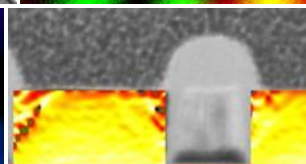
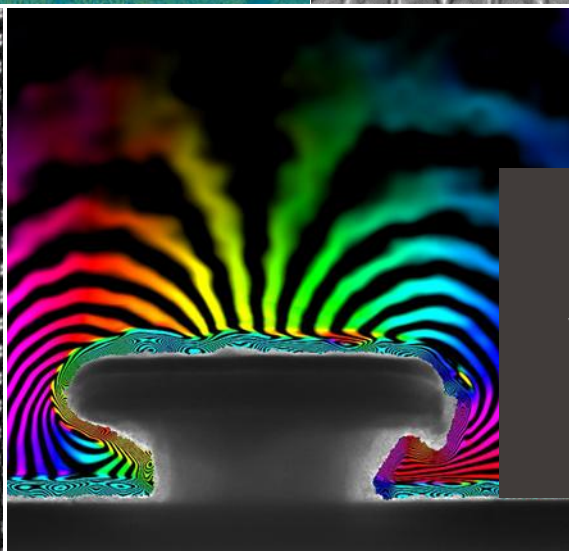
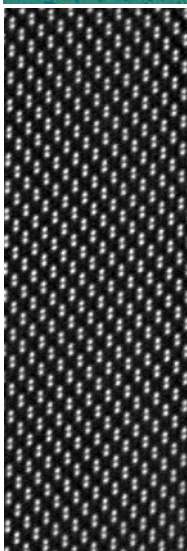
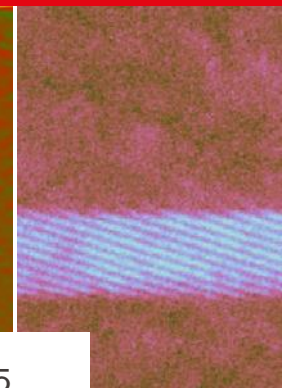
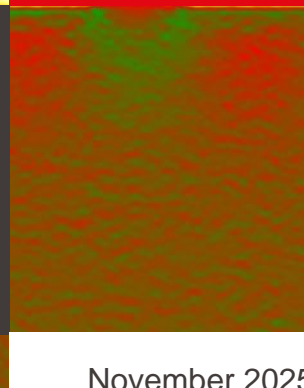


MSE-735
Advanced Transmission
Electron Microscopy

3 – STEM beyond conventional
imaging (with pixelated
detectors)



Victor Boureau

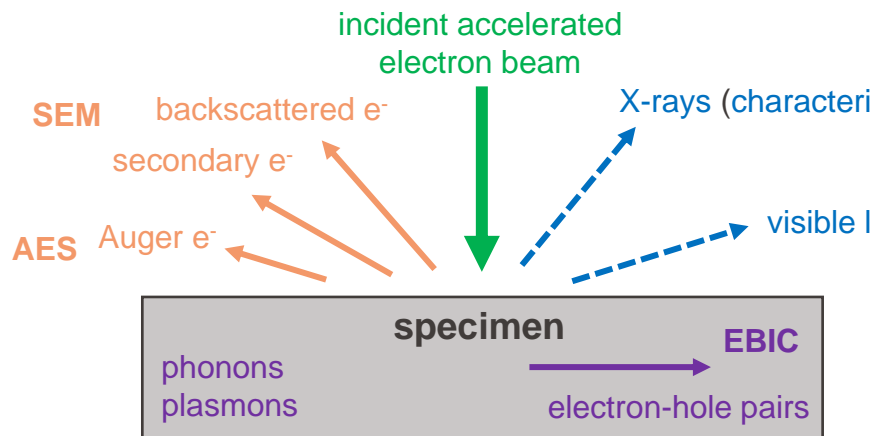




Outline

1. **STEM basics**
2. Pixelated STEM detectors
3. DPC
4. 4D-STEM
5. Conclusion

EPFL Signals in STEM mode



EELS
inelastically scattered e^-

transmitted e^-
BF
ABF

ADF
HAADF



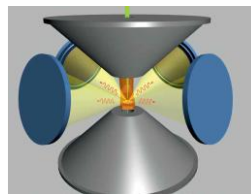
GIF continuum, Gatan



HAADF detector, Gatan

STEM spectroscopy

EDX
CL



Super-X system, ThermoFisher

STEM imaging

ABF: annular bright-field
HAADF: high-angle annular dark-field

STEM imaging detectors are:

- Annular
- Monolithic



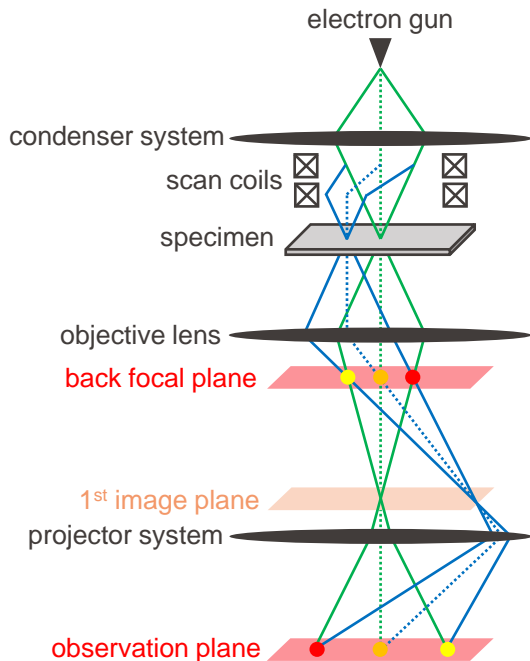
EDX / CL

Detectors

EELS

EPFL Imaging with STEM detectors

STEM optical diagram



STEM diagram

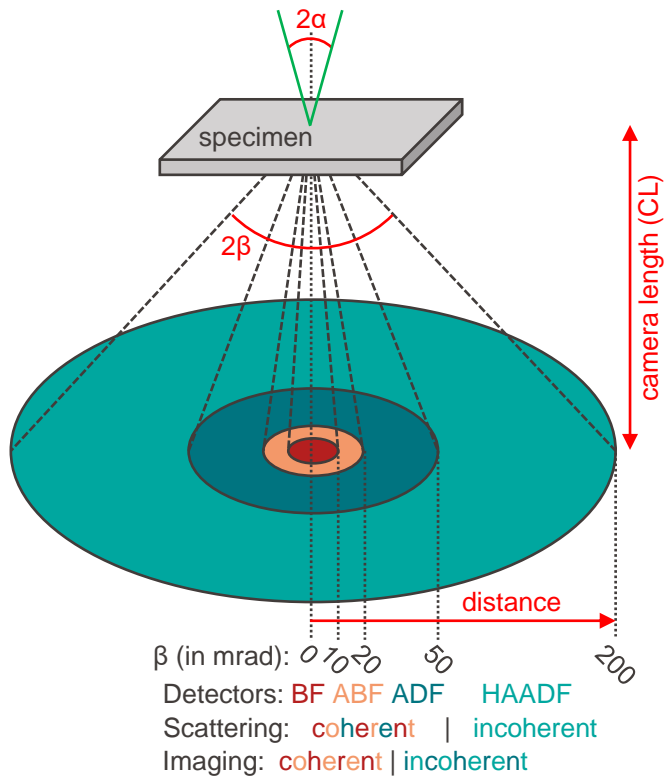
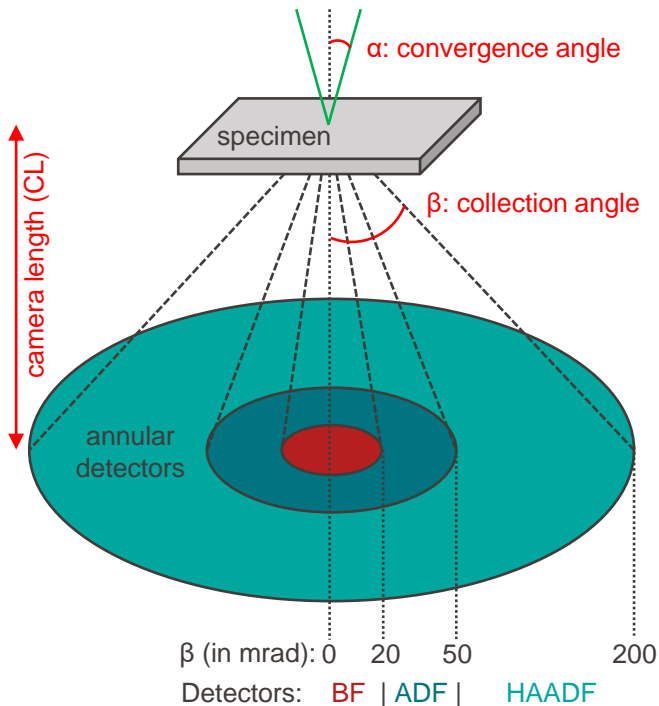


Image capture in STEM:

- Convergent beam raster-scanned on the sample
- Detectors placed in the diffraction plane

- Convergence angle α : defined by condenser system
- Camera length CL: defined by projector lens system
- **Diffraction plane: distance \propto scattering angle**

STEM diagram

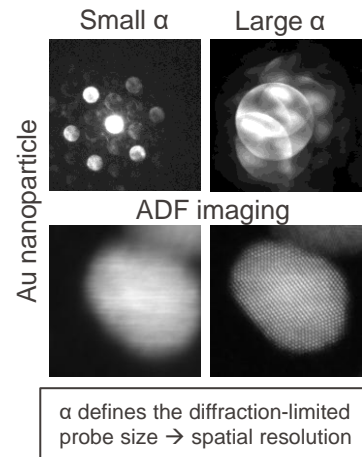


Are there other types of STEM detectors?

