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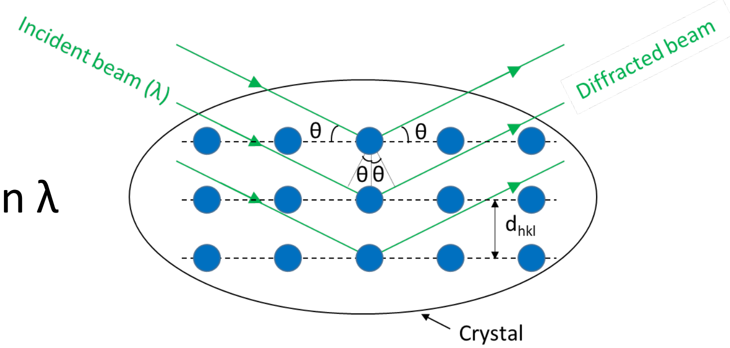
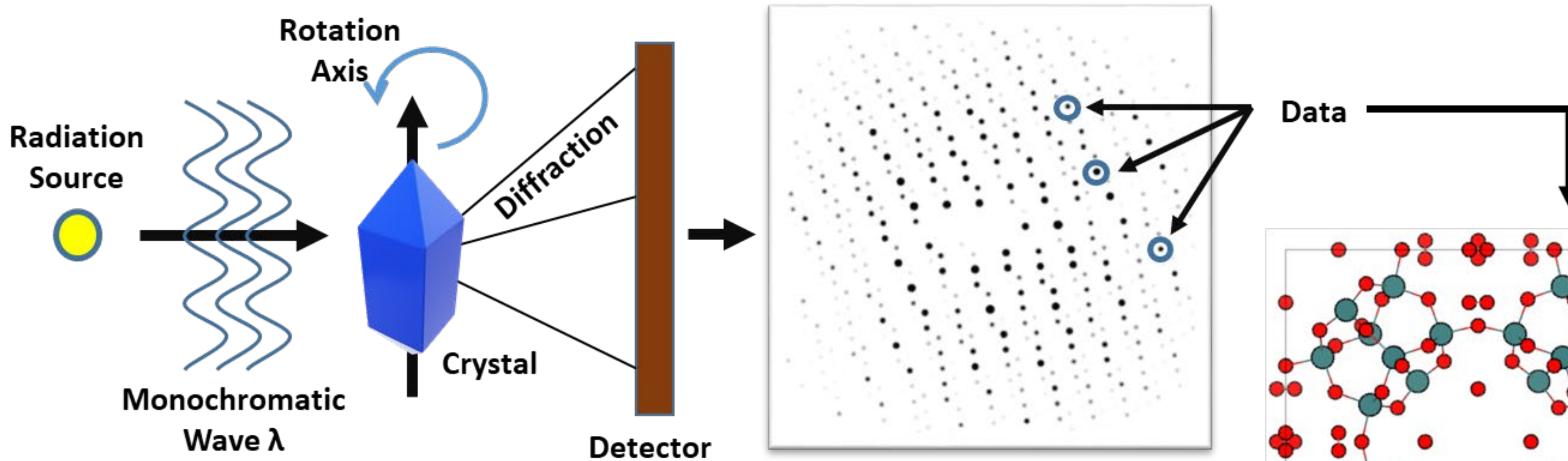
Transmission electron microscopy in materials science: Advances in electron crystallography

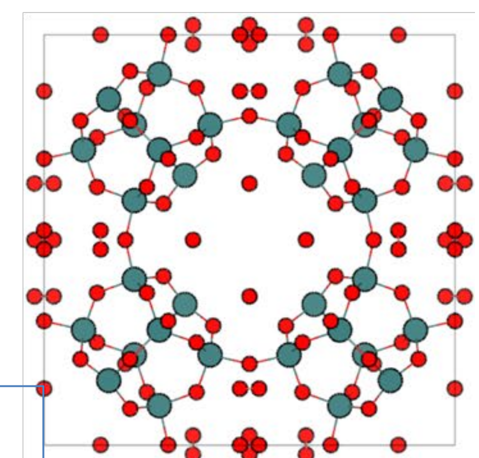
New Inorganic Functional Oxides: Synthesis, Characterisation and Simulations
Orléans, 4-6 october, 2023

Investigating the structure of matter: diffraction experiment

Bragg's law: $2\, d_{hkl} \sin\theta = n\,\lambda$







Most common source: X-Rays

Diffraction angles => periodicity
Intensities => motif. I(hkl) proportional to |F(hkl)|^2

Figure: courtesy of E. YORUK (2022) – PhD Defense

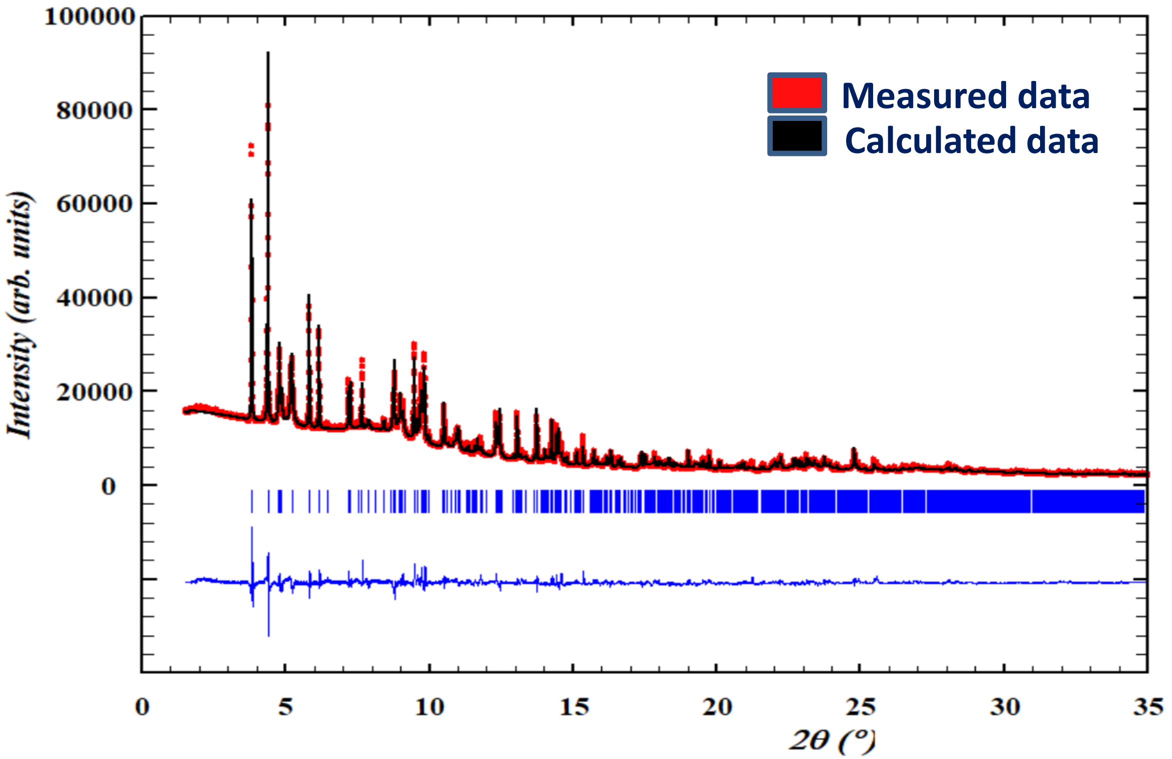
Limitations of X-Ray diffraction

Single Crystal X-Ray Diffraction:

Difficulties in growing crystals to sufficient size

Powder X-Ray Diffraction:

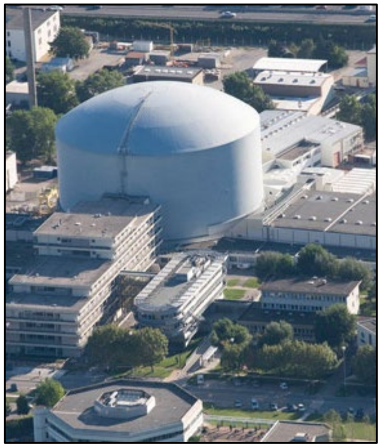
Reflection overlapping due to mixtures and structure complexity



Slide: courtesy of E. YORUK (2022) – PhD Defense

Using electrons

Electrons interact strongly with matter,
an extraordinary advantage for studying nano-sized materials.

