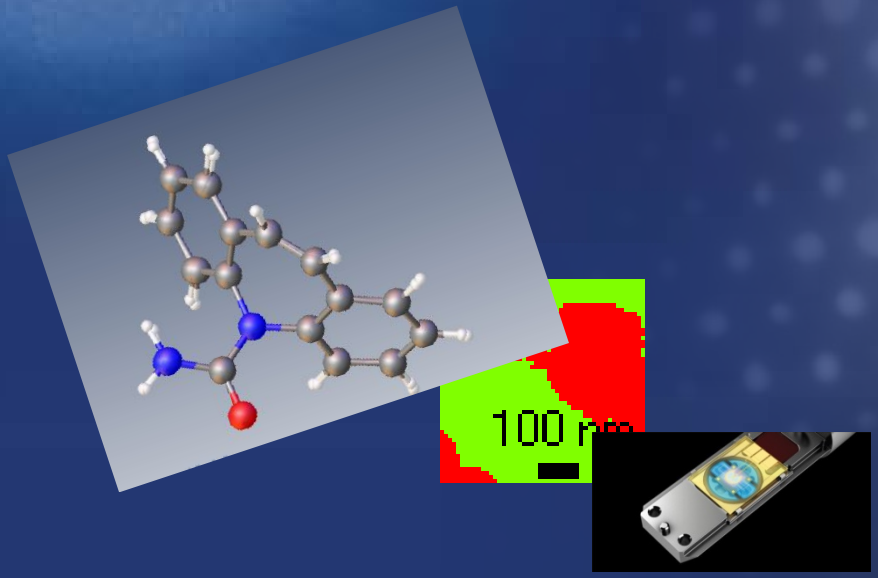
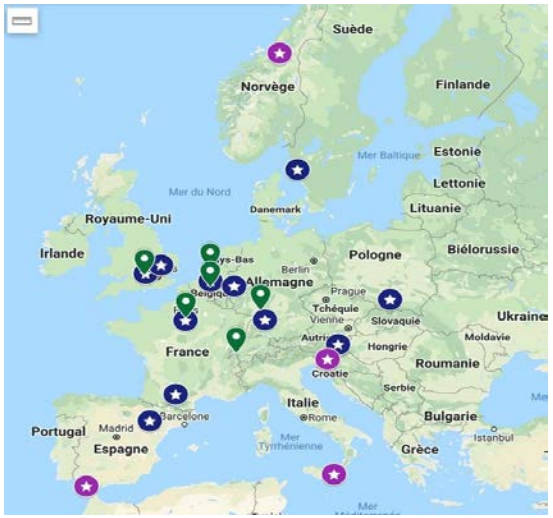
In situ materials characterization with 4D STEM scanning precession diffraction using novel pixelated detectors

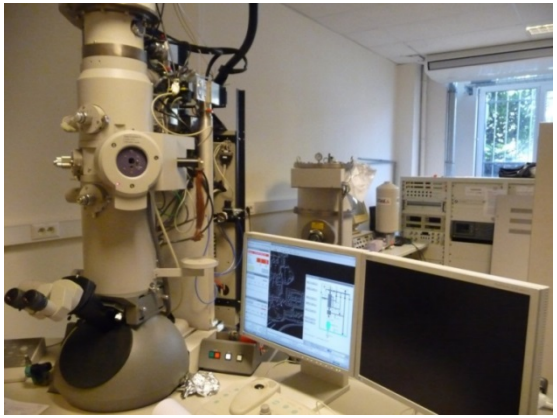


Dr. Stavros Nicolopoulos
Director NanoMEGAS

GROUPEMENT NATIONAL DE MICROSCOPIE ELECTRONIQUE A BALAYAGE ET DE MICROANALYSES
En convention de coopération avec la Société Française de Physique