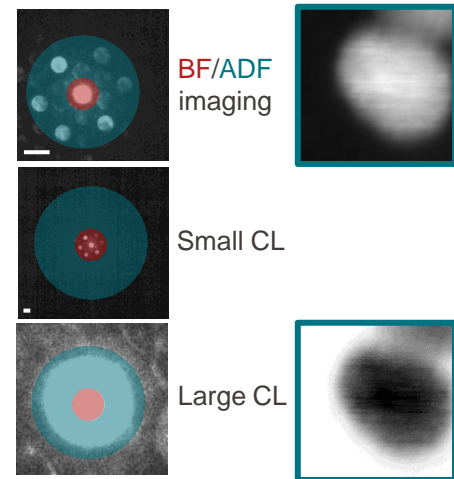
- Not annular
- Not monolithic

Experimental parameters

➤ Convergence angle:

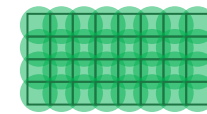
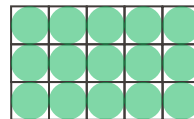


➤ Camera length:



- Probe current
- Dwell time
- Step size:

Electron dose: used to mitigate beam-induced damage



Under-sampled

Over-sampled



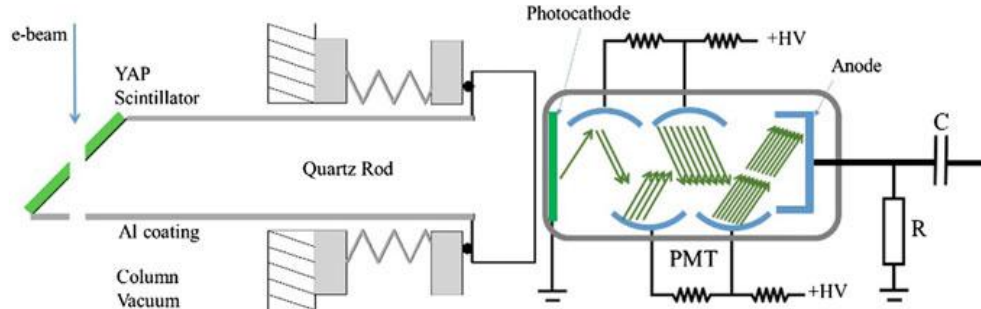
Outline

1. STEM basics
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Scintillator-photomultiplier detector

Principle

1. Scintillator: conversion of incident e^- into photons
2. Optical coupling of photons
3. Photomultiplier (photocathode + dynodes + anode): detection of photons



Zuo & Spence, Advanced TEM (2017)

Specification

- Speed ~ 1 MHz
- Low noise
- Sensitive to beam damages

Application

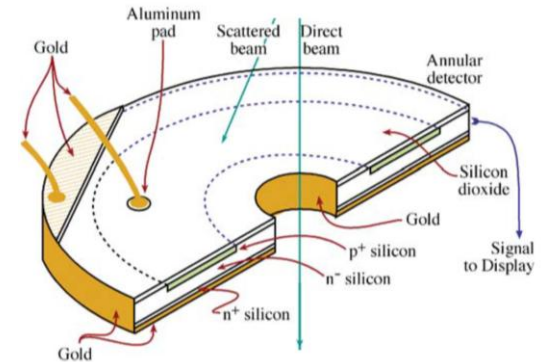
- Imaging: HAADF

Semiconductor detector

Principle

Si pn diode, covered with metal contacts

1. Incident electrons generate e^- -hole pairs (3.6 eV)
2. Dissociation of e^- -hole pairs with built-in potential
3. Collection of current



Williams & Carter, TEM (2009)

Specification

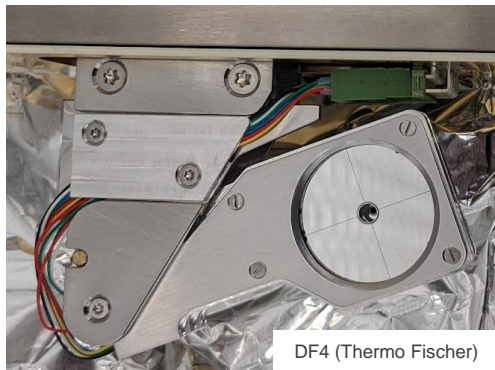
- Speed ~ 1 MHz
- Dark noise
- Cheap, any shape

Application

- Imaging: BF, ABF, ADF

Segmented detector

4-segment detector:

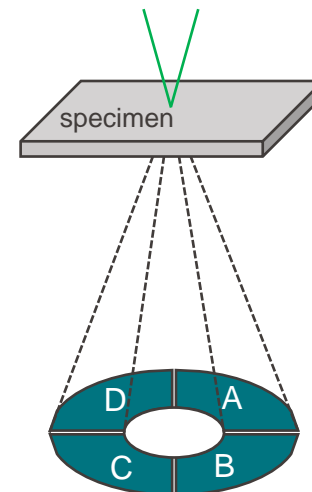


- Segmented detector is a **semiconductor detector** with independent active areas
- Exists since the 1980's, nowadays 16-segments detectors commercially available

Specification
<ul style="list-style-type: none">▪ Cheap▪ 4 to 16 segments▪ Speed ~1 MHz STEM dwell time ~μs
Application
<ul style="list-style-type: none">▪ Imaging (BF/ABF/ADF)▪ Differential phase contrast (DPC)

This is a 4-pixel detector!
➤ Equips most of the STEM nowadays

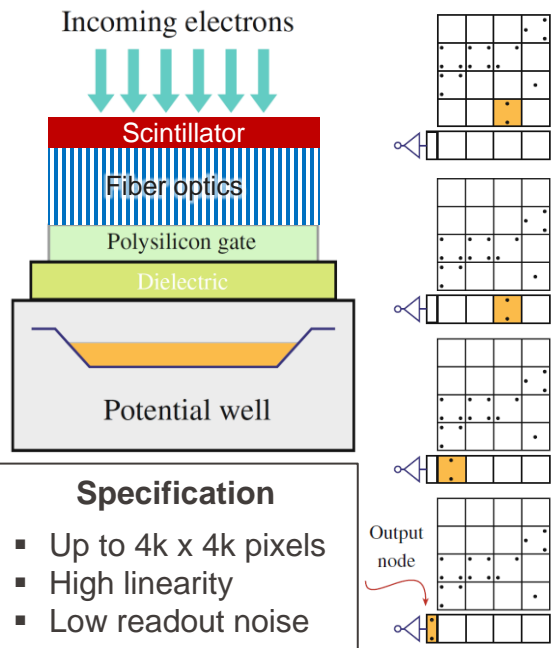
STEM diagram:



Charge-coupled device (CCD)

Principle

1. Scintillator: conversion of incident e^- into photons:
2. Optical coupling of photons: fiber optics
3. Array of Si pn diodes, biased to use it as potential well
4. Readout system using the capacitors to transfer the charges between neighboring pixels toward the output node



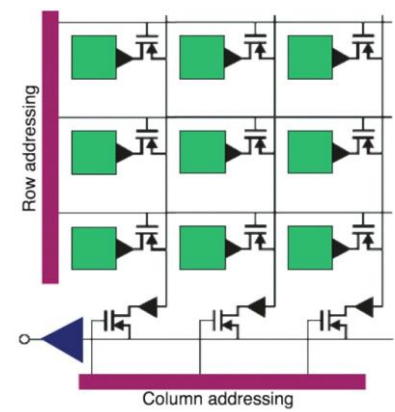
Specification

- Up to 4k x 4k pixels
- High linearity
- Low readout noise

Complementary metal-oxide-semiconductor (CMOS)

Principle

1. } Similar as CCD, to collect the signal
2. }
3. }
4. Dedicated readout for each pixel, addressed by row and column as in a memory chip, to convert charges to voltage



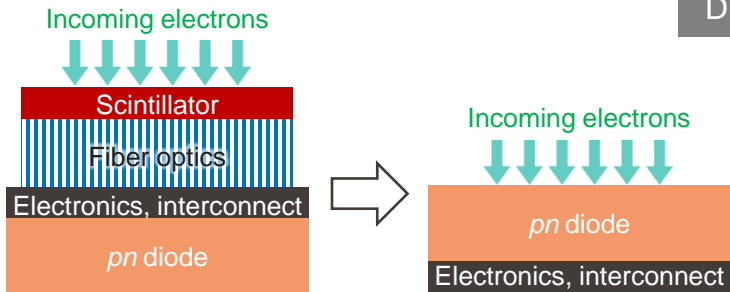
Specification w.r.t. CCD

- Faster
- Cheaper
- Higher readout noise

Not suitable for STEM!