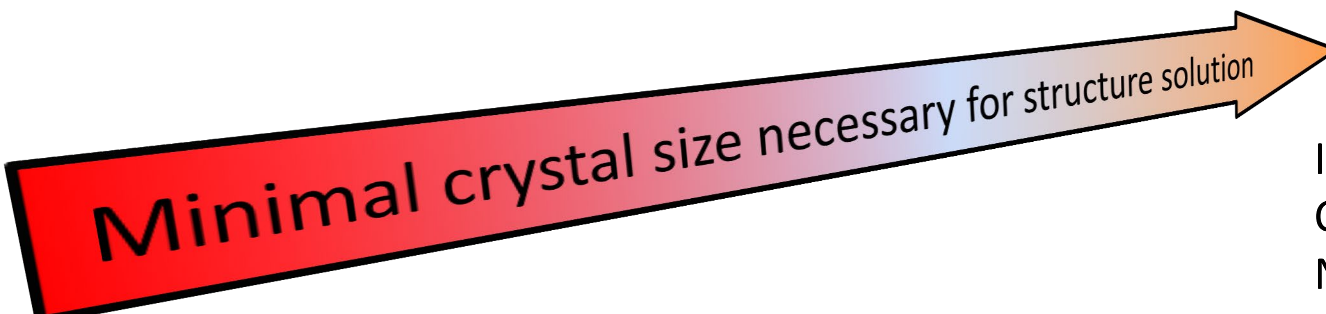


Neutrons
1 mm

Laboratory X-Rays
10-100 µm

Synchrotron X-Rays
1-100 µm

Transmission Electron Microscope (TEM)
100-500 nm



Ideal for
Complex structures
Nanocrystals,
Polyphased powder
…

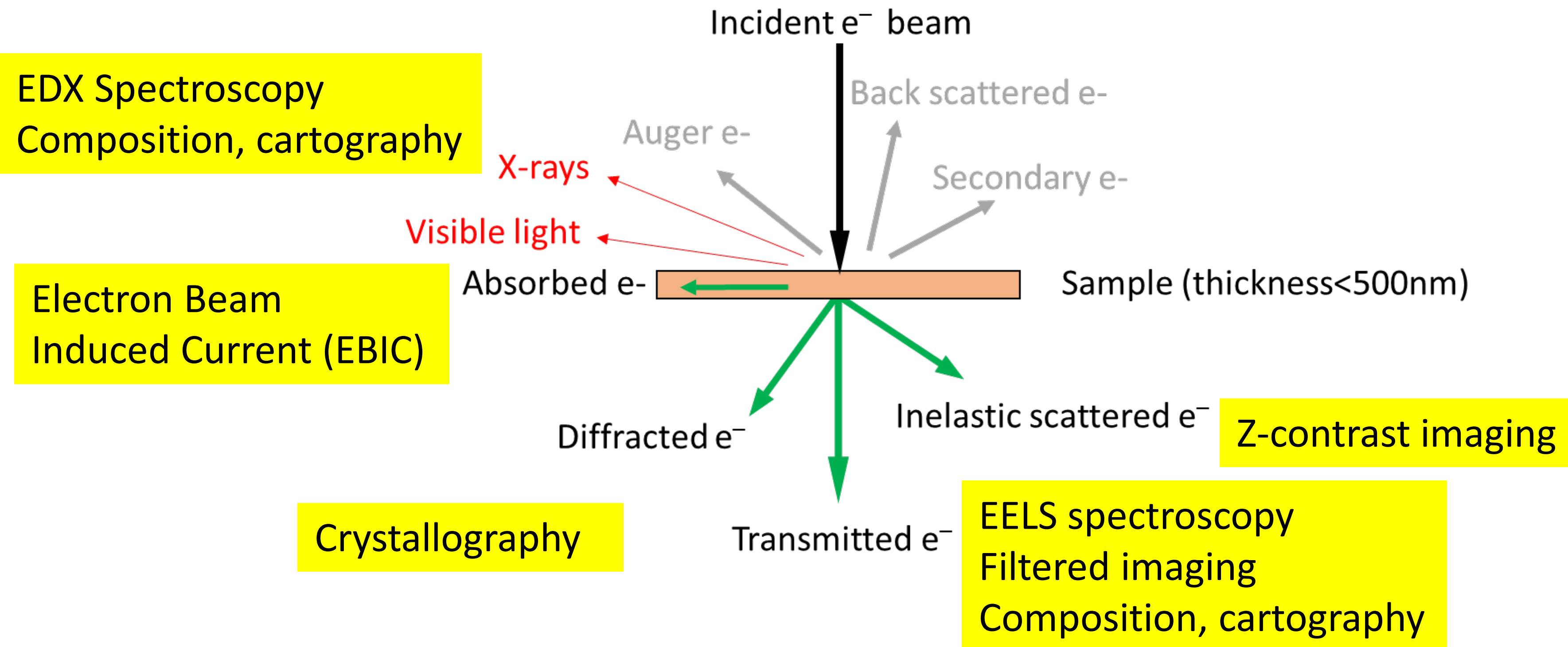
OUTLINE

- Introduction
- Particularities of transmission electron microscopy
- Particularities of electron diffraction
- 3D electron diffraction: data collection and treatment
- 3D electron diffraction at Institut Néel
- Conclusion

Particularities of transmission electron microscopy (TEM)

Particularities of TEM: inelastic interactions

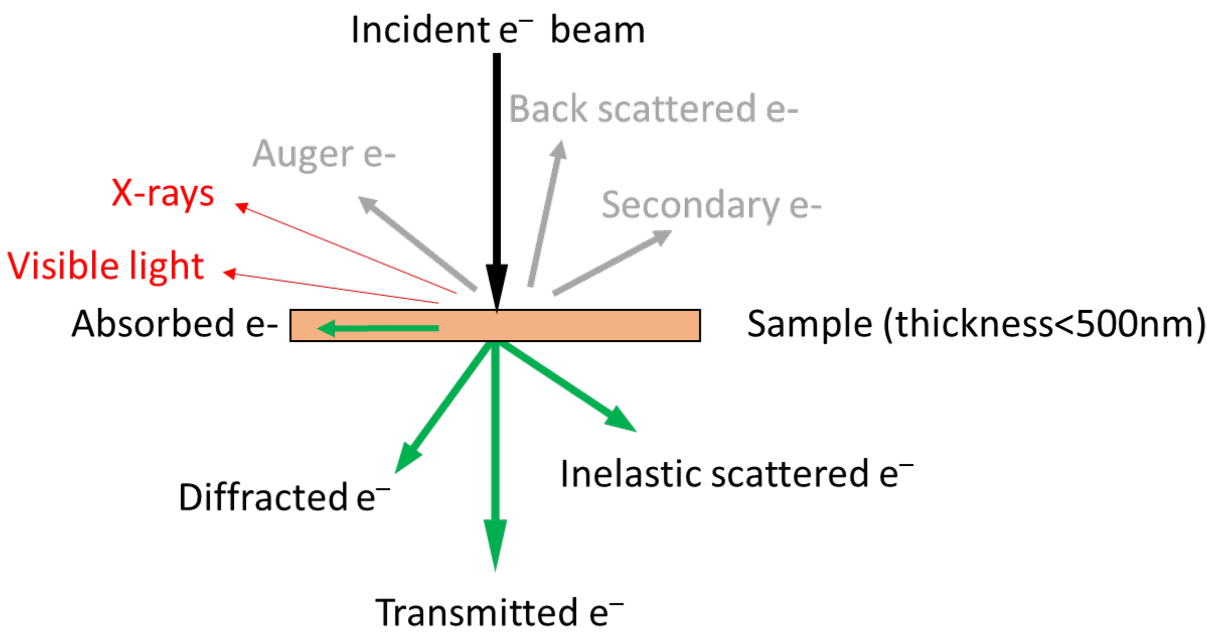
Strong interaction of electrons with matter (with nucleus and electronic 'clouds')



Many signals can be used
TEM is a **powerful tool** for sample characterization

Particularities of TEM: inelastic interactions

Strong interaction of electrons with matter (with nucleus and electronic 'clouds')



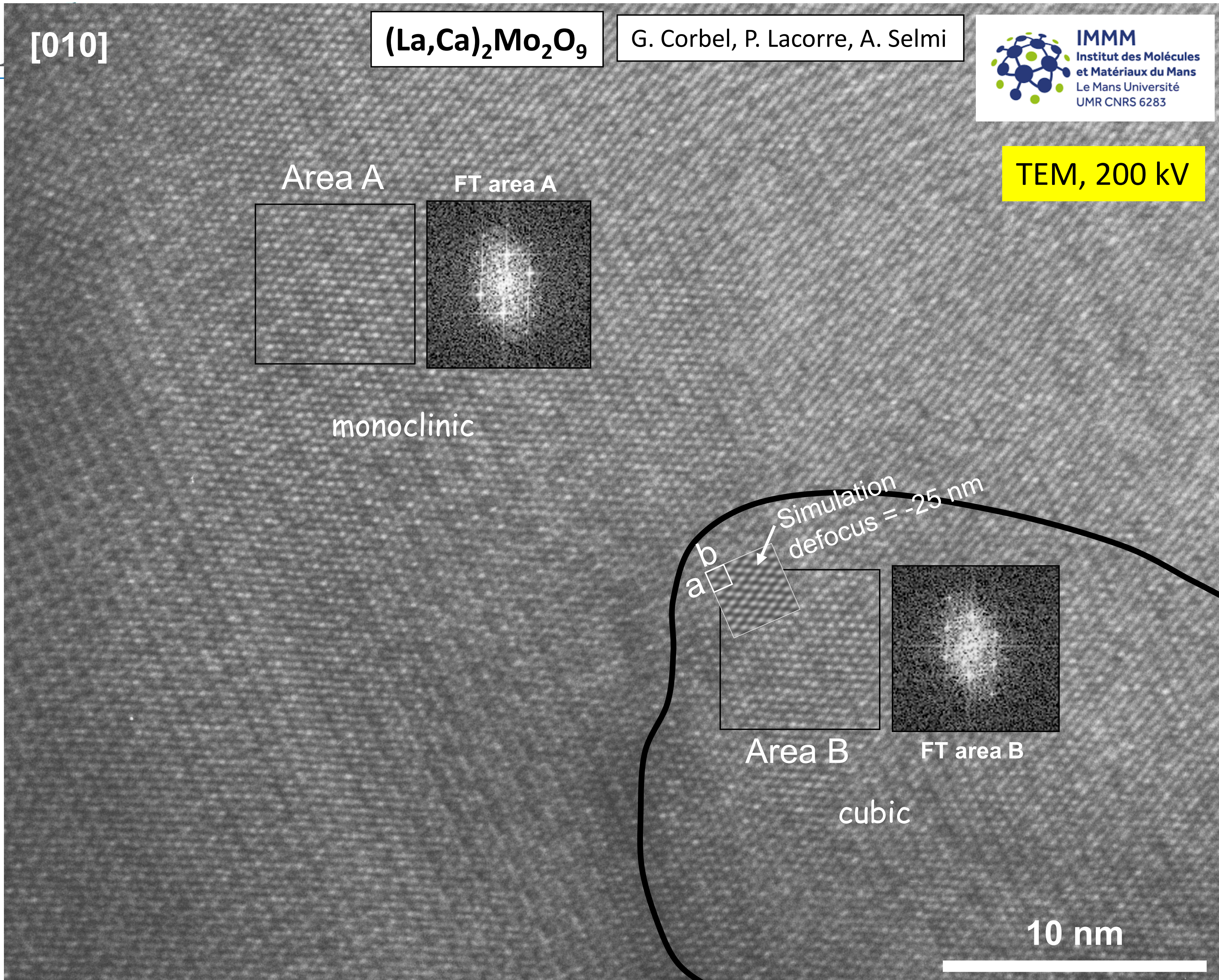
Inelastic interactions affect the structure and/or the chemistry
$\Rightarrow$ specimen is not representative of its parent material

