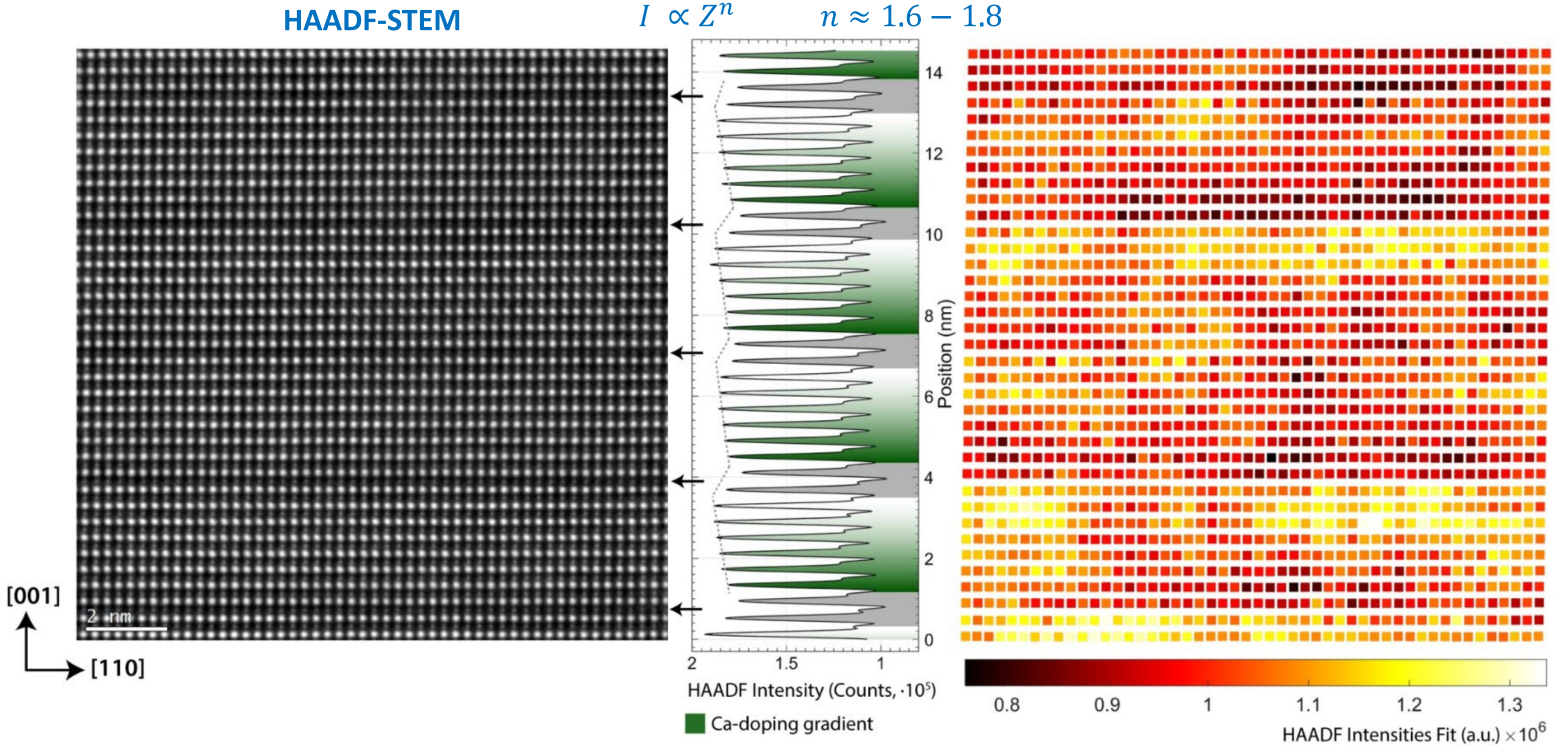
Qualitative analysis of the HAADF STEM intensity.

$I \propto Z^n \qquad n \approx 1.6 - 1.8$



Identification of local Ca gradients.