- Slow (~10-100 Hz)
- Low dynamic range
- Sensitive to beam damages

Direct detection cameras



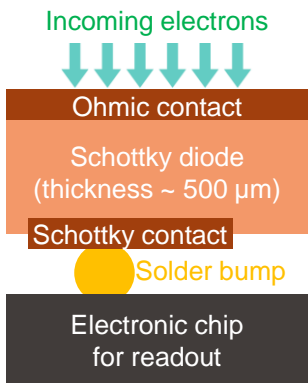
CMOS technology with no scintillator, no optical coupling
 Revolution in the STEM world in 2015's

- **Robust to beam damages**
- **Single electron sensitivity (very high DQE)**
- **Fast**

PAD: pixel array detector

Principle

1. Array of Schottky diodes (thick Si chip)
2. Backside bonding to the readout chip for independent pixel reading



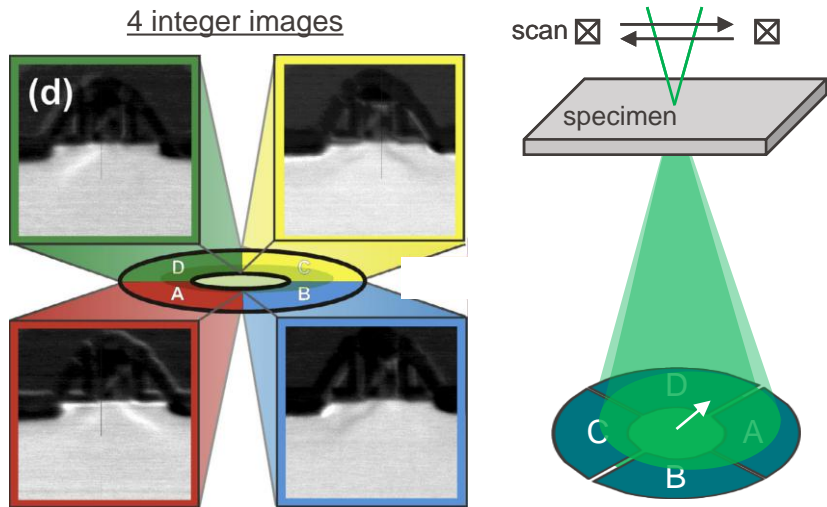
Specification
<ul style="list-style-type: none"> ▪ Up to 512 x 512 pix ▪ High dynamic range ▪ Speed ~1-10 kHz <p style="text-align: center;">STEM dwell time ~ms</p>
Application
<ul style="list-style-type: none"> ▪ 4D-STEM



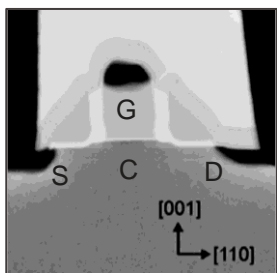
Outline

1. STEM basics
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Segmented detector acquisition



Si-doped MOSFET

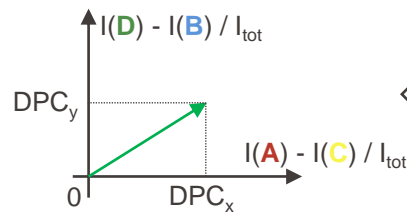


Monolithic reading:

- Annular detector
- ABF imaging

Data representation: vector image

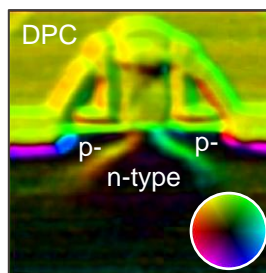
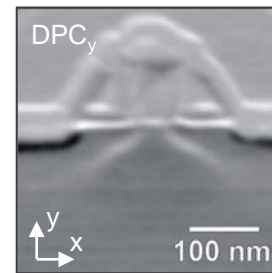
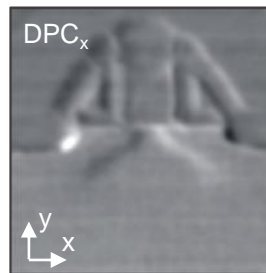
Movement of intensity of the transmitted beam



Center-of-mass (CoM) for an array of n.m pixels:

$$\text{CoM}_x = \sum_{n,m} \frac{n \cdot I_{n,m}}{I_{n,m}}$$

$$\text{CoM}_y = \sum_{n,m} \frac{m \cdot I_{n,m}}{I_{n,m}}$$

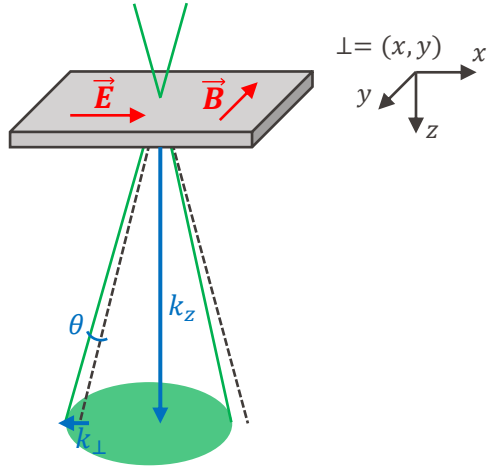


DPC imaging reveal the deflection of the transmitted beam:

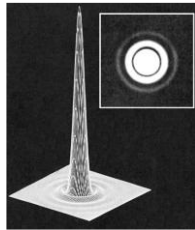
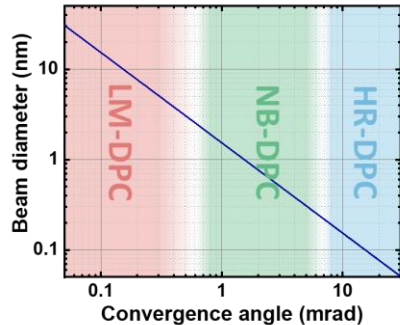
- Calculated by CoM

What information about the sample contains the DPC map?

Hypothesis: electron probe \ll field variation



Diffraction-limited probe size (no aberrations):



Williams & Carter, TEM (2009)

Classical mechanics formalism

Lorentz force: $\vec{F}_L = -e(\vec{E} + \vec{v} \times \vec{B})$

Newton 2nd law: $\vec{F} = m\vec{a} = m \frac{d\vec{v}}{d\tau} = \frac{d\vec{p}_\perp}{d\tau}$

➤ Momentum transfer for electric field only: $\vec{p}_\perp = -e \int \vec{E}_\perp d\tau$

Definition: $p = hk = mv = \frac{h}{\lambda}$

Time to go through the specimen: $d\tau = \frac{dz}{v}$

➤ Beam deflection: $\theta \approx \frac{k_\perp}{k_z} = \frac{p_\perp}{p_z} = \frac{-e \int E_\perp d\tau}{mv} = -\frac{e\lambda}{hv} \int E_\perp dz$

Lorentz deflection: $\theta = \begin{pmatrix} \theta_x \\ \theta_y \end{pmatrix} = -\frac{e\lambda}{hv} \int \begin{pmatrix} E_x \\ E_y \end{pmatrix} dz + \frac{e\lambda}{h} \int \begin{pmatrix} B_y \\ -B_x \end{pmatrix} dz$

➤ DPC signal, mapped by CoM

DPC enables quantitative mapping of the EM fields:

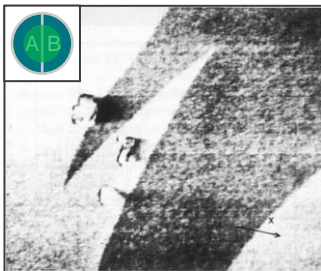
- Electric field
- Magnetic induction field