Observing the specimen can change it

$(La,Ca)_2Mo_2O_9$

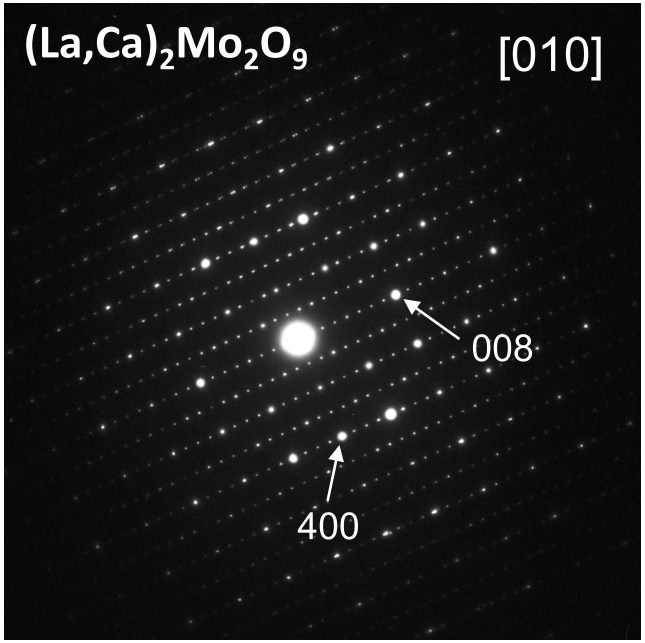
G. Corbel, P. Lacorre, A. Selmi

IMMM Institut des Molécules et Matériaux du Mans Le Mans Université UMR CNRS 6283



Inelastic interactions: phase transition

Experimental conditions : selected area electron diffraction, room temperature, 200 kV

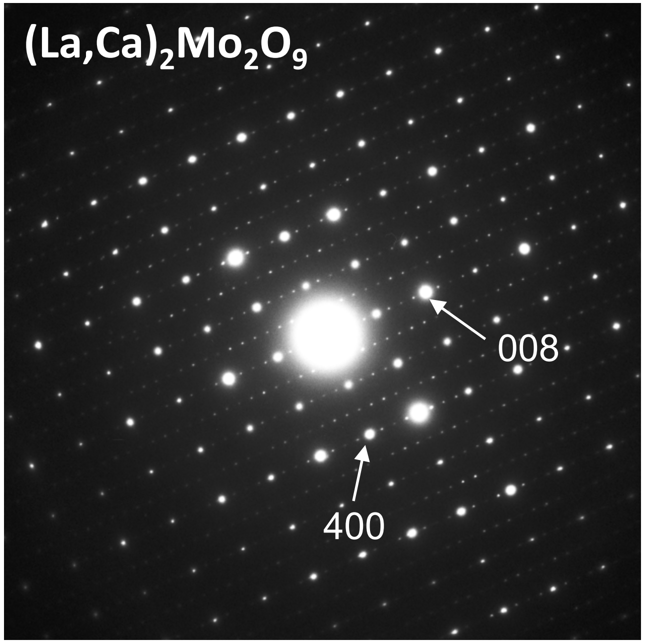


Superstructure x2 x3 x4

α-$La_2Mo_2O_9$ (Monoclinique $P2_1$)
a = 14.325(3) Å, b= 21.482 (4) Å, c= 28.585 (6) Å
β = 90.40 (3) °

A few minutes Irradiation

Phase transition



α-$La_2Mo_2O_9$ (Monoclinique $P2_1$)
+
β-$La_2Mo_2O_9$ (Cubique $P2_13$)
a= 7.2351 (1) Å

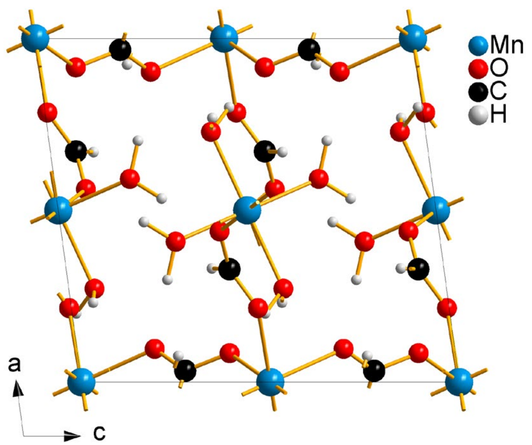
Complex effect of partial substitution of La^{3+} by Ca^{2+} on the stability of fast oxide-ion conductor $La_2Mo_2O_9$
A Selmi, G Corbel, S Kodjikian, V Voronkova, P Lacorre   Eur. J. Inorg. Chem. (2008) 1813-1821

IMMM Institut des Molécules et Matériaux du Mans
Le Mans Université
UMR CNRS 6283

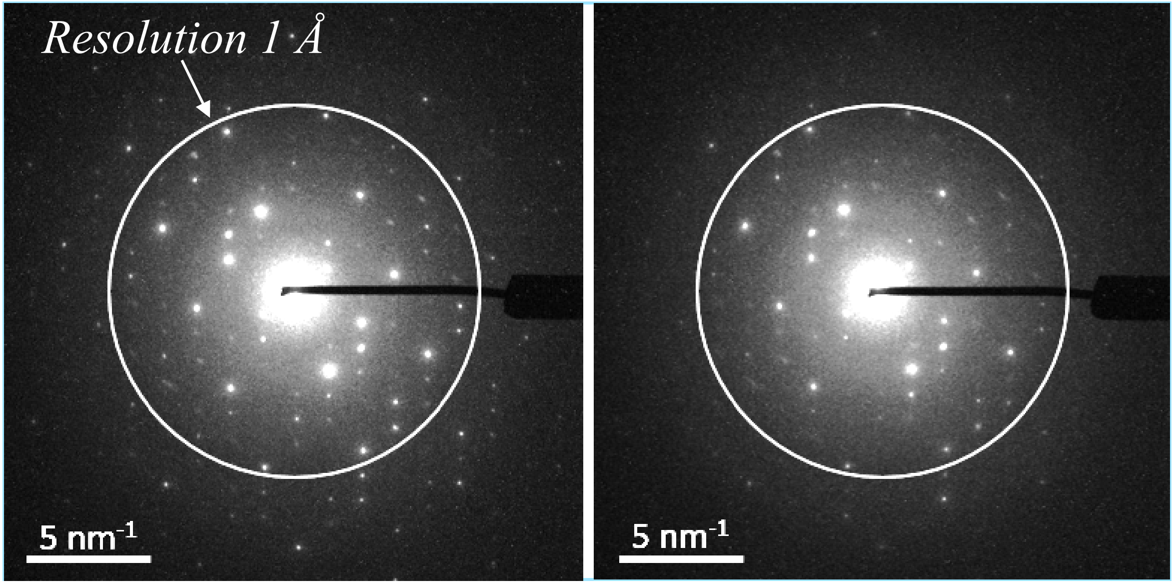
Inelastic interactions: cristallinity loss

Manganese formate

$[Mn(HCOO)_2(H_2O)_2]_\infty$



Diffraction fading



At the beginning of the data acquisition

After the data acquisition (same orientation)

Maximal irradiation dose: 0.15 $e^-/Å^2$

*300 kV, Crystal size: 0.7 µm*0.9 µm*

Low-Dose Electron Crystallography: Structure solution and refinement, H. Klein, S. Kodjikian, E. Yörük, P. Bordet, Symmetry 2022, 14 (2), 245