PARTNER IN TEM MICROSCOPY INNOVATION NETWORK IN EUROPE

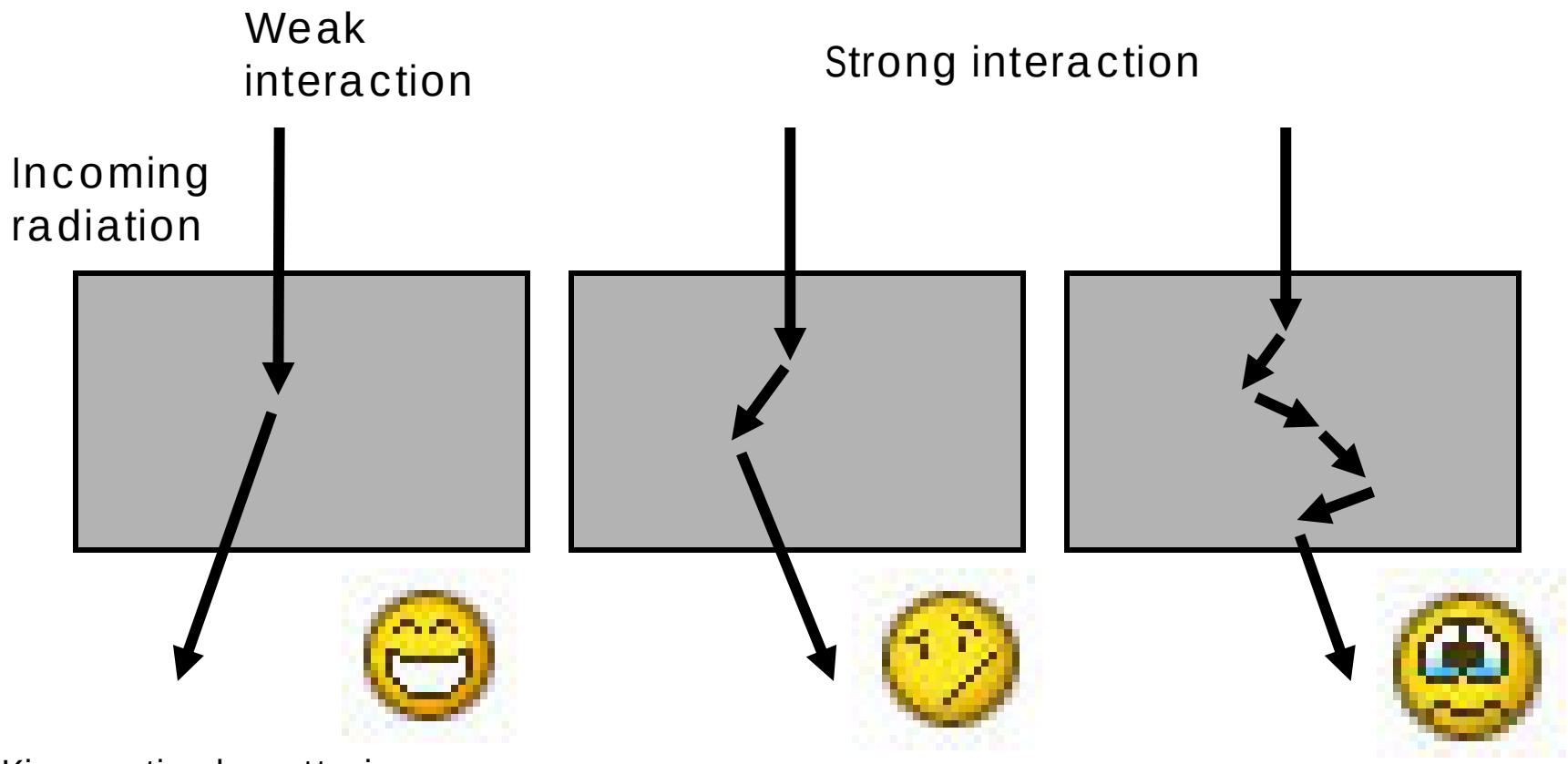




esteem3

BRUSSELS RESEARCH & DEVELOPMENT FACILITY

Electron diffraction : Dynamical effects



Kinematical scattering
Single scattering
$I_{hkl} \sim (F_{hkl})^2$