- The integral over the electron path is observed
- Insensitive to the out-of-plane component

Magnetic measurements

Permalloy (NiFe), ferromagnetic material:

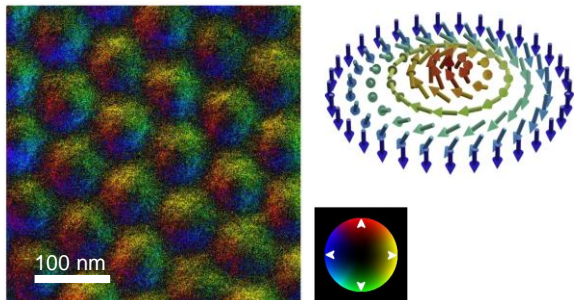
- Magnetization domains



Chapman et al., Ultramicroscopy 3, 203 (1978)

Bloch-type skyrmions lattice in FeGe:

- In-plane component of magnetic induction

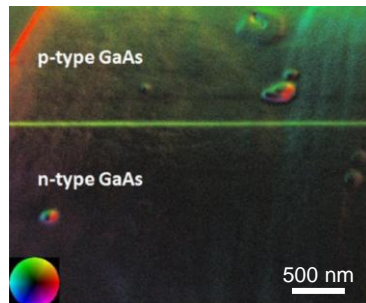


McGrouther et al., New J. Phys. 9, 095005 (2016)

Electric measurements

pn junction in GaAs:

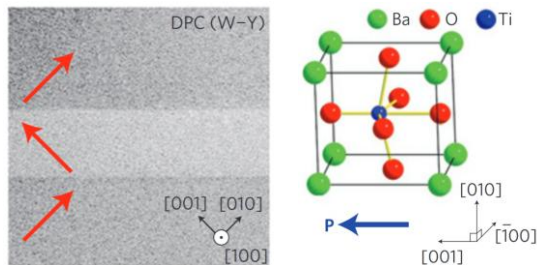
- Built-in electric field



Seki et al., Microscopy 70, 148-160 (2021)

BaTiO₃, ferroelectric material (tetragonal):

- Polarization domains



Shibata et al., Nature Physics 8, 611-615 (2012)

Restriction

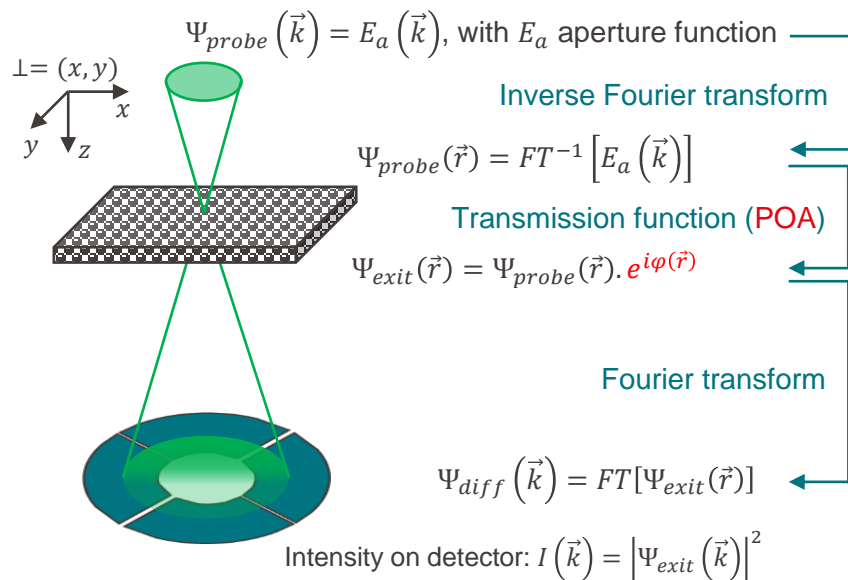
- Unwanted contrasts from:
 - Variation of specimen thickness
 - Inhomogeneous material
 - Change of diffraction conditions
- Qualitative measurement in practice
 - DPC is more quantitative with 4D-STEM...

What happens at atomic resolution?

Hypothesis: electron probe \gg field variation

Fourier optics

Unit plane wave, time-independent writing, propagation along z, no initial phase shift: $\Psi_0(\vec{r}) = A_0(\vec{r})e^{i(2\pi\vec{k}_0 \cdot \vec{r} - \omega_0 t + \varphi_0)} = e^{i(2\pi k_z \vec{r})}$



Quantum mechanics

It can be shown [2]: $\varphi(\vec{r}) = \sigma \int V(\vec{r}) dz - \sigma v \int A_z(\vec{r}) dz$

with: $\sigma = \frac{2\pi m e \lambda}{h^2} = \frac{2\pi e}{h v}$ the interaction constant

V is the electrostatic potential

A_z is the z component of the magnetic vector potential

DPC is sensitive to the gradient of the potentials, i.e. to the electric and magnetic fields

Fields derive from a potential:

$$\vec{E} = -\vec{\nabla}V$$

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

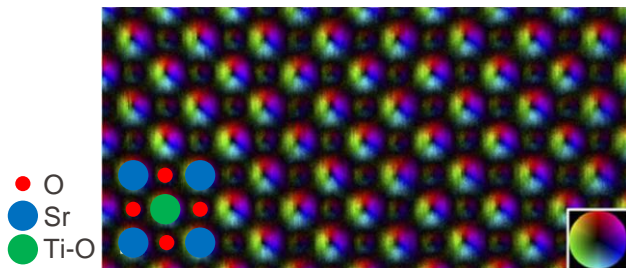
DPC signal is [1]: $CoM[I(\vec{k})] = \frac{1}{2\pi} \int |\Psi_{probe}(\vec{r})|^2 \otimes \vec{\nabla} \varphi(\vec{r}) dz$

DPC = “differential phase contrast”

➤ Probes the gradient of the phase shift induced by the sample

SrTiO₃ crystal (8 nm thick):

- Map $\propto \int \vec{E}_\perp dz$ field



Shibata et al., Nat. comm. 8, 15631 (2017)

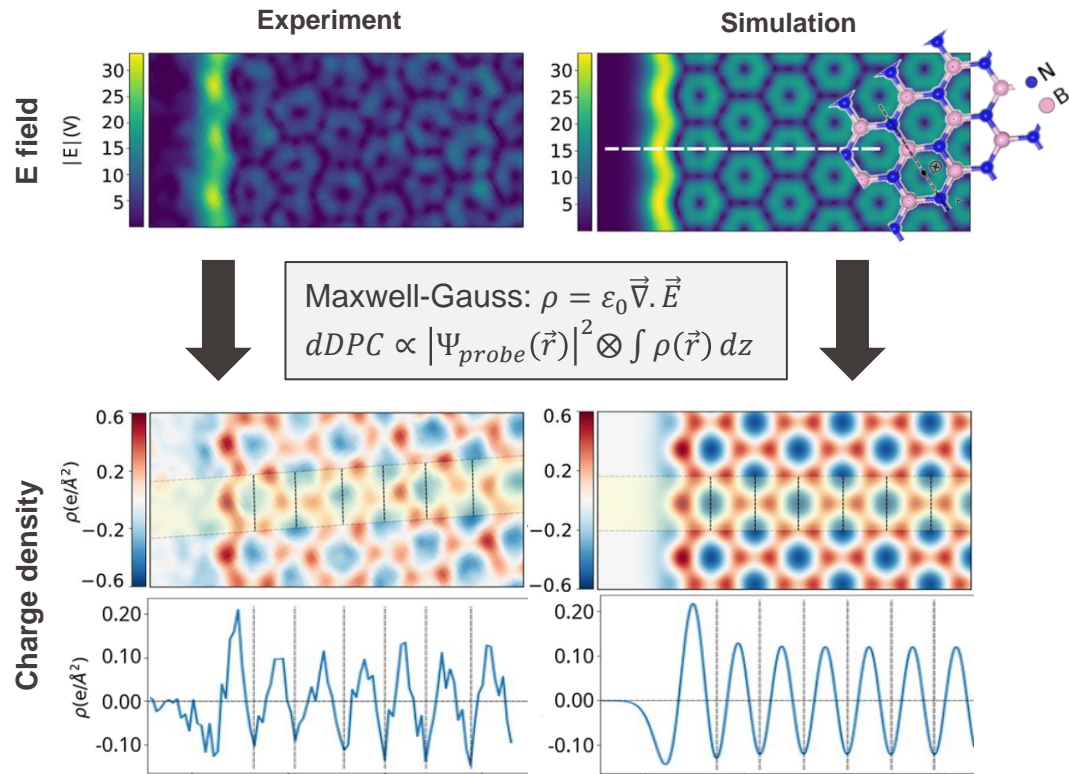
Restriction

- Unwanted contrasts from:
 - Variation of specimen thickness
 - Change of diffraction conditions
- Requires extremely thin materials, <10 nm
 - Phase object approximation (POA)