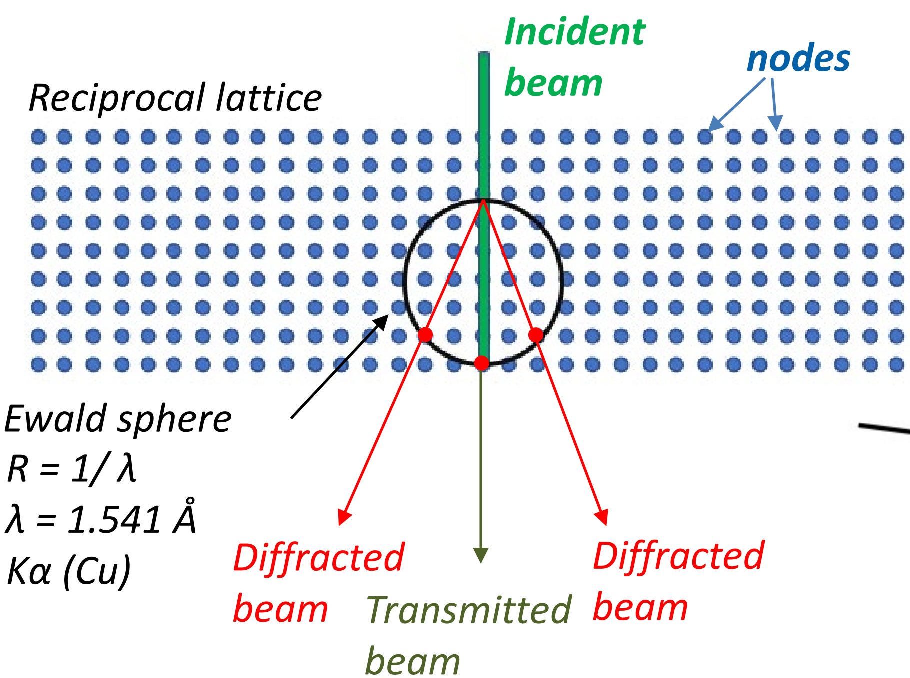
Particularities of Electron diffraction

Particularities of electron diffraction: rods and Ewald sphere

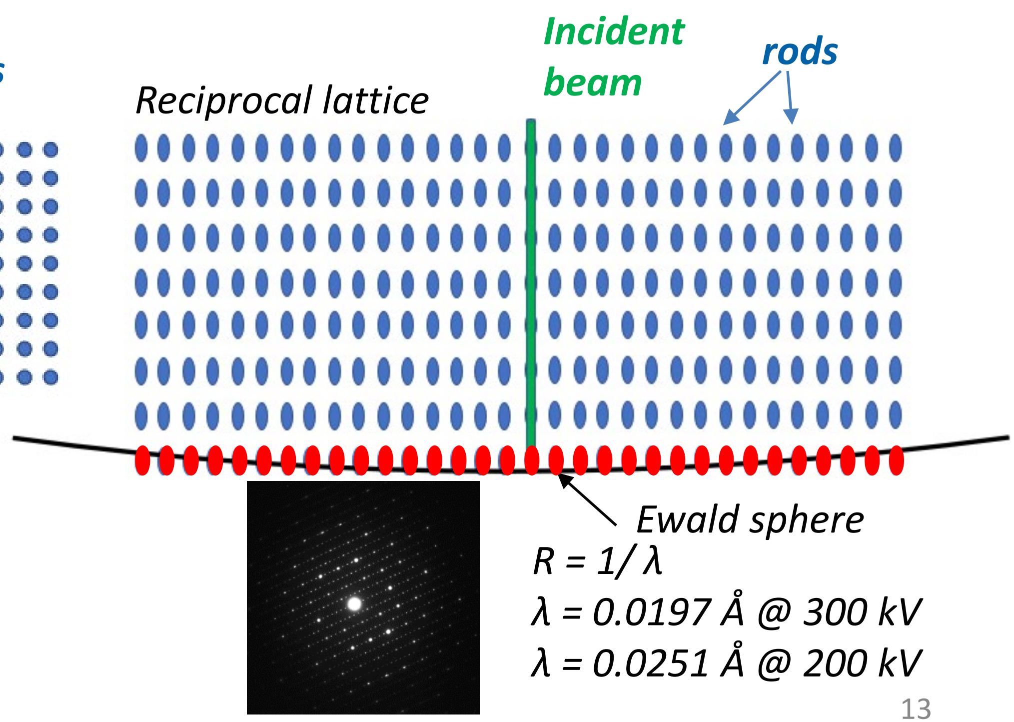
- **Thin** specimen => spatial extension of nodes (**rods**)
- **Small** wavelength => Ewald sphere **intersects a large number** of rods

Bragg's law: $2\, d_{hkl} \sin \theta = n\, \lambda$

X-ray diffraction

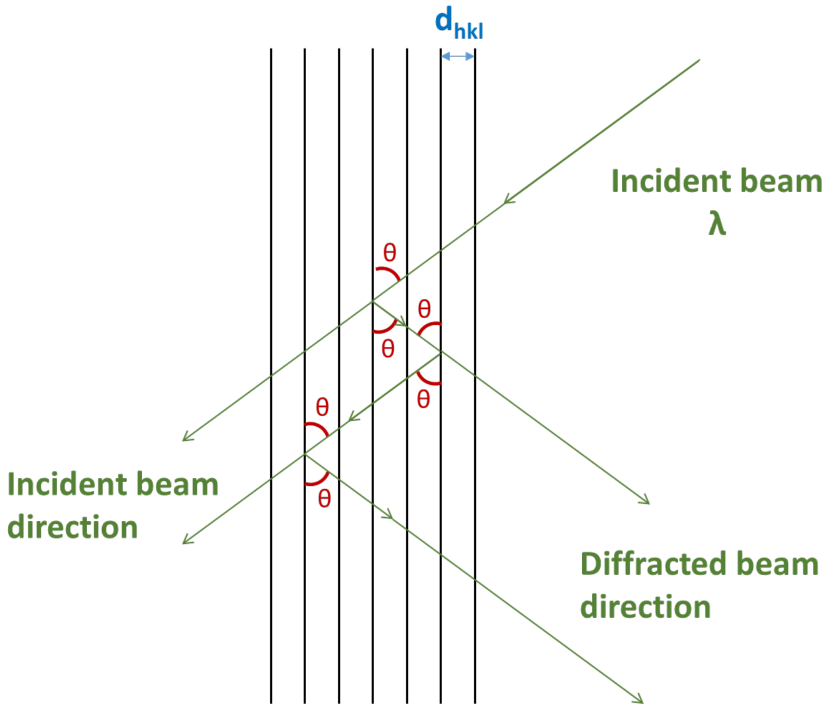


Electron diffraction



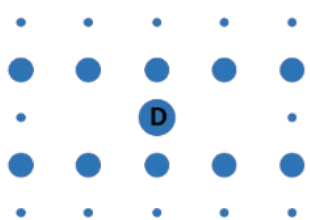
Figures: adapted from Emre YORUK, Institut Néel Grenoble and FZU Prague (PhD manuscript)

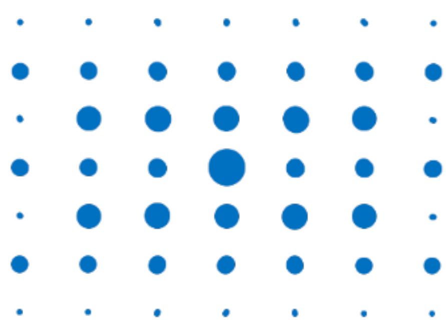
Particularities of electron diffraction: dynamical effects



$$2\,d \sin\theta = n\,\lambda$$

$$I(hkl) \propto |F(hkl)|^2$$





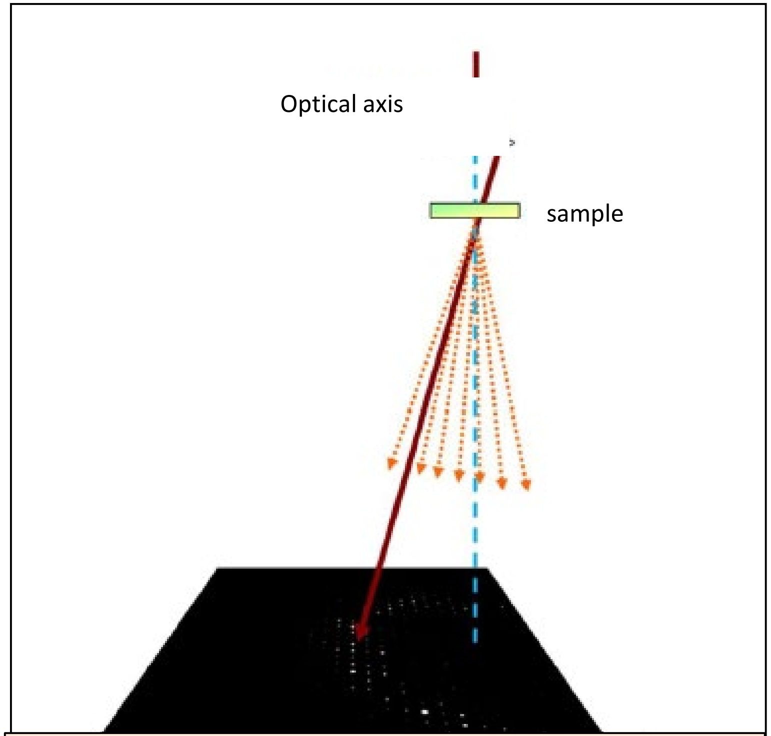
*Relative **intensities are modified** due to dynamical diffraction*

Kinematical diffraction pattern *Dynamical diffraction pattern*

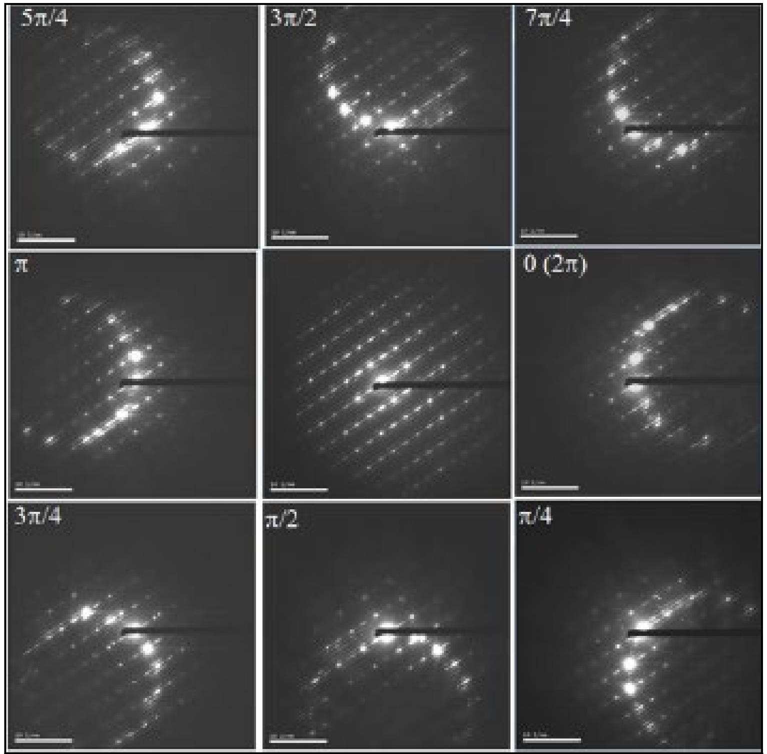
Electron Diffraction: Recent Breakthroughs

❑ Precession Electron Diffraction (1994)

Vincent & Midgley, Ultramicroscopy 53 (3), 1994



Beam Precession
Limits dynamical effects



Central snapshot = sum of the snapshots for each direction of the incident beam.