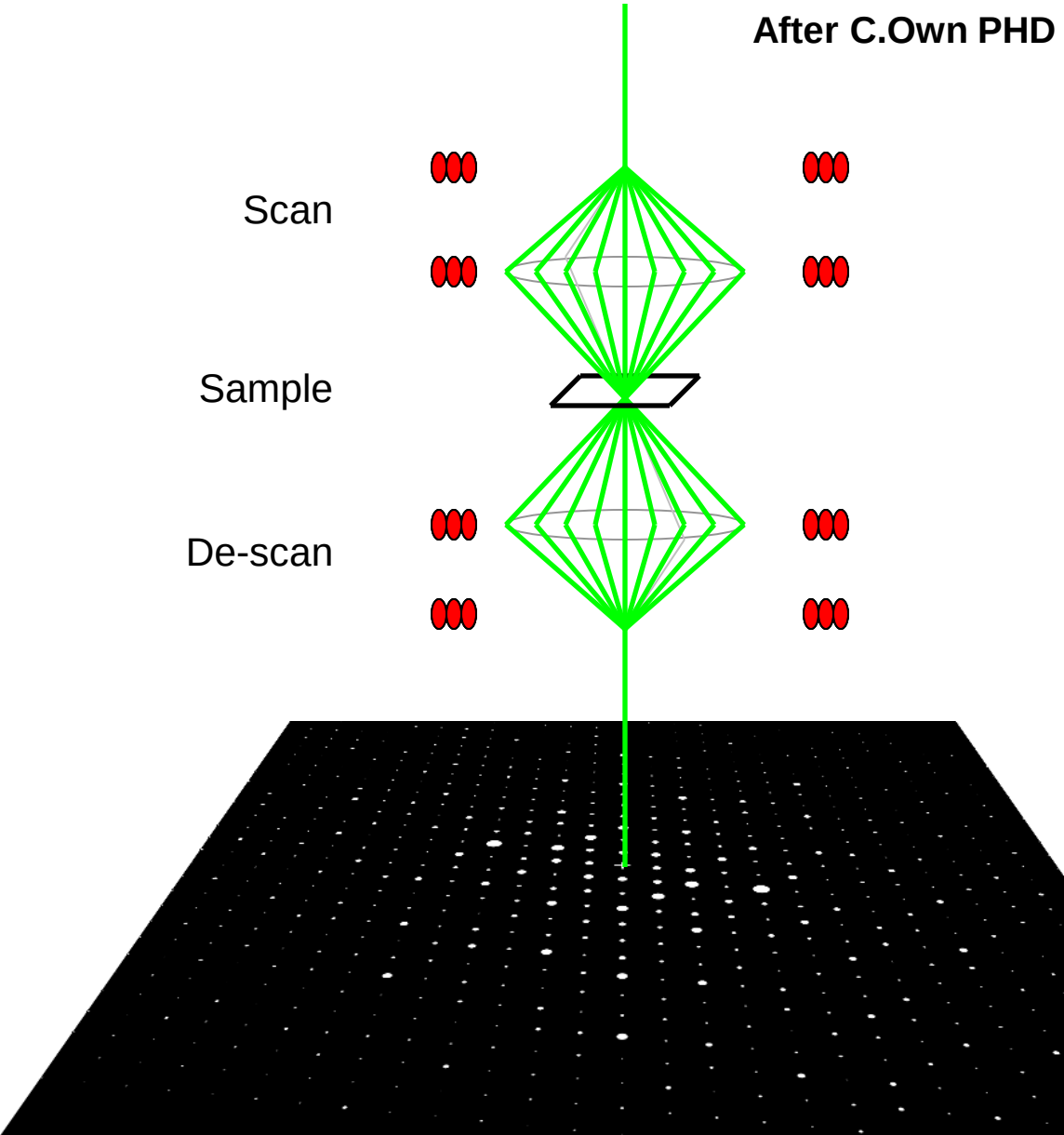
Always the case for X-ray

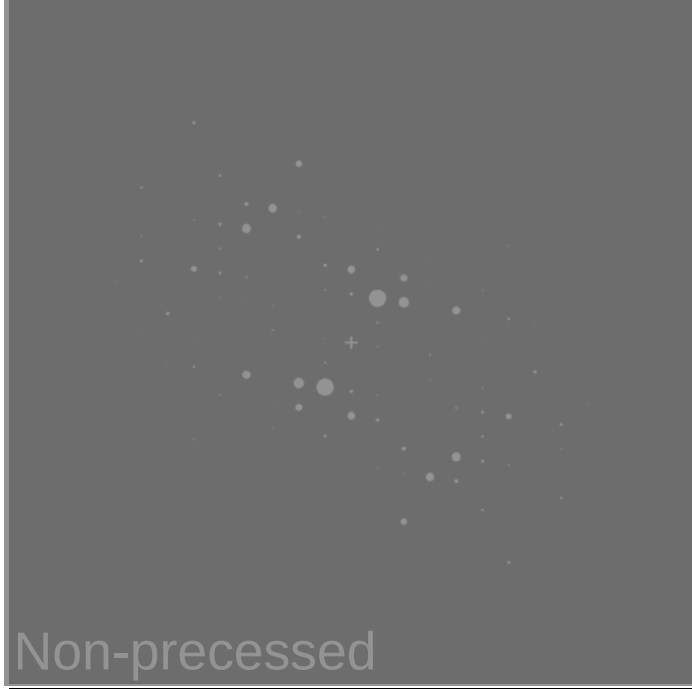
Dynamical scattering
2-beam scattering
Blackman formula
$I_{hkl} \sim F_{hkl}$

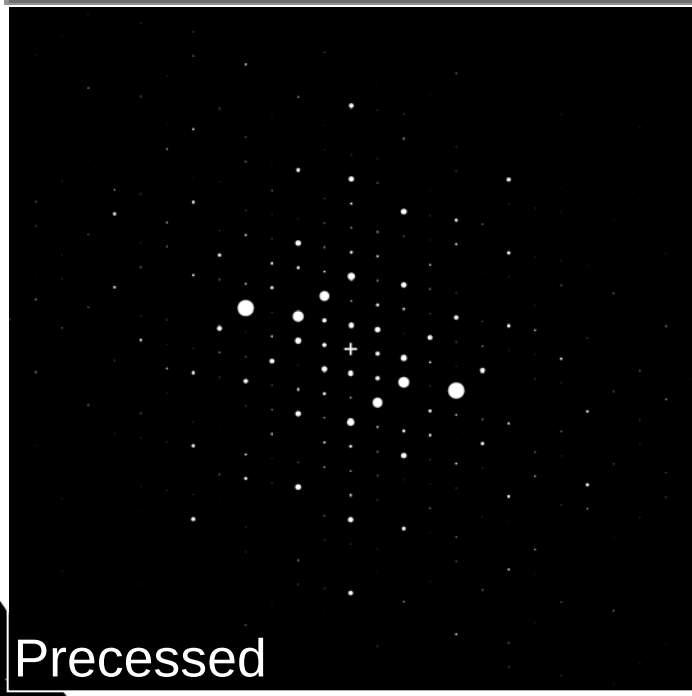
Dynamical scattering
Multi-beam?