Derivative of the DPC signal:

- dDPC \propto charge density ρ

Monolayer of h-BN (hexagonal boron nitride):



$$\text{Maxwell-Gauss: } \rho = \epsilon_0 \vec{\nabla} \cdot \vec{E}$$

$$dDPC \propto |\Psi_{probe}(\vec{r})|^2 \otimes \int \rho(\vec{r}) dz$$

Susana et al., ACS Nano 18, 7424-7432 (2024)

Principle [1]

DPC is sensitive to the electric field:

$$DPC \propto |\Psi_{probe}(\vec{r})|^2 \otimes \int \vec{E}(\vec{r}) dz$$

$$\vec{E} = -\vec{\nabla}V$$

$$iDPC \propto |\Psi_{probe}(\vec{r})|^2 \otimes \int V(\vec{r}) dz$$

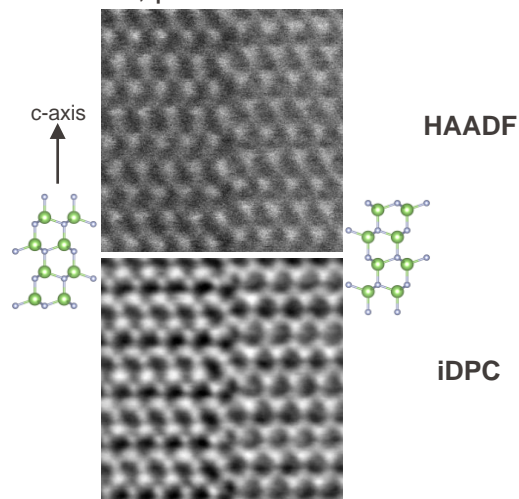
Integration of the DPC signal:
 ➤ iDPC \propto electric potential

iDPC is popular for atomic resolution imaging

1. Good contrast with light atoms
 - Intensity scales with Z (vs. $\sim Z^2$ for HAADF)
2. High dose efficiency
 - Collects the “strong” transmitted beam (vs. thermal diffuse scattering for HAADF)

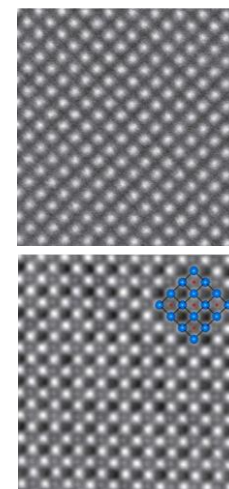
Examples

GaN, polar inversion:



© V. Boureau

TiH crystal:



de Graaf et al., Sci. Adv. 6, eaay4312 (2020)

Restriction

- Phase contrast image: coherent
 - Contrast changes with material thickness, defocus, tilt, etc.
- iDPC imaging also works for “thicker” samples 😊



Outline

1. STEM basics
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EPFL Recording new class of signal: 4D-STEM

scan 



Convergent beam raster-scanned on the sample:

- **2D image of the specimen**
- Pixels defined by probe position (STEM)

At each probe position:

- **2D image of the diffraction pattern**
- Recorded by the fast camera



4D-STEM dataset

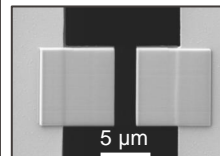
- 2D in real space + 2D in diffraction space
- Collection of local diffraction patterns

Why?

- Comprehensive information of the diffraction
- Allows in-depth analysis in post processing

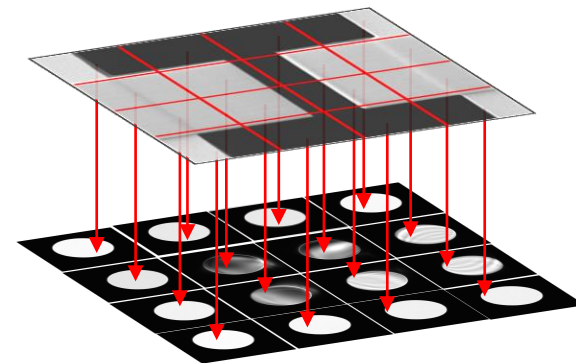
Example of data

STEM



Micro-capacitor

4D-STEM



Challenge of 4D-STEM: data handling (storage, analysis)

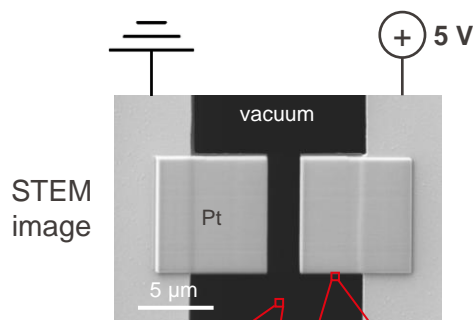
Example (MerlinEM camera):

- 512 x 512 pixels STEM image
- 256 x 256 pixels diffraction patterns, 12 bit depth
- 25 Gb dataset, acquired in 3 min!

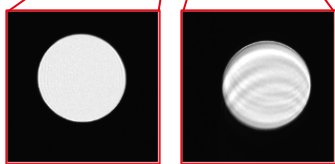
➢ **Do not do 4D-STEM when not necessary!**

Example: Planar capacitor, biased [2]

Data acquisition



Diffraction patterns



Transmitted beam

Data processing: DPC signal

Center-of-mass (CoM) for an array of $n \cdot m$ pixels:

$$\text{CoM}_x = \sum_{n,m} \frac{n \cdot I_{n,m}}{I_{n,m}}$$

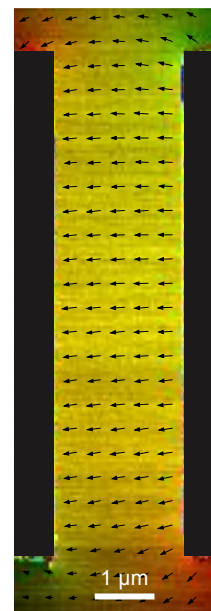
$$\text{CoM}_y = \sum_{n,m} \frac{m \cdot I_{n,m}}{I_{n,m}}$$

DPC with 4D-STEM configuration [2]

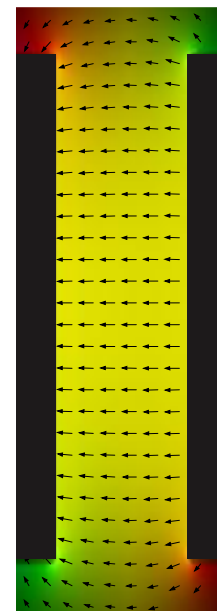
- Mapping of \vec{E} and \vec{B} fields
- Long-range fields: ☺
 - More easily quantitative
- Atomic fields: ☹
 - Too slow vs. segmented detector

Plot of $\int \vec{E} dz$

Measurement



Simulation (FEM)



[1] Ranieri et al., submitted to Ultramicroscopy

[2] Boureau et al., J. Phys. D 54, 085001 (2021)

EPFL What are the applications of 4D-STEM?

Electromagnetic fields mapping

DPC
iDPC, dDPC

Imaging

Virtual imaging

Phase contrast imaging

iDPC
Ptychography

Crystal analysis

Crystal phase and orientation mapping (ASTAR)
Strain and rotation maps
HOLZ analysis
Symmetry analysis

Amorphous

Short-range ordering
Amorphous phase classification
Strain maps

Degree of crystallization

Fluctuation microscopy

Organic solids

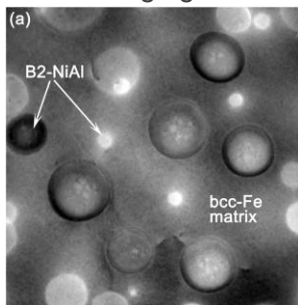
Medium-range ordering

4D-STEM is a method of recording STEM data

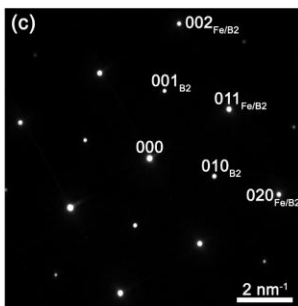
- Encompasses **many established techniques** for a wide range of applications
- 4D-STEM records all local diffractions :
 - Smart and **flexible data analysis** to retrieve the information of interest
 - **Specific acquisition parameters** should be used for a specific technique!