Figures: C. Lepoittevin

Electron Diffraction: Recent Breakthroughs

- **Precession Electron Diffraction (1994)** → **Dynamical effects reduced**
  Vincent & Midgley, Ultramicroscopy 53 (3), 1994

- **Automated Diffraction Tomography (2007)**
  Kolb et al., Ultramicroscopy 107 (6-7), 2007
- **Precession Electron Diffraction Tomography (2009)**
  Mugnaioli et al., Ultramicroscopy 109 (6), 2009
- **Continuous Rotation Electron Diffraction (2013)**
  Nederlof et al.,Acta Cryst. D 69 (7), 2013. Etc…

→ **Faster data acquisition: 3D Electron Diffraction**

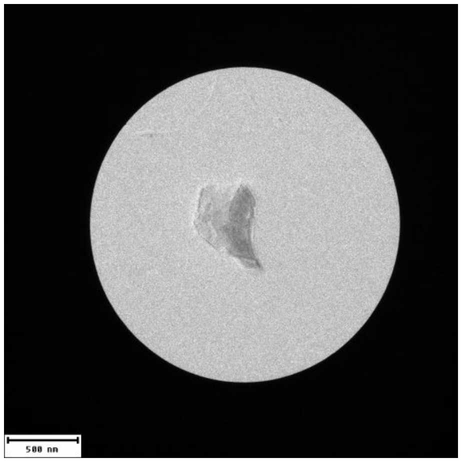
- **Dynamical refinement (2015)** → **Consideration of dynamical diffraction in data processing**
  Palatinus et al., Acta Cryst. A 71 (2), 2015

Slide: courtesy of E. YORUK (2022) – PhD Defense

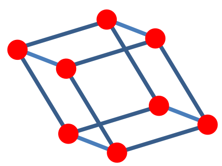
3D electron diffraction: Data collection and treatment

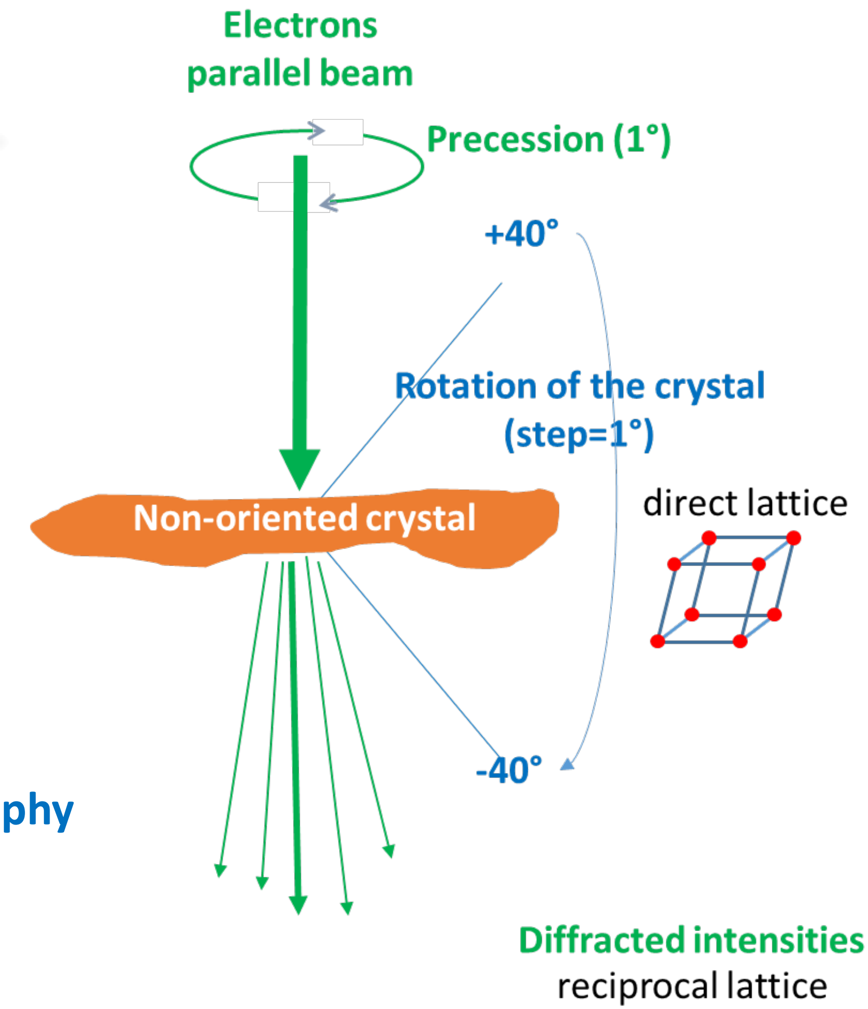
Data collection: Low Dose Electron Diffraction Tomography

S. Kodjikian and H. Klein, Ultramicroscopy, 200, 2019, pp. 12-19



Non-oriented crystal



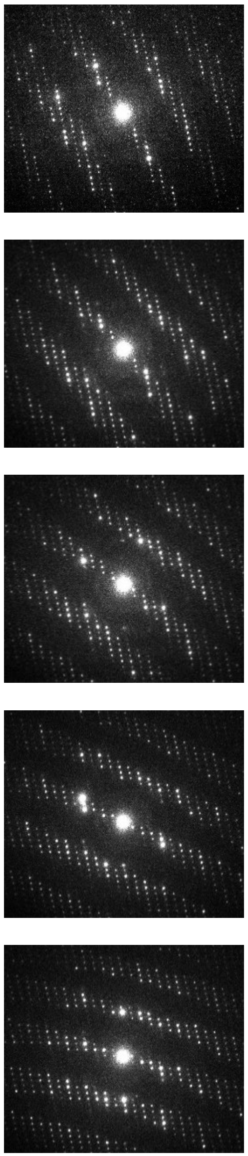


Low Dose –Electron Diffraction Tomography

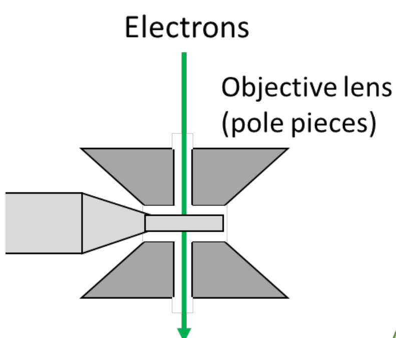
- Step by step (step = 1°)
- Beam precession (half-angle = 1°)
- Beam blanking between two frames.

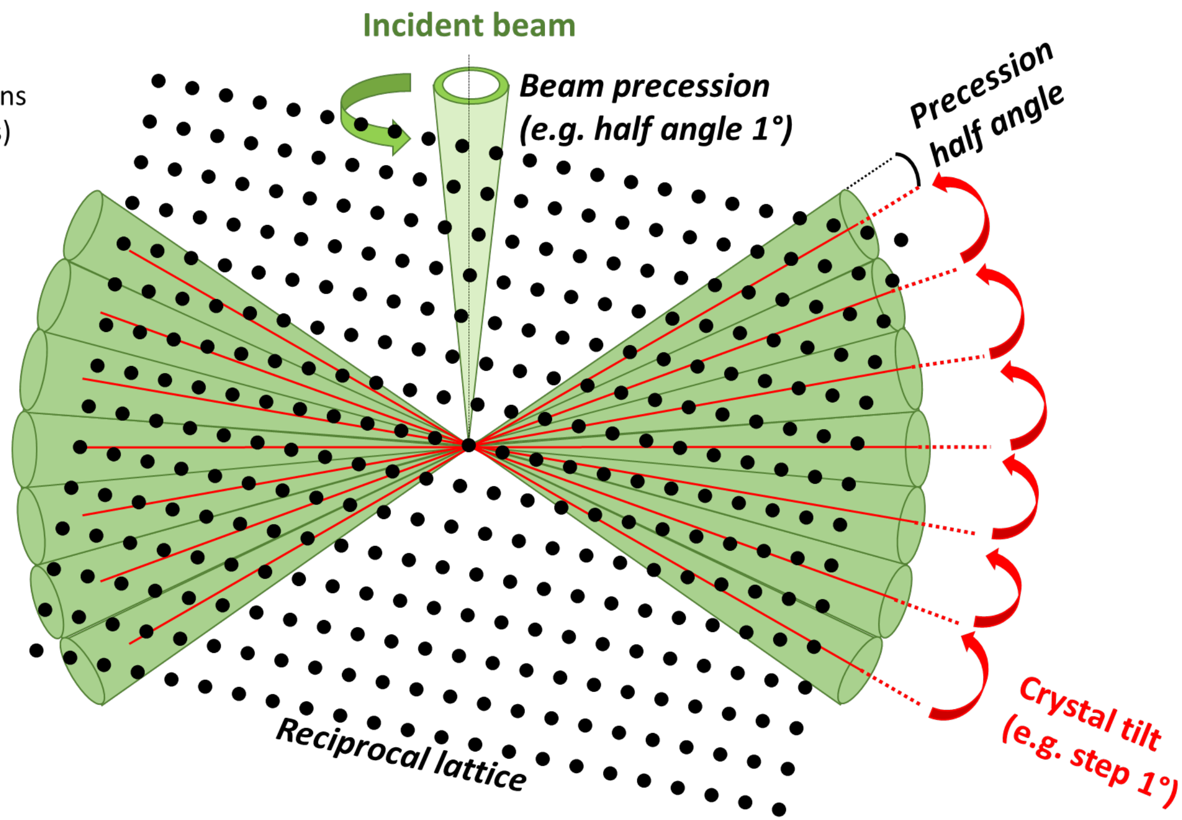
Data collection: example of LD-EDT method