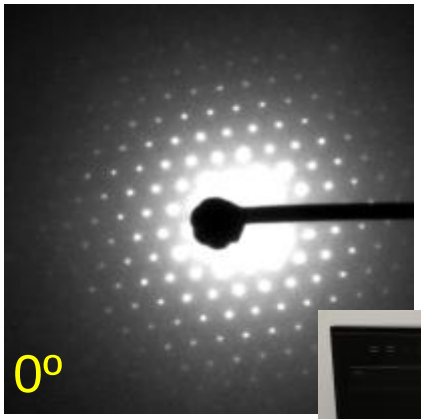
Courtesy Dr. E.Mugnaioli Univ of Sienna

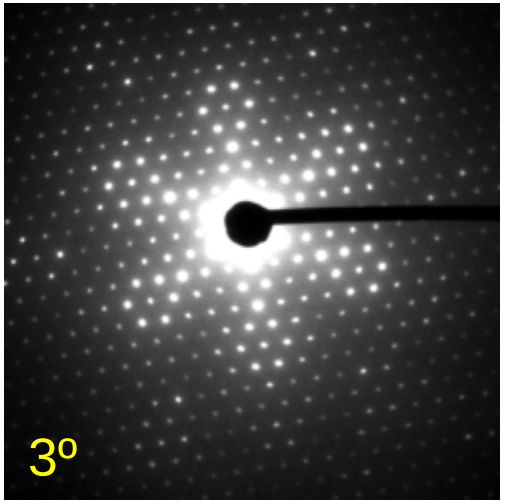
Vincent-Midgley Precession Method





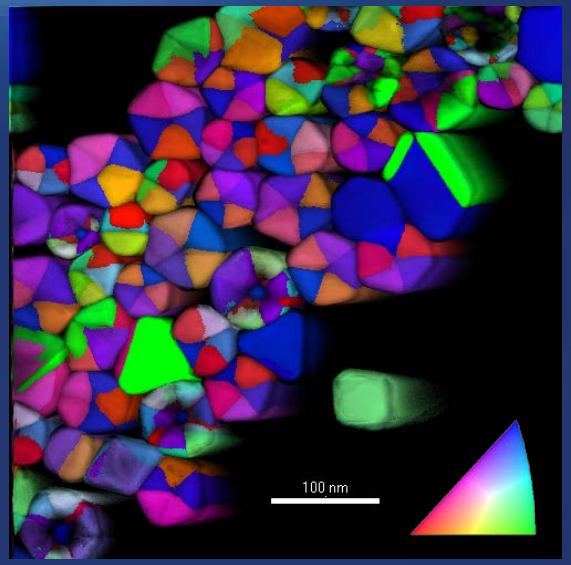






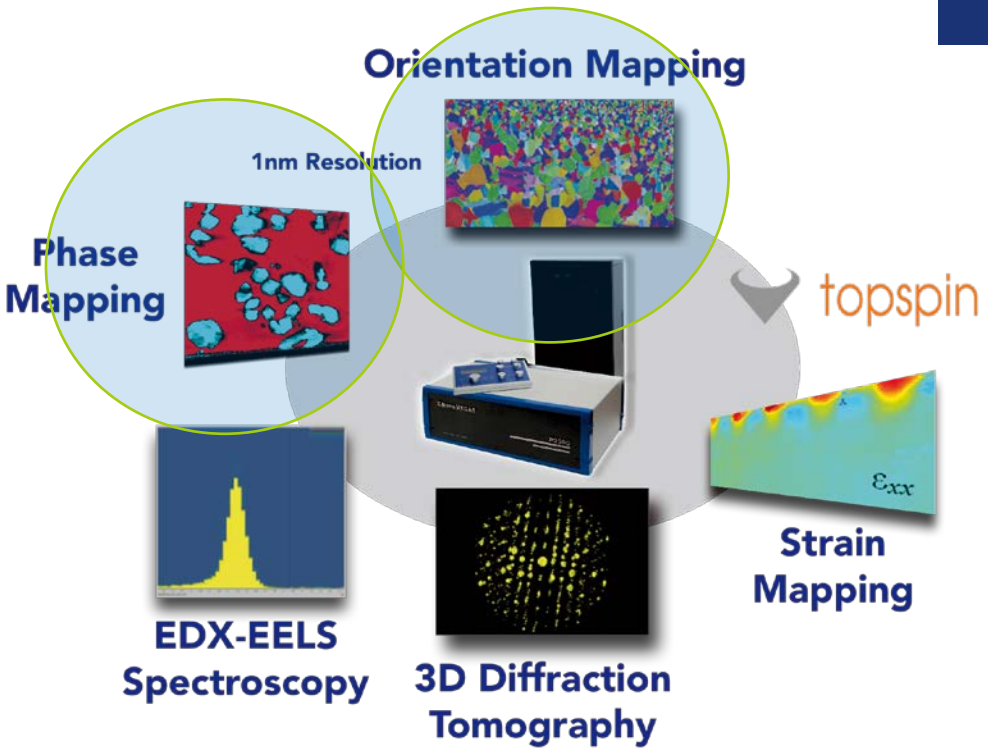
Precession unit Digistar
more kinematical ED intensities

ASTAR : orientation & phase mapping



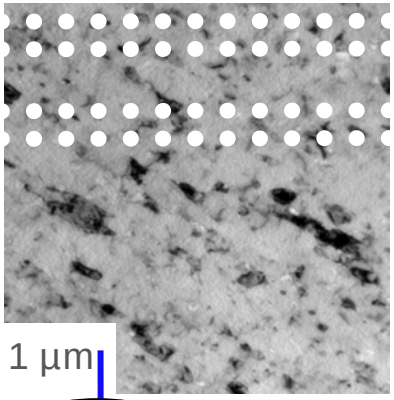
ASTAR: TEM Orientation and Phase Mapping