M. Campanini *et al.* Nano Lett. **18**, 717-717 (2018)

Oxygen vacancies in Ca-$BiFeO_3$: ABF-STEM

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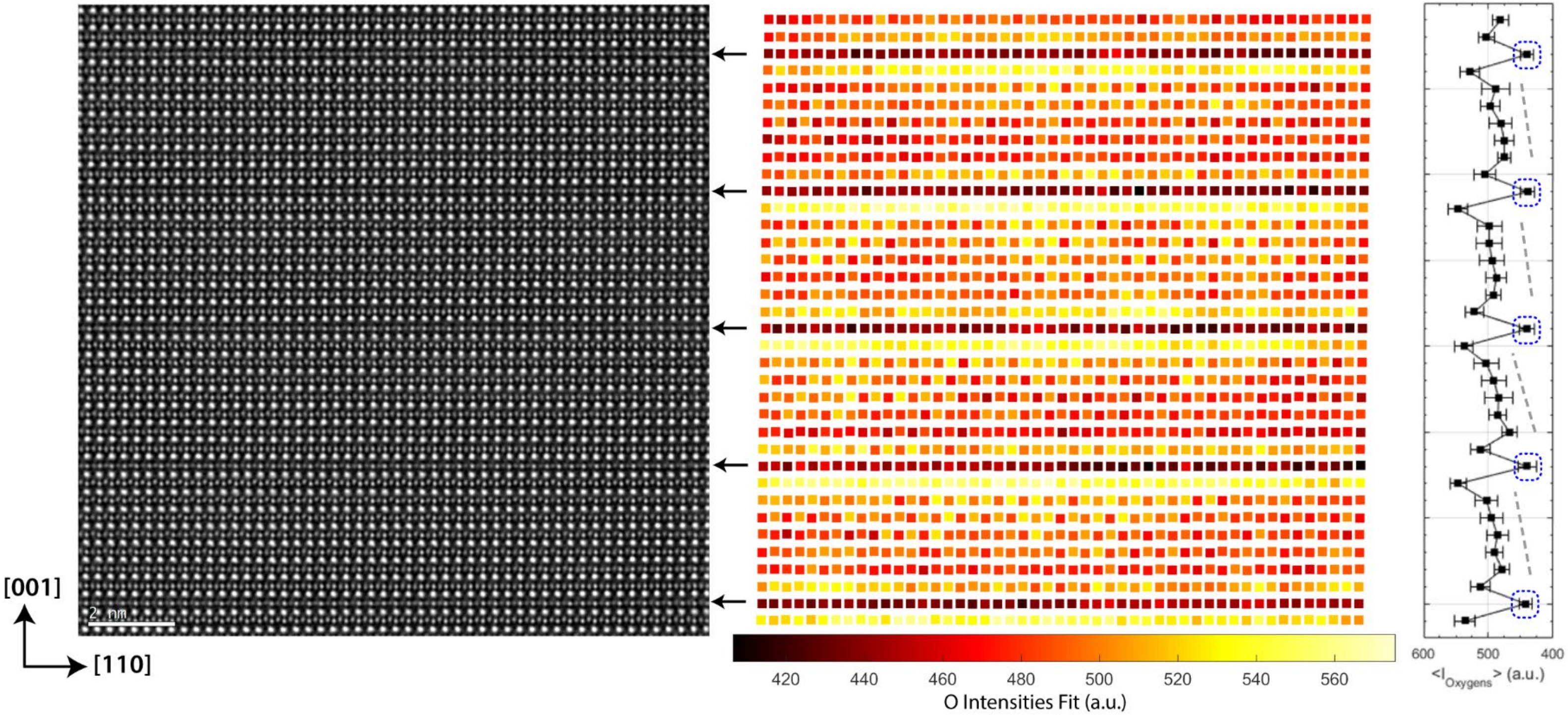
Qualitative analysis of the ABF STEM intensity.