S. Kodjikian and H. Klein, Ultramicroscopy, 200, 2019, pp. 12-19



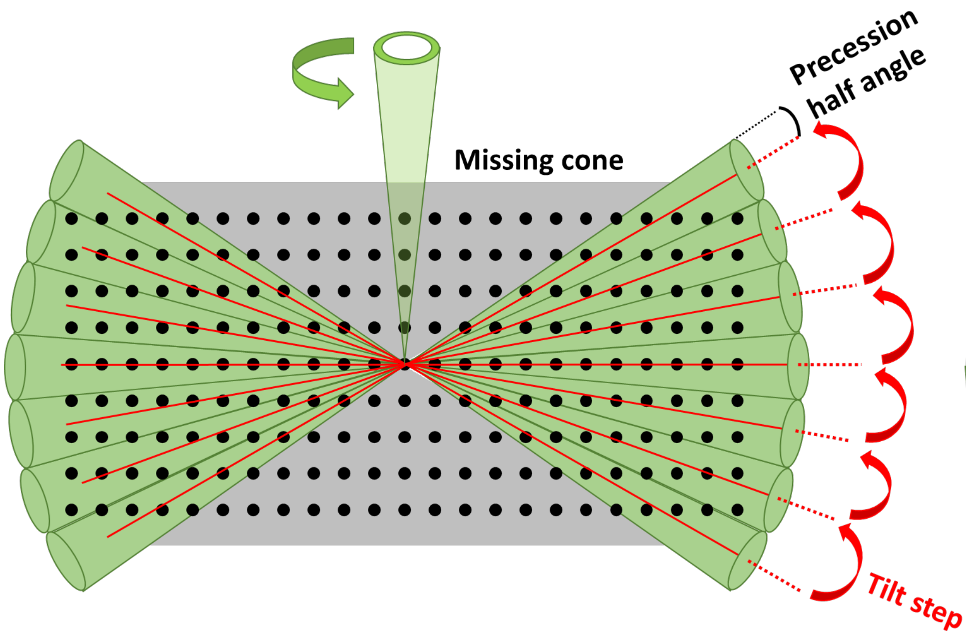
… 3D Reconstruction
of the reciprocal lattice

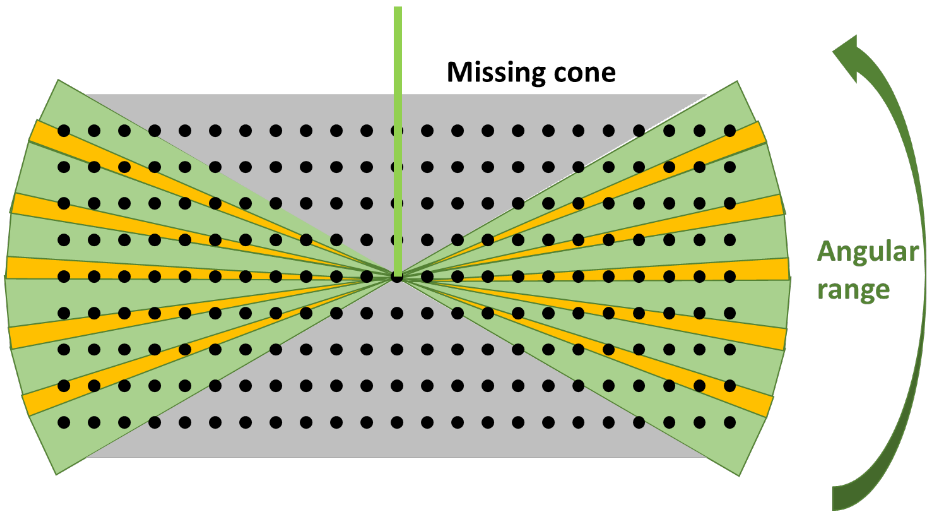




3D Electron Diffraction – data collection

3D ED: *Collecting ED data from a single crystal while tilting it around an arbitrary axis*





Step-wise rotation, with beam precession (ADT, PEDT, LD-EDT)

- ✓ **Possibility to re-center the sample**
- ✓ **Time consuming (10 min to 45 min)**
- ✓ **Requires beam precession**

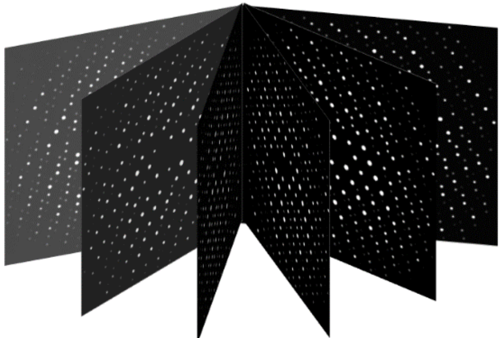
=> LOW DOSE (beam blanking)

Continuous rotation (cRED, MicroED)

- ✓ **Very fast : 30 s to 5 min**
- ✓ **Requires**
  - **- very stable goniometer & sample holder**
  - **- fast detector**

=> LOW DOSE

3D Electron Diffraction – data treatment

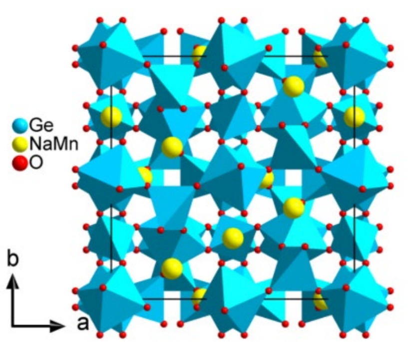


Peak Search → Tilt Axis → Unit Cell & Orientation Matrix → Reflection Profile → Frame Geometry → Final Integration → **hkl file**

Phasing by
- Direct Methods
- Charge Flipping
- Molecular Replacement

→ Kinematical + Dynamical Refinement → Final Structure

Structural model



Kinematical refinement

- $I_{hkl} \propto |F_{hkl}|^2$
- One intensity per reflection

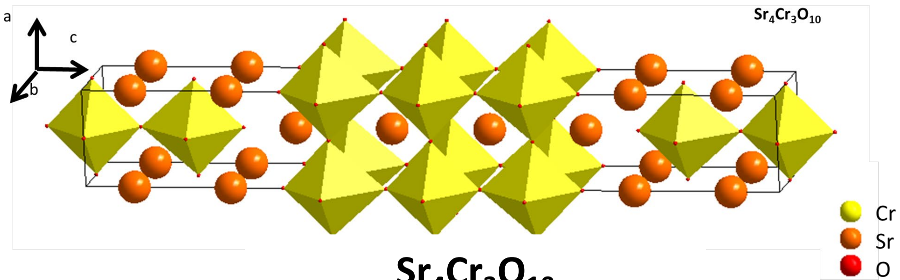
Dynamical refinement

- $I_{hkl} \propto$ multiple $|F|^2$
- Reflections considered frame by frame

3D ED @ Institut Néel

Some unknown structures solved at Institut Néel

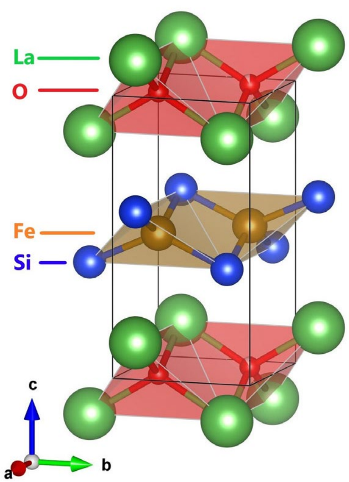
Superconductivity



$Sr_4Cr_3O_{10}$
Tetragonal, *I4/mmm*
a= 3.8 Å, *c* = 27 Å

J. Jeanneau *et al. Journal of Solid State Chemistry 251 (2017) 164-169*

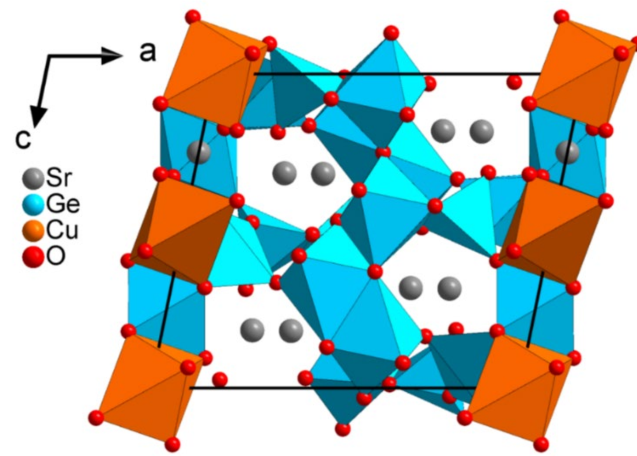
Superconductivity, Tc = 10 K



$LaFeSiO_{1-\delta}$
P4/nmm
a = 4.1085(4) Å,
c =8.132(2) Å

M.F. Hansen et al. Npj Quantum Materials, 2022, 7 (1), pp.86

Magnetic properties / multiferroism



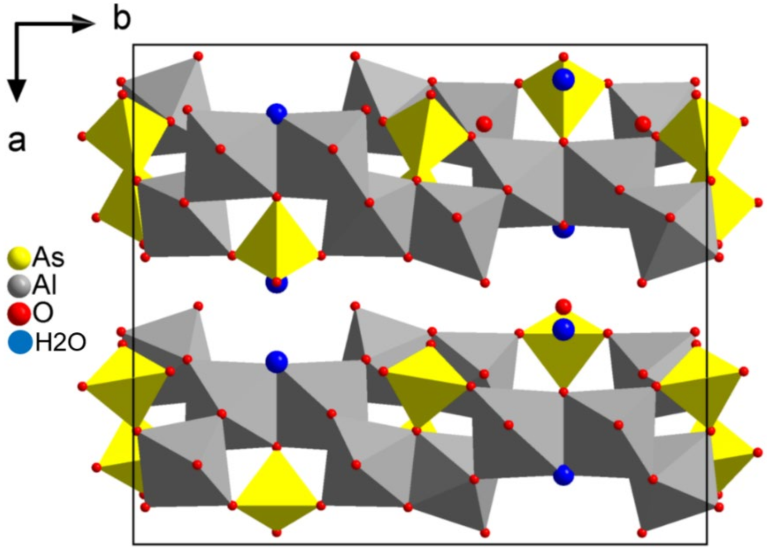
$Sr_5CuGe_9O_{24}$
Monoclinic *P2/c*
a = 11.8817(3) Å
b = 8.1928(2) Å
c = 10.3237(2) Å
β = 101.60(1)°