➢ **180 installations world-wide in TEM**



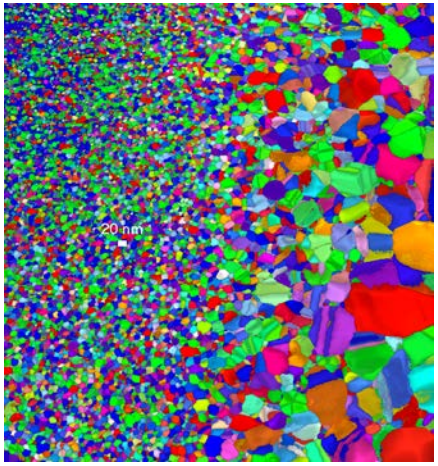
ASTAR : EBSD type tool for TEM

ASTAR : Automated Crystal Orientation Mapping

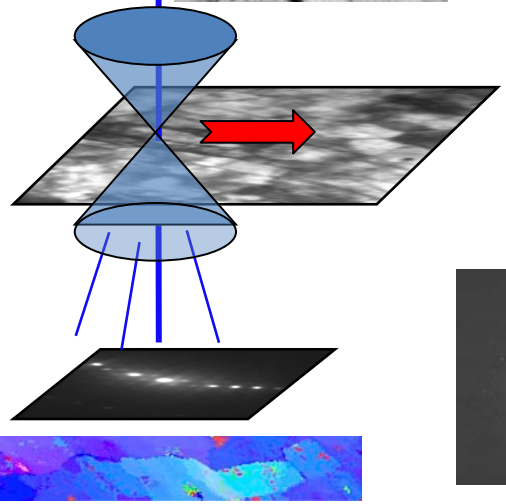


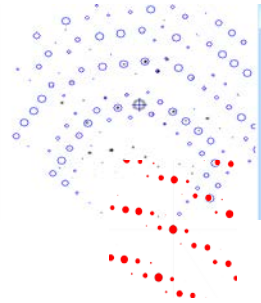
1 µm

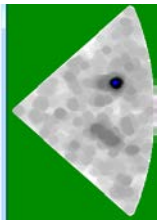
Scan sample area



Orientation map





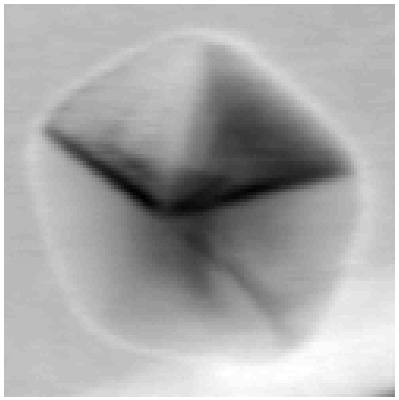


Orientation map

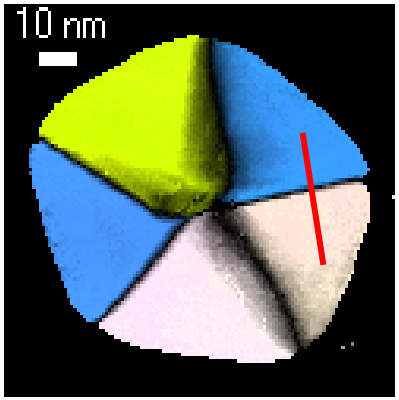
ASTAR : EBSD type tool for TEM

ASTAR : 1 nm spatial resolution orientation map

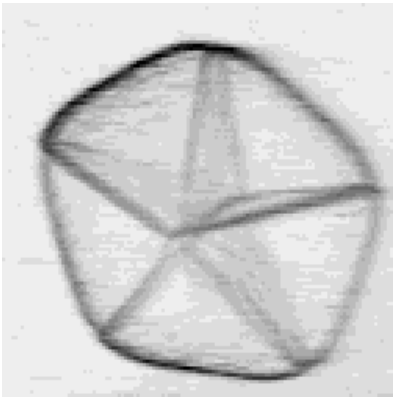
Multi-twinned gold particles (JEOL ARM 200)