Inverted Annular Bright-Field STEM

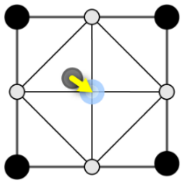
$I \propto Z^n \qquad n \approx 0.3$

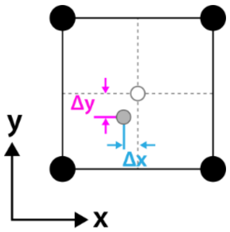


Oxygen vacancies correlate with Ca distribution.

M. Campanini *et al.* Nano Lett. **18**, 717-717 (2018)

Atomic displacements: polarization map [100]

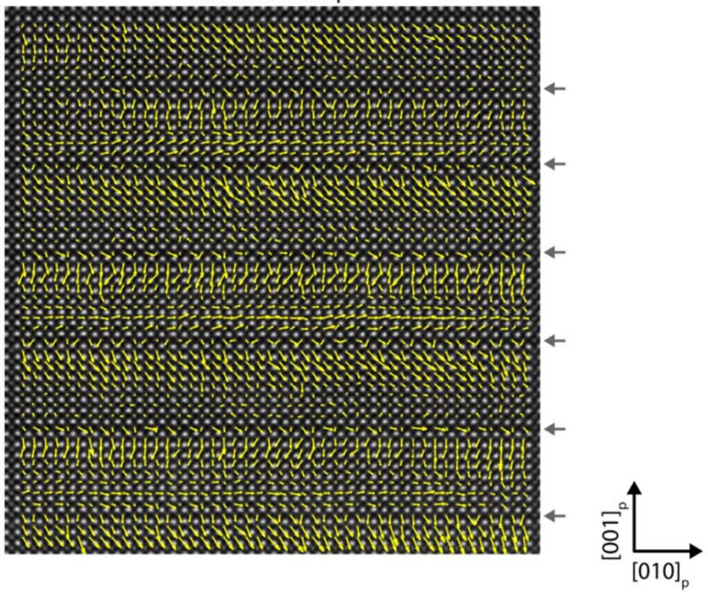




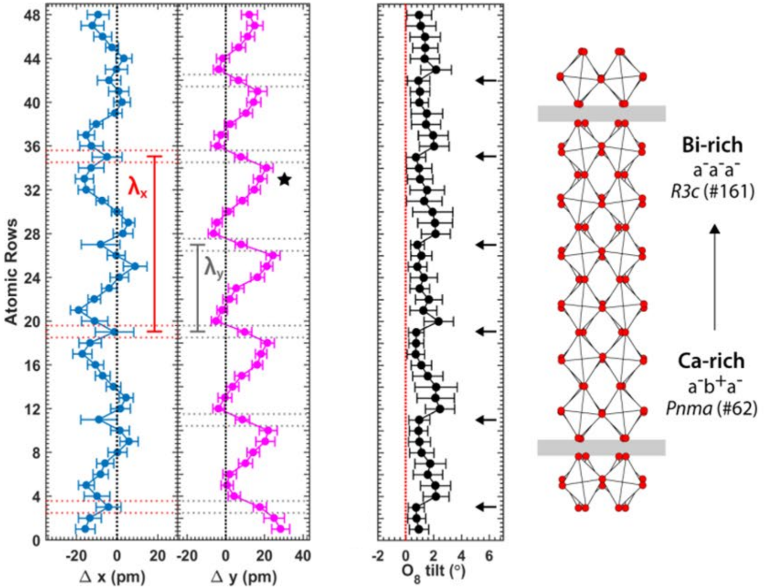
Polarization estimation
(Born effective charge (BEC) approximation)
P_{max} = 76 μC/cm^2
P_{min} = 8 μC/cm^2