*H. Klein et al. Acta Cryst. (2020) B**76**, (5), pp.727-732*

Synthesized at HP/HT
3 Ge environments:
Tetrahedra, octaedra, five-fold pyramid

Some unknown sensitive materials solved at Institut Néel

Mineral



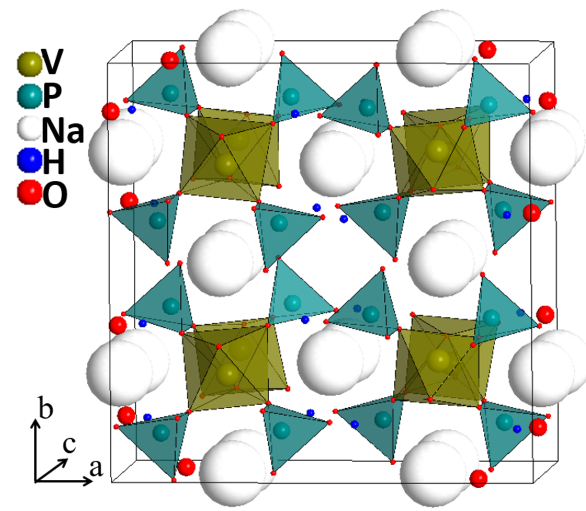
$[Al_6(AsO_4)_3(OH)_9(H_2O)_4]\cdot 2H_2O$

Pnma, *a* = 15.4 Å, *b* = 17.7 Å, *c* = 7.81 Å

Total dose : 3 $e^-/Å^2$

I.E. Grey et al. Mineralogical Magazine (2020), 84, 608–615

Na-ions batteries



$Na_2VO(HPO_4)_2$

*Iba*2

a = 13.86852(19) Å

b = 13.7985(2) Å

c = 7.47677(9) Å

C. *Lepoittevin et al, Dalton Trans., 2021,* ***50****, 9725-9734*

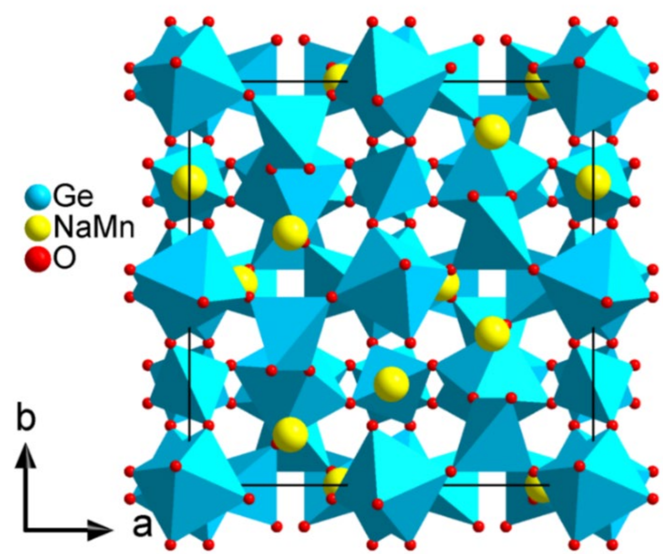
Quasi-1D magnetism, Multiferroism

$(Na_{2/3}Mn_{1/3})_3Ge_2Ge_3O_{12}$

Cubic Ia-3d, a = 11.9860(3) Å

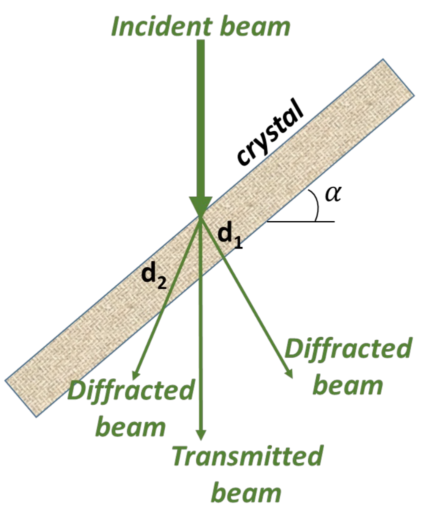
Total dose : 0.13 $e^-/Å^2$

H. Klein et al. Symmetry 2022, 14 (2), 245



3D Electron Diffraction at Institut Néel: improvements
Dose Symmetric Electron Diffraction Tomography (DS-EDT)

✸ When the crystal is tilted,
diffracted beams experience **different apparent thicknesses**.

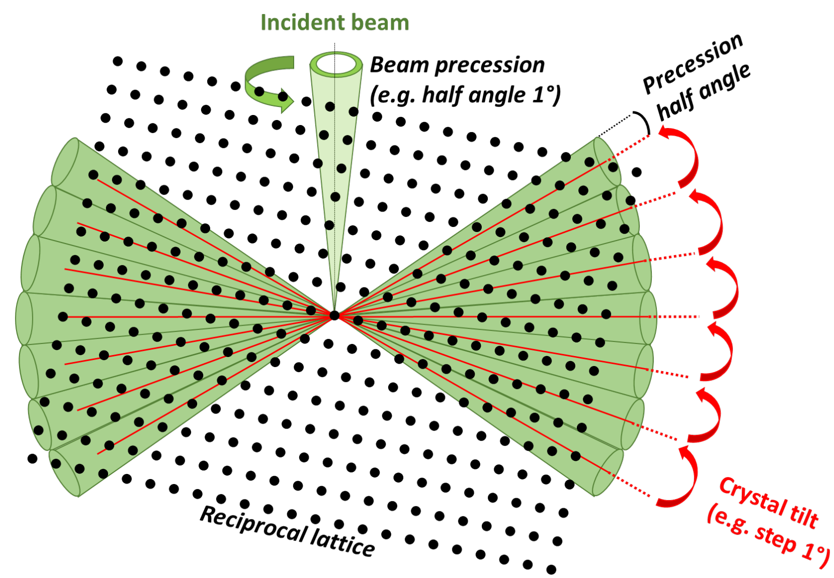


Differences in absorption and dynamical effects

Low tilt
⇒ low apparent thickness
⇒ High resolution

PhD Emre YORUK
2019-2022

✸ Typical step by step tomography in 3D ED



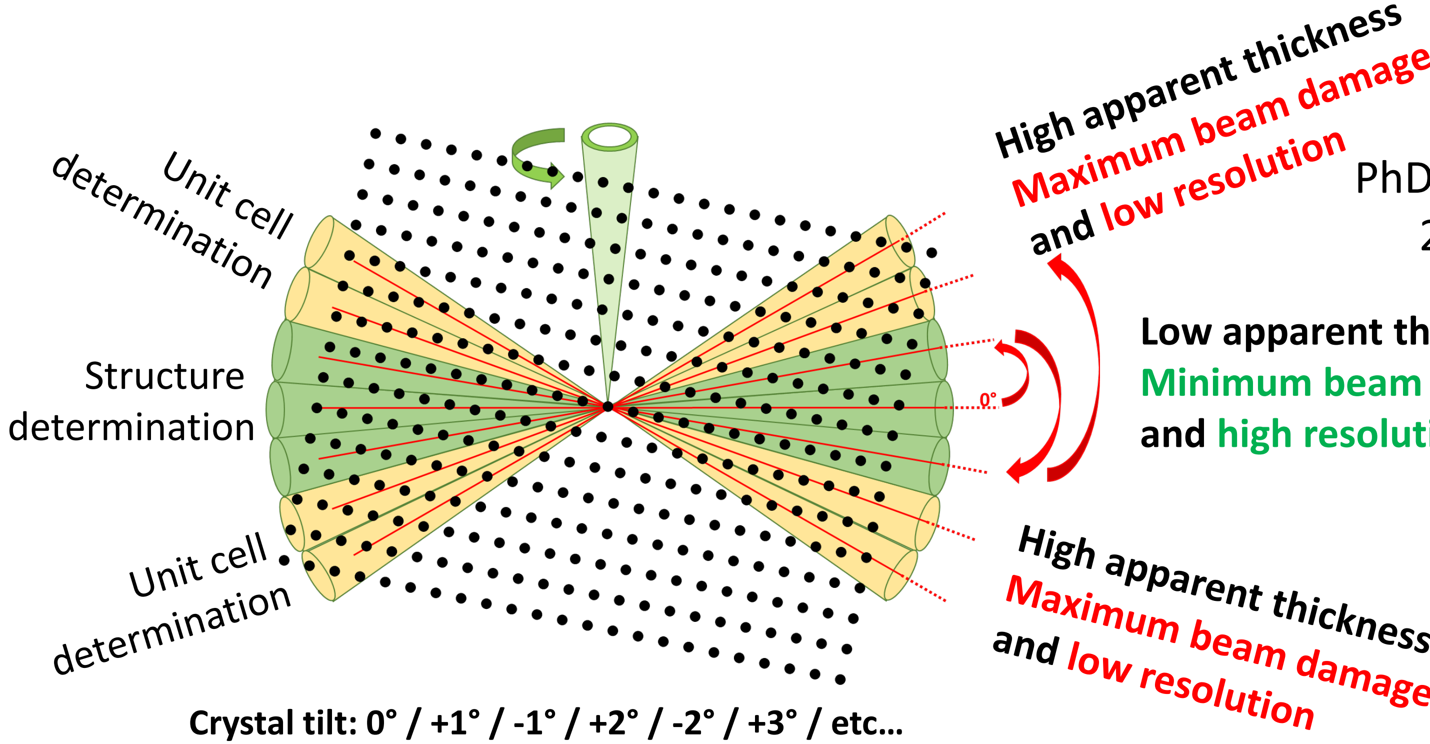
The initially recorded high tilt frames are the least damaged,
while the damage accumulates throughout the acquisition.