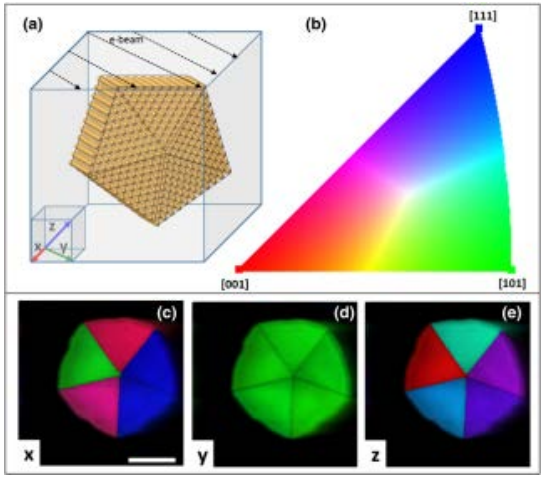
Virtual Bright-Field

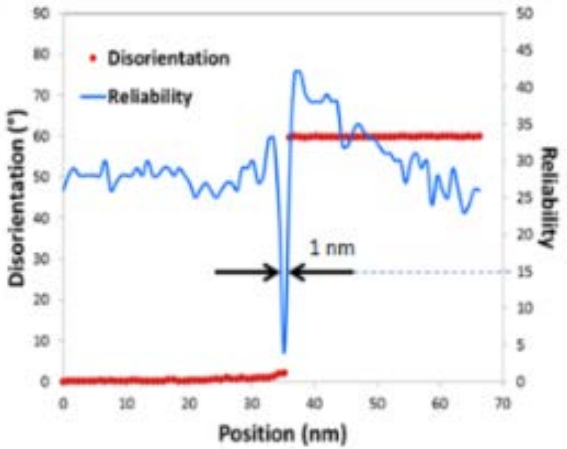


Orientation + Reliability

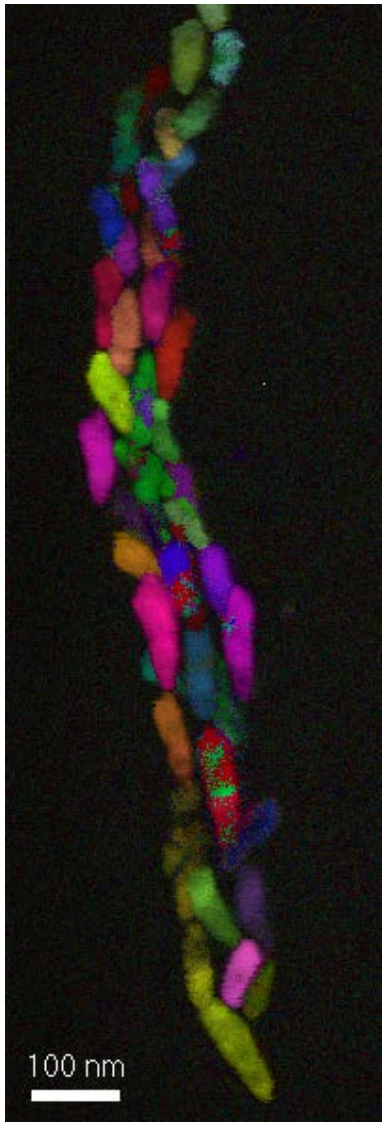


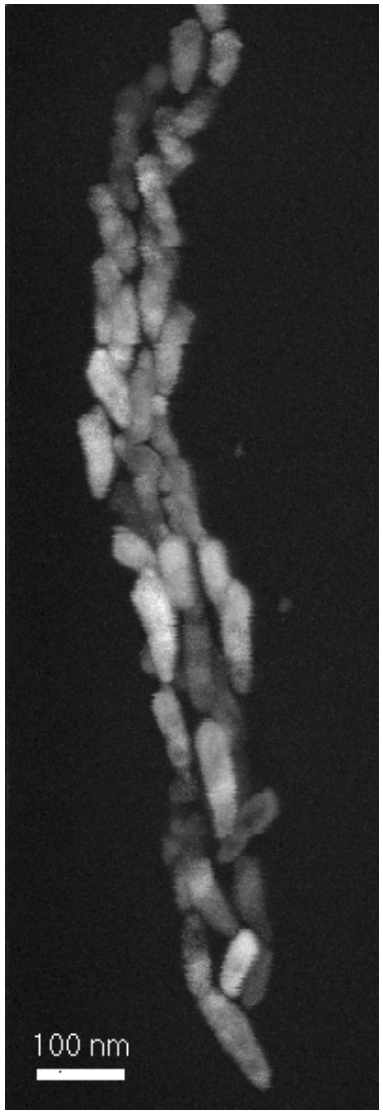
DP cross-correlation



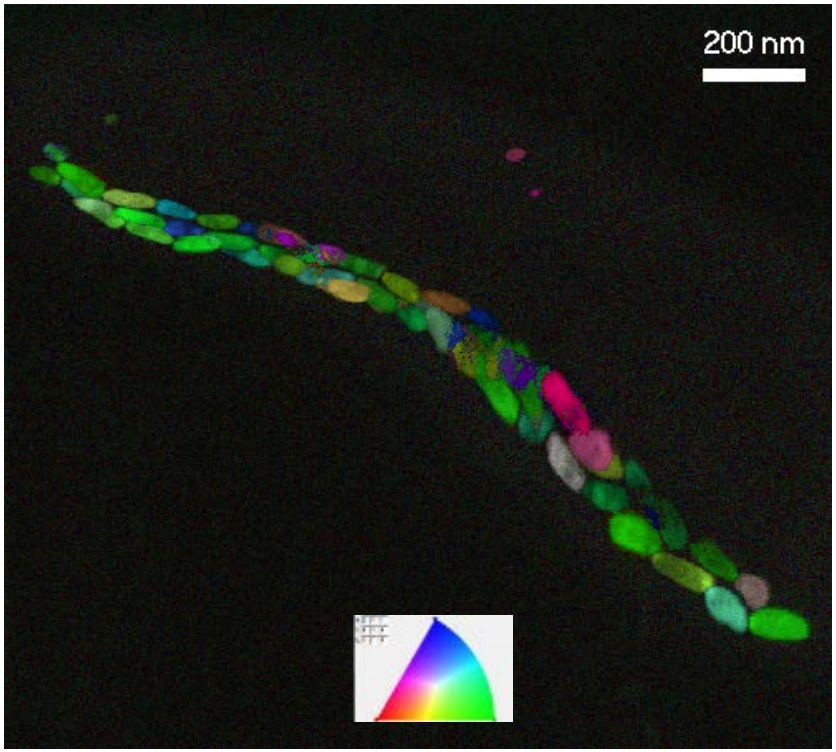


ASTAR : EBSD type tool for TEM





ASTAR orientation map

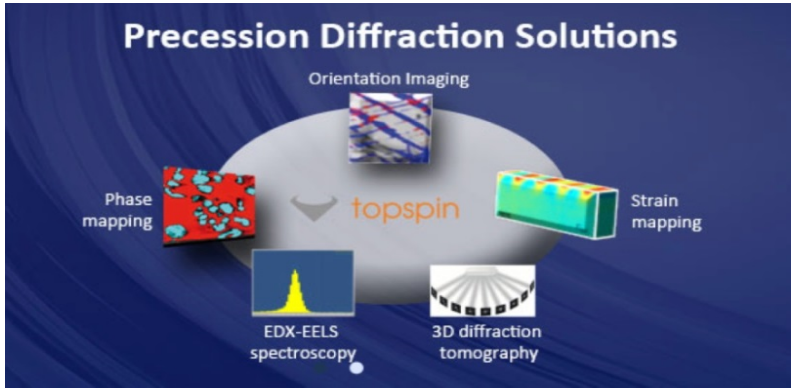


Data, coutesy Dr. J.Bourgon CNRS Thiais

Magnetite nanocrystals and magnetotactic BACTERIA

NanoMEGAS - TEM Cs corr / high end microscopes

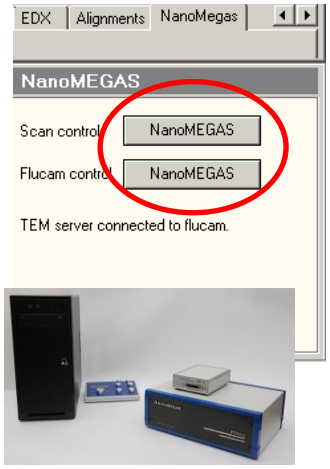
TITAN HIGH Base



> 400 PED related articles in 12 years
> 180 installations worldwide

ARM 200 FEG Double Cs

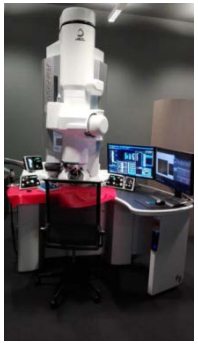
ARM 300 Double Cs



TITAN LOW Base

TALOS

HF5000

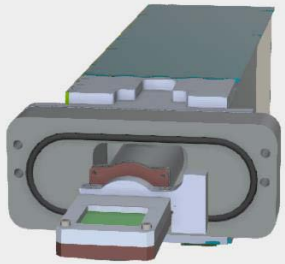


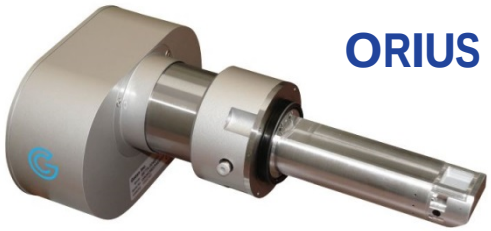
F200

ASTAR and PIXELATED DETECTORS

Quantum DETECTORS