$\lambda_x = 2\,\lambda_y$

Polarization map



Atomic displacements

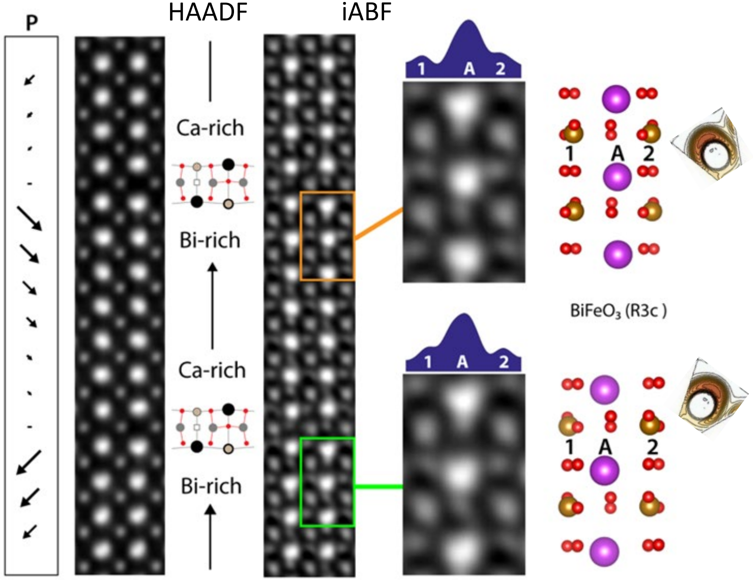


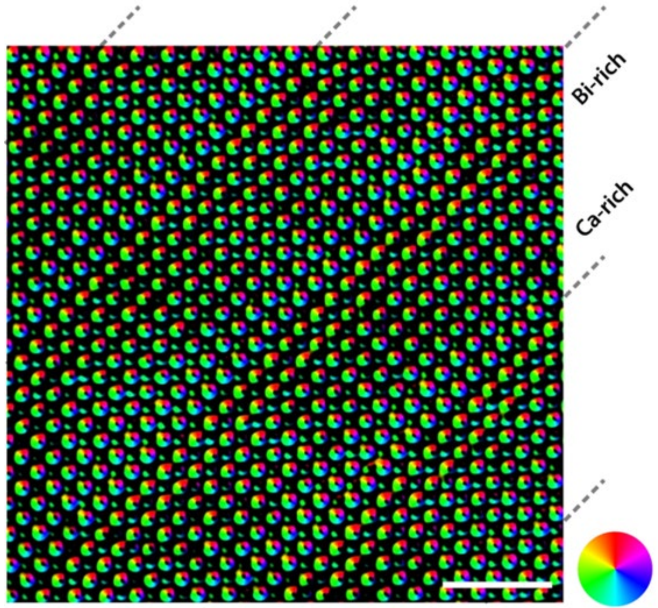
M. Campanini *et al.* Nano Lett. **18**, 717-717 (2018)

Structure-property relation: DPC STEM

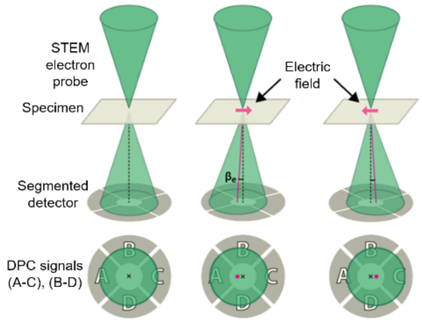
Ferroelectricity in $BiFeO_3$: determined by a lone pair associated with Bi

Can we see the lone pair by Differential Phase Contrast STEM?





Electrostatic field map from DPC STEM



DPC STEM does not see the lone electron pair, but the ferroelectric polarization.

Ca-rich areas: Ca destroys lone pair ordering

Ca-poor areas: lone pair ordering as expected for (bulk) $BiFeO_3$

M. Campanini *et al.* Nano Lett. **18**, 717-717 (2018)

Summary

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- Spending hours tuning the corrector is often not necessary: a reasonable, reliable tuning is often sufficient. Measuring a unique peak value of the correction state is often not representative.

- Not only lateral resolution matters, but also the depth of field, particularly for tomography or samples that cannot be prepared super thin.

- Aberration-corrected STEM provides a versatility of imaging modalities: ABF, HAADF, BF, DPC, 4D

- STEM settings can be optimized according to the requirement of the sample and according to the data are needed: beam current, electron energy, convergence angle etc.

- Combining aberration-corrected STEM with analytics (EELS, EDX, CL) opens up additional dimensions, benefiting from enhanced beam current!

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