⇒ Record low tilt frames first
Minimum beam damage and **high resolution**

3D Electron Diffraction at Institut Néel: improvements
Dose Symmetric Electron Diffraction Tomography (DS-EDT)

E. Yoruk et al. Ultramicroscopy 16 sept. 2023, DOI: 10.1016/j.ultramic.2023.113857

- Data collection begins at low tilt, and alternates between increasingly positive & negative tilts
- **Low tilt frames with high-resolution information are least irradiated**
- Damaged high tilt frames used to determine the unit cell and the orientation matrix



PhD Emre YORUK
2019-2022

- Only low tilt frames are used for structure determination, preserving data from beam damage

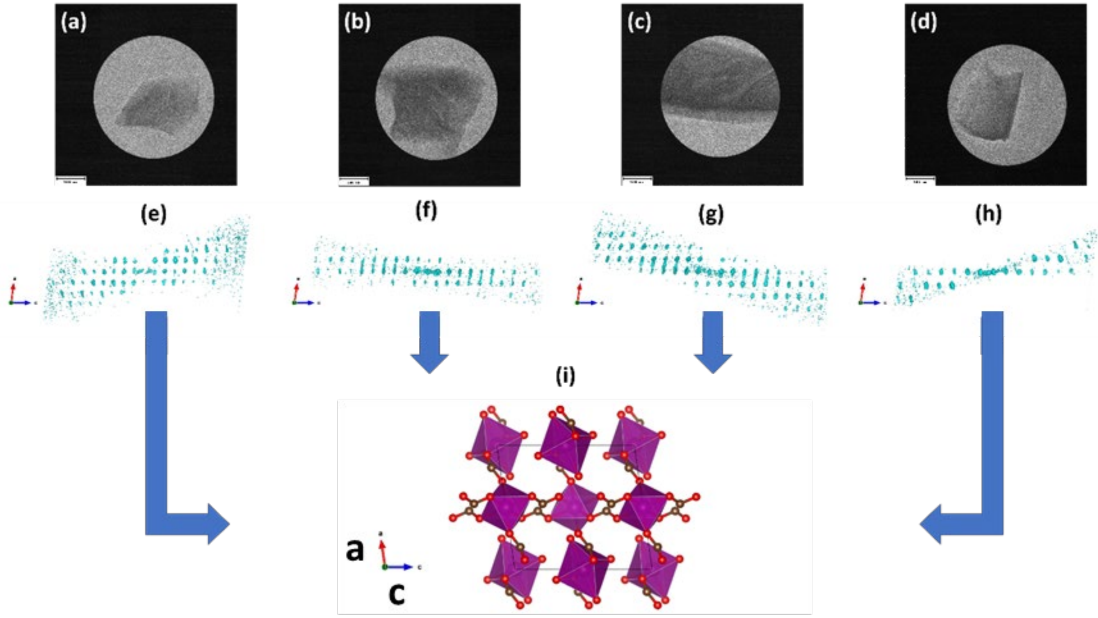
→ **Lower dose per particle without lowering the signal to noise ratio**

3D Electron Diffraction at Institut Néel: improvements
Dose Symmetric Electron Diffraction Tomography (DS-EDT)

E. Yoruk et al. Ultramicroscopy 16 sept. 2023, DOI: 10.1016/j.ultramic.2023.113857

- Low tilt data from multiple crystals is merged for data completeness

Software
Pets 2
Jana 2020



Example:
Mn formate
$Mn_2(COOH)_2(H_2O)_2$
Monoclinic $P2_1/c$
a = 8.8263 Å,
b = 7.2247 Å,
c = 9.6305 Å
β = 97.689°

- Structure solution and dynamical refinement
- **High accuracy** of the atom positions
- Possible using **only low-tilt data** from **multiple particles**, down to **ranges of +/- 5°** per particle

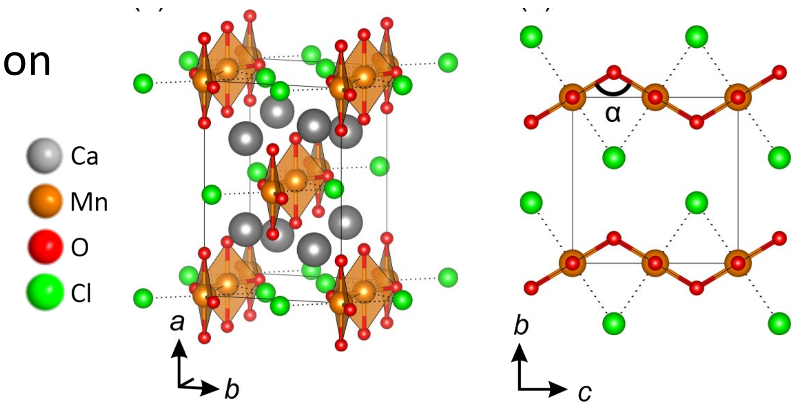
3D Electron Diffraction at Institut Néel: Ca_2MnO_3Cl

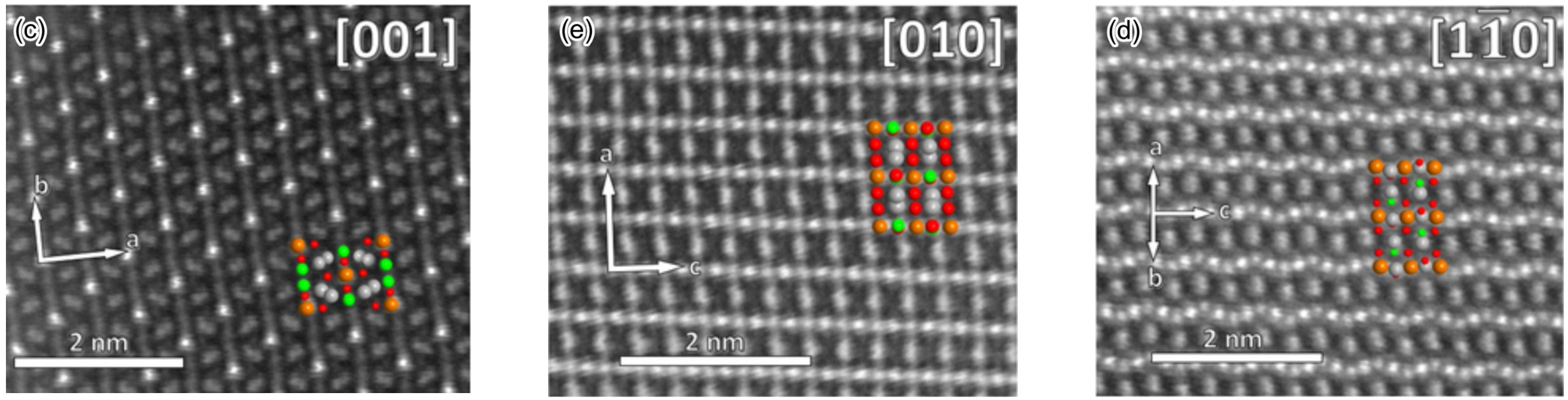
1-dimensional ferromagnetic chains

✶ **TEM:** **Composition** from Energy Dispersive X-Ray Spectroscopy: Ca, Mn, O, Cl
Structural model from 3D electron diffraction
Comparison of the structural model with STEM HAADF images

✶ **Powder X-Ray diffraction:**
Unit cell /space group confirmation
Structure refinement

F. Denis Romero et al.,
Accepted by Journal of the American Chemical Society





STEM-HAADF Images: C. Lepoittevin

Conclusion

Conclusion

- ✓ 3D Electron diffraction suitable for a wide range of samples
  - Nanocrystals
  - Mixtures
  - Domains
- ✓ New developments in data collection and treatment
  - Detectors
  - Software
- ✓ New developments for beam sensitive materials
  - Preparation
  - Cryo
  - Low dose
  - New methods (merging data)

Aknowledgments

Emre YORUK (*now in Prague*)
Holger KLEIN
Christophe LEPOITTEVIN
Martien den HERTOG

Pierre BORDET
Céline DARIE
Fabio DENIS ROMERO
Lei DING
Mads HANSEN
Justin JEANNEAU
Olivier LEYNAUD
Rémy PHILIPPE
Pierre TOULEMONDE

FZU Institute of Physics of the Czech Academy of Sciences

Ian GREY
CSIRO Melbourne

Valérie PRALONG
Crismat Caen

Dominique LUNEAU
LMI Lyon

L'EUROPE S'ENGAGE en région Auvergne-Rhône-Alpes avec le FEDER
UNION EUROPÉENNE
La Région Auvergne-Rhône-Alpes