AMSTERDAM SCIENTIFIC INSTRUMENTS





ORIUS

GATAN

OneView

GATAN

ASTAR compatible with Direct Detection cameras

DECTRIS
detecting the future

NanoMEGAS
Advanced Tools for electron diffraction

www.nanomegas.com

ASTAR and PIXELATED DETECTORS

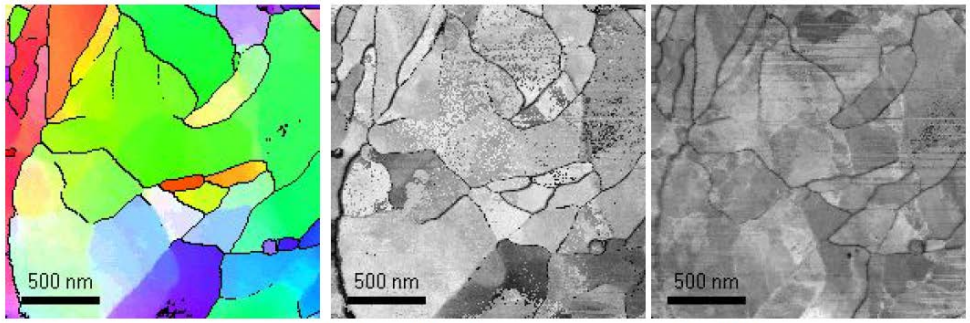


Fig. 1 Orientation mapping results from diffraction patterns acquired with Dectris camera. From left to right: Color coded orientation map with grain boundaries, orientation reliability map and index map

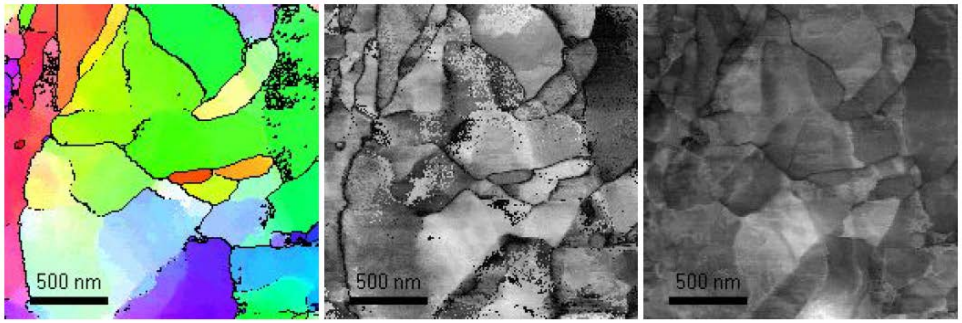
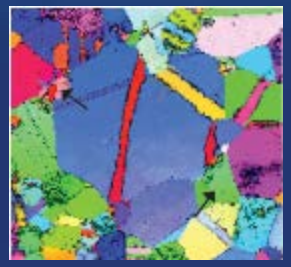


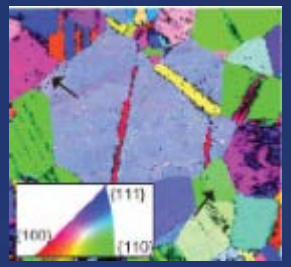
Fig. 2 Orientation mapping results from diffraction patterns acquired with Stingray camera. From left to right: Color coded orientation map with grain boundaries, orientation reliability map and index map

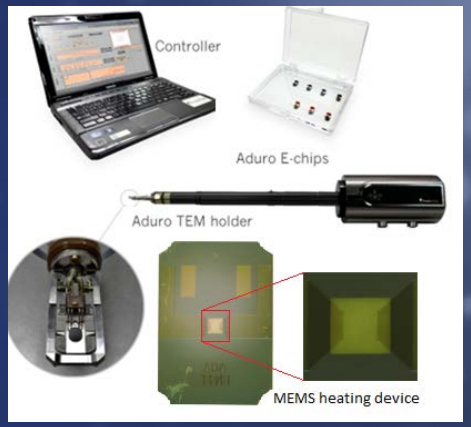
ASTAR orientation / phase mapping : in SITU and correlative microscopy