Example: Phase analysis of a complex FeAlNiCr alloy [1]

TEM data:
Imaging

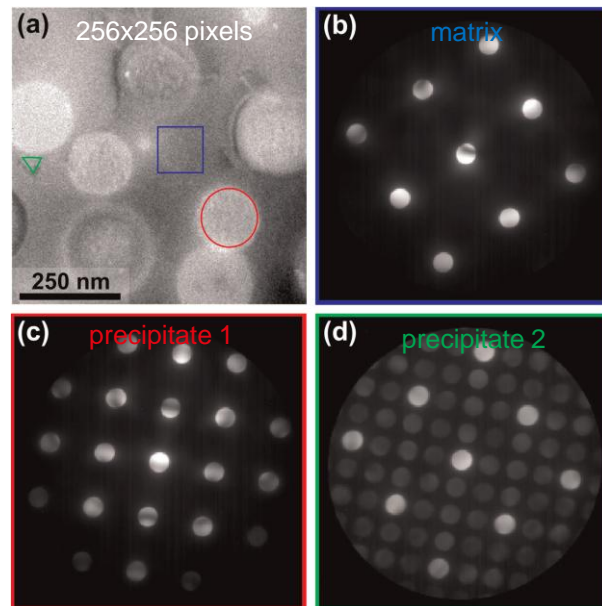


Diffraction



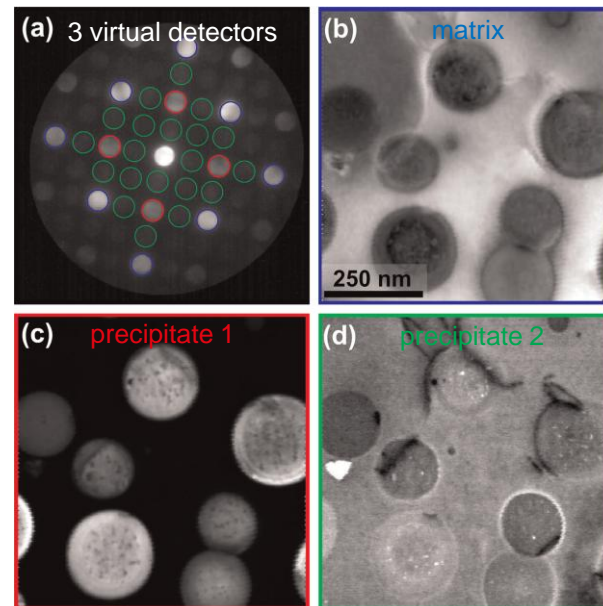
4D-STEM dataset:

Diffraction pattern at each pixel



Virtual dark-field imaging:

Image contrast built from virtual detectors



Strengths

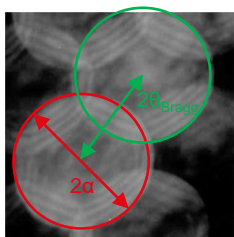
- Image reconstruction for any size/shape of virtual detector
- Versatile analysis of diffraction contrasts

Weaknesses

- Heavy dataset
- Slow acquisition vs. annular STEM detector

EPFL 4D-STEM for super-resolution imaging: ptychography

Example: MoS₂ monolayer^[1]



Pennycook & Nellist, STEM (2011)

Ptychographic imaging

Iterative image reconstruction of the exit wavefunction

- Different class of algorithm: ePie, SSB, WDD^[2]
- This is a phase imaging technique
- Allows for deconvolution of the probe aberrations

Interferences in the Bragg disks overlapping:

- Information limit for coherent STEM imaging
- Atomic plane resolved if $\theta_{\text{Bragg}} < \alpha$

Strengths

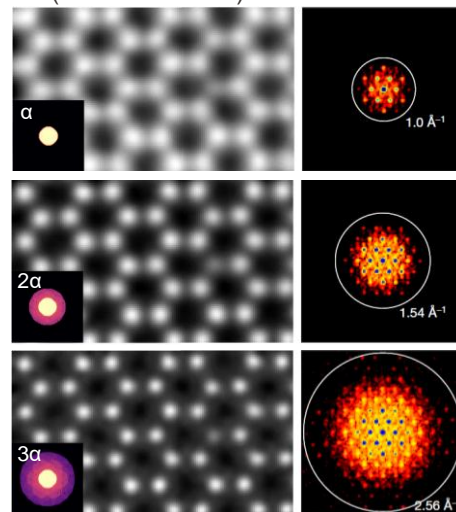
- Very high dose efficiency
- Super-resolution, beyond the diffraction limit set by aperture

Weaknesses

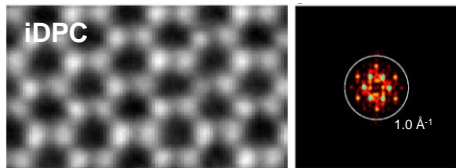
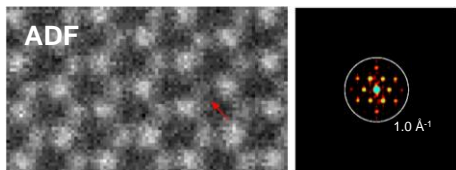
- Advanced method and algorithms
- Limited to very thin samples (POA)
- Early results with iterative multislice reconstruction for thicker samples^[3]

Ptychographic imaging

(different cut-off): FFT:



STEM imaging:



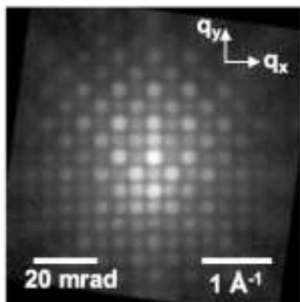
[1] Jiang et al., Nature 559, 343 (2018)

[2] O'Leary et al., Ultramicroscopy 221, 113189 (2021)

[3] Chen et al., Science 372, 826 (2021)

Principle

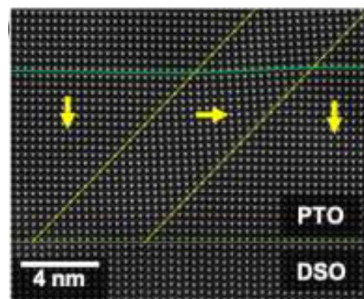
1. 4D-STEM acquisition



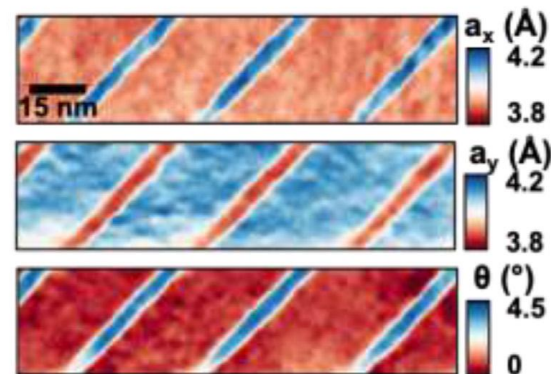
2. For each diffraction pattern, compute the Bragg vectors position (\vec{g})
 - Different algorithms exist!
3. Compute the local strains and rotation (or lattice parameters), from the local \vec{g} vectors
 - Strain field: $\varepsilon = \frac{g^{ref} - g}{g}$
 - Lattice d-spacing: $d_{hkl} = \frac{1}{g_{hkl}}$

Example: PbTiO₃ grown on DyScO₃ [1]

HAADF STEM image



Strain and rotation maps:

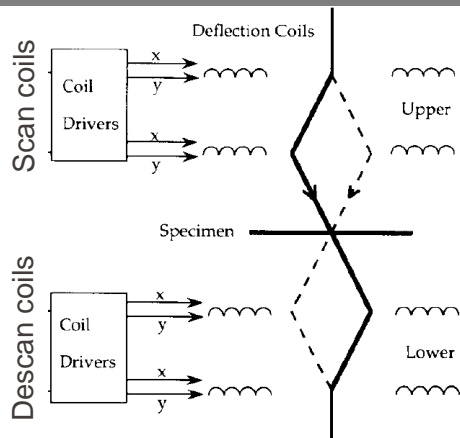


Evidence of lattice distortions induced by ferroelectric domains

Elastic strain mapping in (mono-)crystalline samples

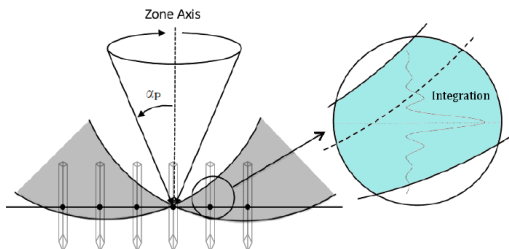
- In-plane components (2D): strain and rotation
- Quantitative measurement
- Beam precession improves accuracy [2]

Principle [1]:



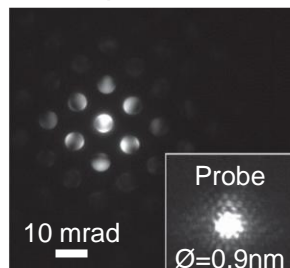
Dynamic tilting of the Ewald sphere during imaging

- Ewald sphere intersection with reciprocal lattice rod (reldod) intensity gives the Bragg intensity
- Precession integrates relrod intensity over the excitation error on the Bragg conditions

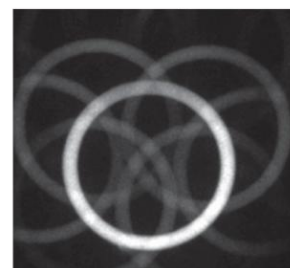


Example: diffraction of Si(110) crystal [2]

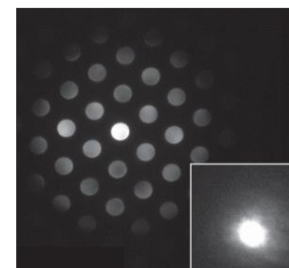
No precession



Precession, no descan



Precession with descan



➤ Pseudo-kinematical diffraction conditions

- Diffraction contrasts weakened
- Diffracted beam intensities closer to the structure factor

Why using precession?

- Reliable Bragg intensities
- Accurate localization of the diffracted beams
 - Improved **crystal strain** measurement [2]
 - Improved **DPC** long-range field mapping [3]
 - Improved **crystal phases and orientation** mapping [4]

[1] Vincent & Midgley, Ultramicroscopy 53, 271 (1994)

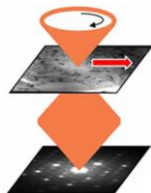
[2] Rouvière et al., Appl. Phys. Lett. 103, 241913 (2013)

[3] Bruas et al., J. App. Phys. 127, 205703 (2020)

[4] Vilado et al., J. of Microscopy 252, 23 (2013)

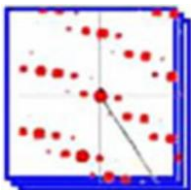
Principle: ASTAR [1]

1. 4D-STEM acquisition, in precession mode



2. Simulation of a database of diffraction patterns

- For all crystal phases in the sample
- For all orientations of the crystals



3. Matching between experimental patterns and the database with correlation-based algorithm

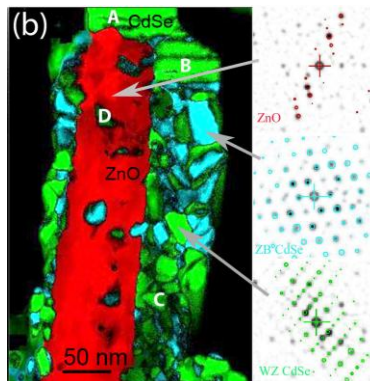
- The most similar diffraction pattern is assigned to each local diffraction

Example: ZnO/CdSe core/shell nanowires [2]

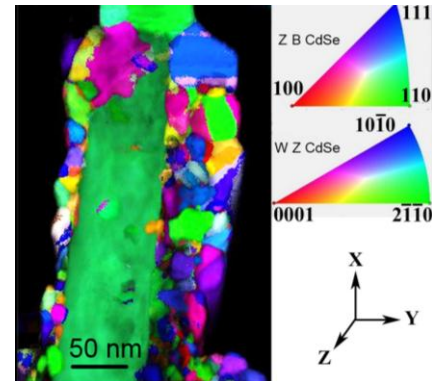
Virtual BF



Crystal phase map:



Orientation map:



ZnO: **wurtzite**

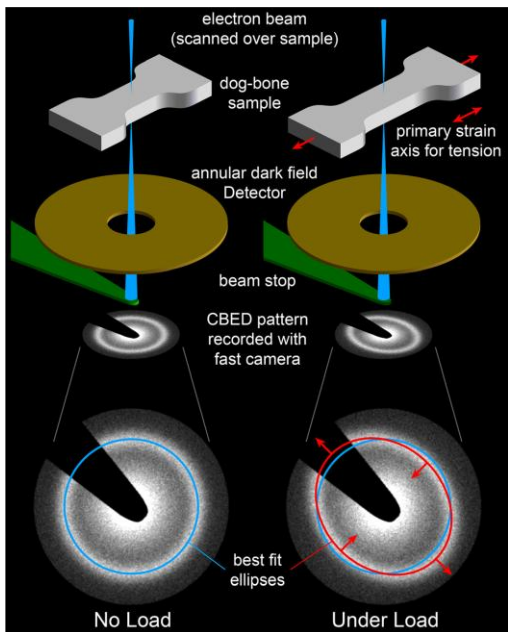
CdSe: **zinc-blende** + **wurtzite**

Crystal phase and orientation mapping in polycrystalline samples

- Crystal grains > specimen thickness
- Requires beam precession to be in pseudo-kinematical diffraction conditions

Principle

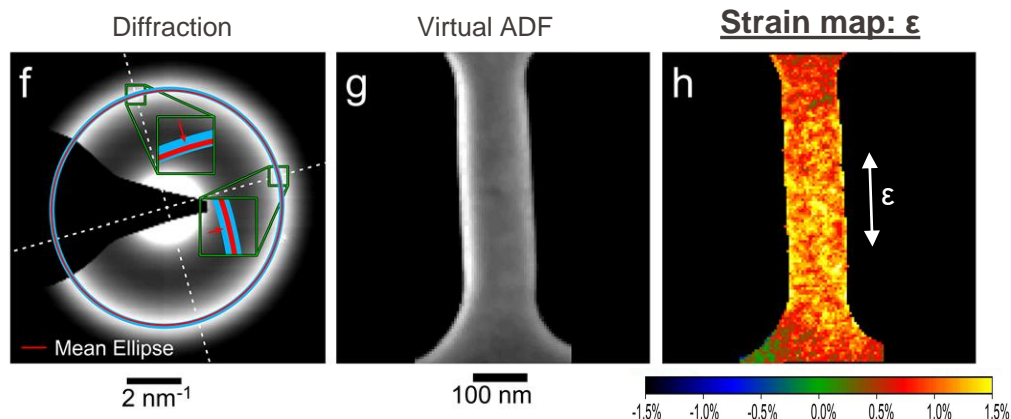
1. 4D-STEM acquisition



2. Fit an ellipse to each amorphous diffraction pattern to compute the strain (and orientation) from the elliptic distortions

Example: In-situ traction of an amorphous CuZrAlAg metallic glass [1]

After application of a tensile strain:

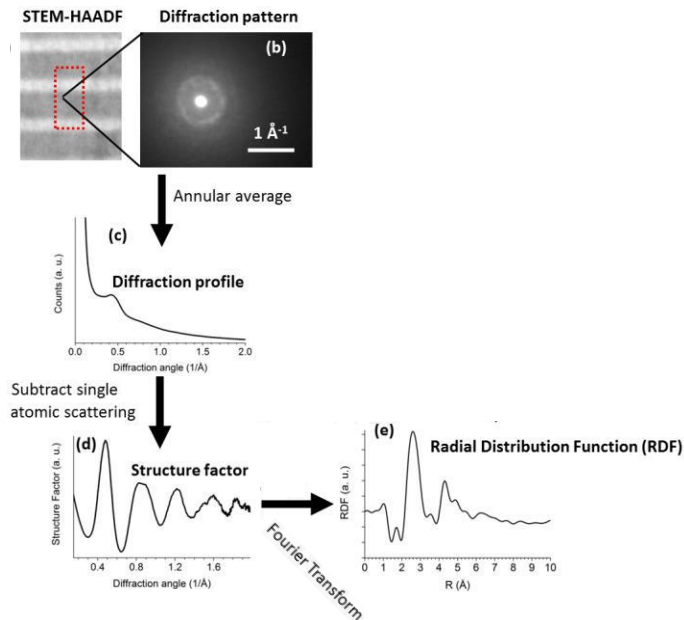


Strain mapping in amorphous samples

- In-plane strain components (2D): magnitude and orientation
- Quantitative measurement

Principle [1]:

1. 4D-STEM acquisition
2. Compute the RDF for each diffraction

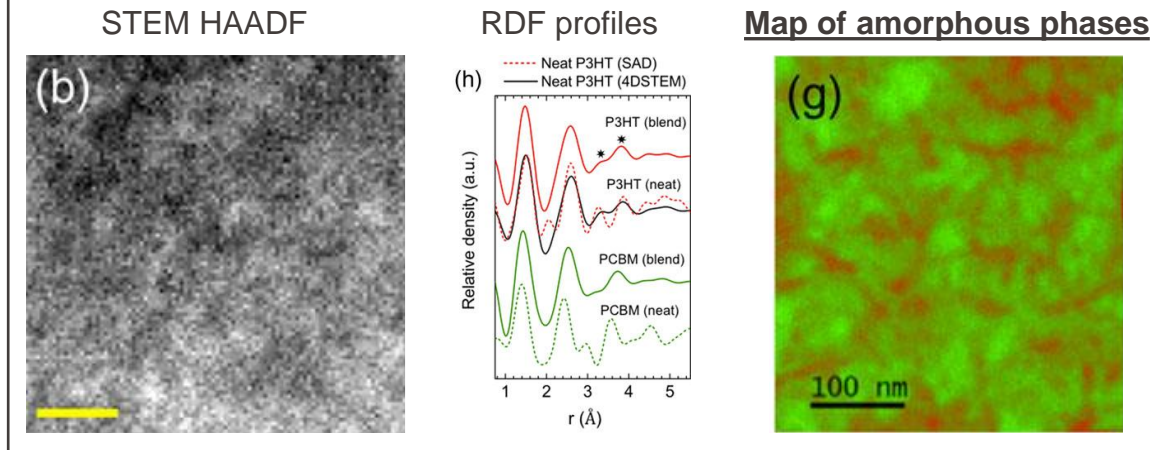


3. Classify the RDF profiles using hyperspectral analysis, e.g. MLLS fitting (multiple linear least square)

Radial distribution function (RDF) shows the short-range atomic order
 RDF \equiv pair distribution function (PDF)

➤ RDF is the fingerprint of the amorphous structure

Example: Mapping of PC₆₁BM and P3HT amorphous materials [2]



Amorphous sample phase mapping

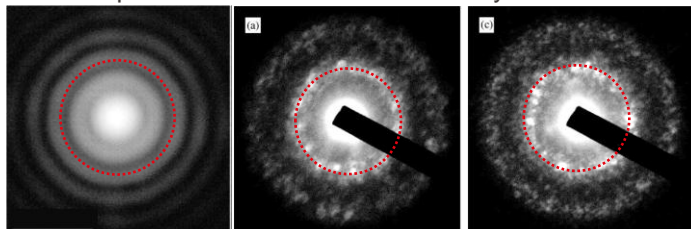
- Requires care with data acquisition:
- Often beam sensitive materials
 - Weak scattering signal

Principle [1]:

1. 4D-STEM acquisition

Amorphous

With nano-crystallites



2. For each diffraction pattern, compute the variance of the azimuthal profile:

$$V = \sigma^2 = \frac{1}{N} \sum_{i=1}^N (x_i - \bar{x})^2$$

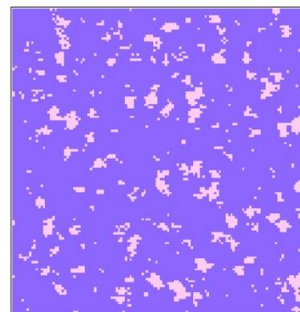
$V \sim 0$ for a perfect amorphous

V increases when crystal ordering increases

3. Data representation

Example: Local heterogeneities in $\text{Zr}_{55}\text{Co}_{25}\text{Al}_{20}$ glass [2]

Distribution of nano-crystallites:



10 nm

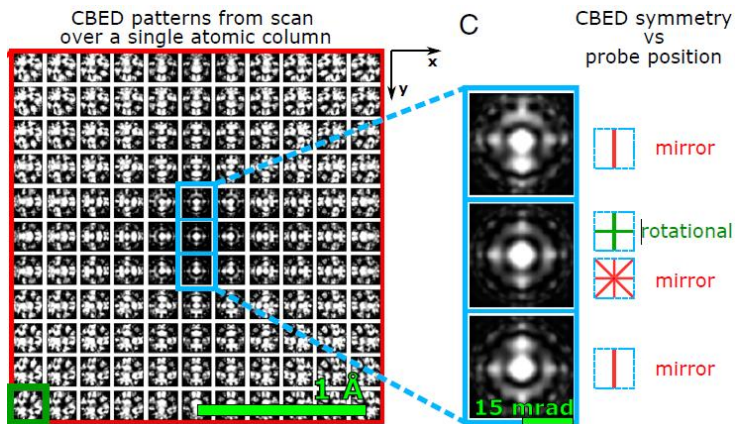
Thresholding of the higher degrees of crystal ordering

Map of the **degree of crystallinity of amorphous / nanocrystalline samples**

- Statistical method
- Observation of crystal nanoclusters in amorphous

Principle:

1. 4D-STEM acquisition

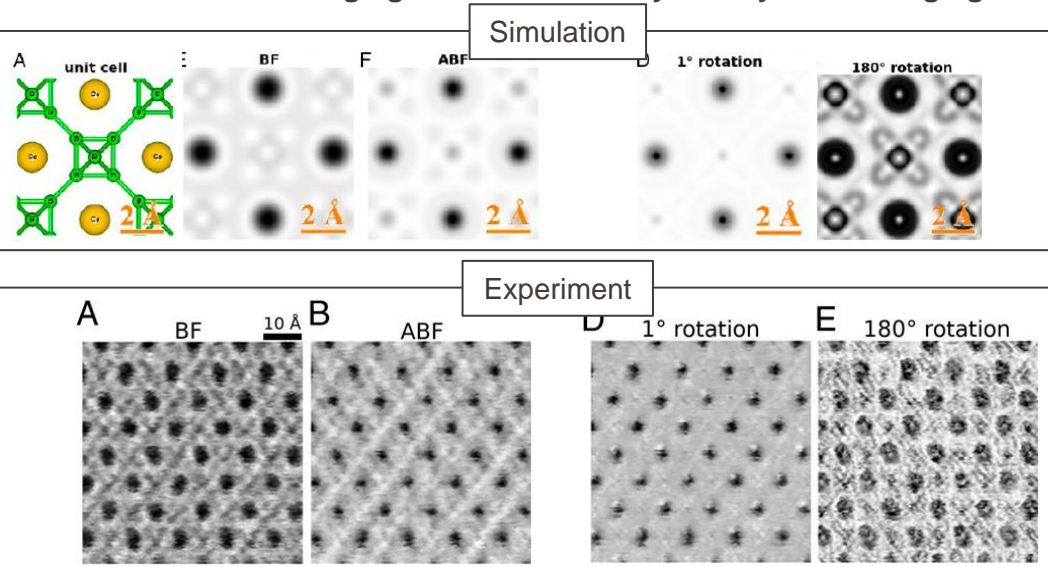


2. Processing to create contrasts according to a certain degree of symmetry

Example: Proof of concept of symmetry imaging on CeB_6 [1]

STEM imaging:

Symmetry STEM imaging:



Atomic resolution imaging with contrast based on local symmetry

- Study of crystal symmetries
- For imaging:
 - Robust contrast vs. defocus, thickness, etc. (incoherent type)
 - Low dose



Outline

1. STEM basics
2. Pixelated STEM detectors
3. DPC
4. 4D-STEM
5. **Conclusion**

- DPC
 - Mapping of phase gradient \equiv in-plane \vec{E} and \vec{B} fields
 - Field quantification difficult, improved with 4D-STEM detector
 - iDPC is great for atomic-resolution imaging, with a segmented detector
 - Light atoms visible
 - Highly dose efficient
- 4D-STEM: method of recording the local diffraction at each pixel of the STEM image
 - Heavy dataset and slow acquisition
 - Better to use conventional STEM approach when possible
 - Give access to a wide range of data analyses
 - Many established techniques to apply
 - Pertinent for quantitative measurement techniques
 - Comprehensive information on the sample to be explored
 - STEM parameters should be chosen wisely!
 - Data processing is often the bottleneck
 - Standard applications have existing resources: Python toolboxes, DigitalMicrograph plugins, etc.
 - Requires advanced coding for fancy applications
- Contact CIME to discuss potential applications to your research 😊

▪ Books

- Williams & Carter, TEM, Springer (2009)
- Reimer & Kohl, TEM, Springer (2008)
- Hawkes & Spence, Science of microscopy, Springer (2007)
- Pennycook & Nellist, STEM: imaging and analysis, Springer (2011)
- Zuo & Spence, Advanced TEM: imaging and diffraction in nanoscience, Springer (2017)
- De Graef & Zhu, Magnetic Imaging and its Applications to Materials, Academic press (2001)

▪ Direct electron detectors

- Faruqi & McMullan, Nucl. Instrum. Methods Phys. Res. A 878, 180 (2018)

▪ Review on 4D-STEM applications and processing

- Ophus, Microsc. Microanal. 25, 563 (2019)
- Savitzky et al., Microsc. Microanal., 1 (2021)

Website: www.epfl.ch/research/facilities/cime

Email: victor.boureau@epfl.ch