0 % strain

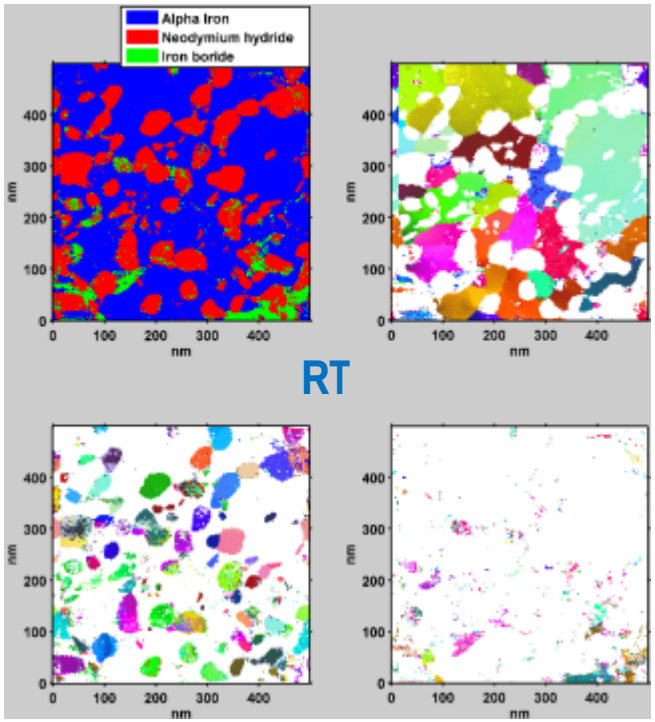


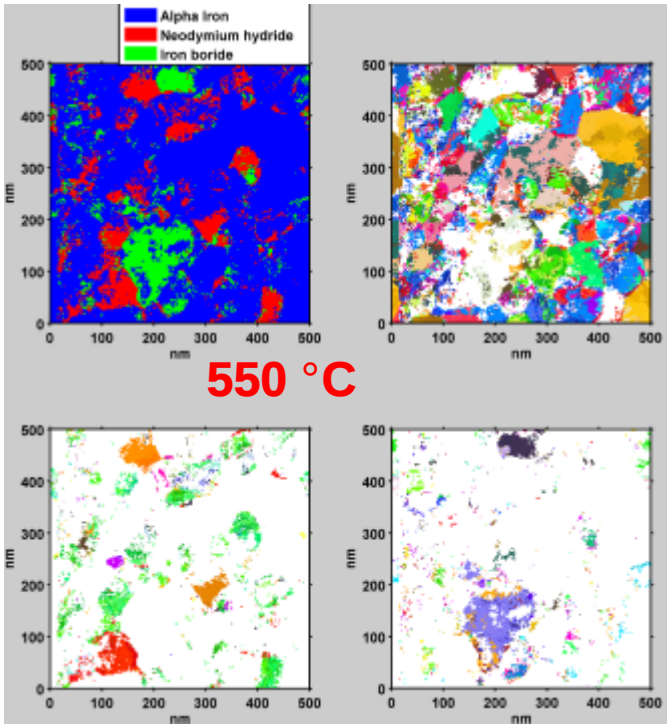
6.5 % strain

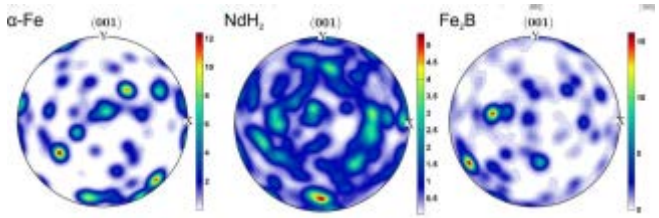


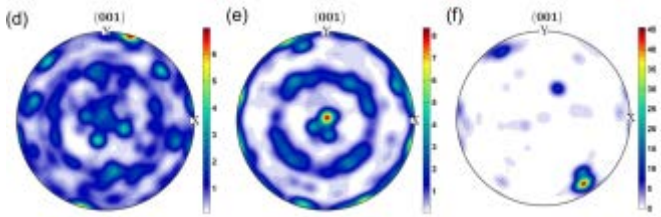


ASTAR - in situ texture analysis and HEATING of Nd-Fe-B powder particles



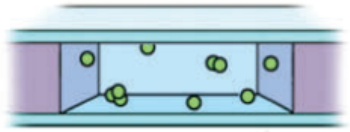






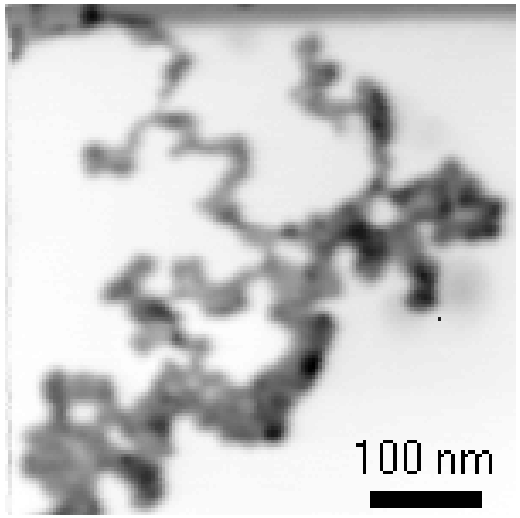
In situ LC- TEM : the Nano-aquarium

Collaboration wiith
Dr. A.Demortiere
Univ Picardie France

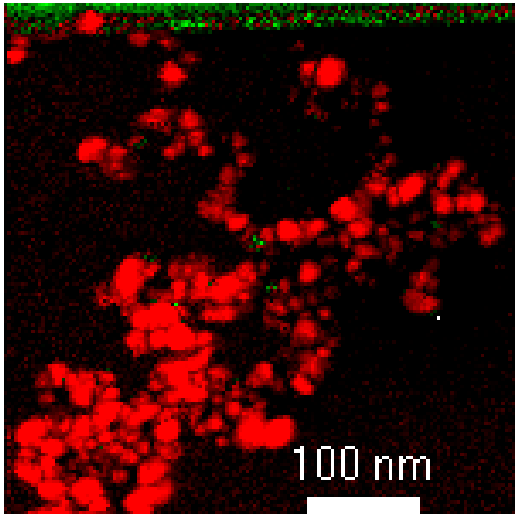


The loaded liquid sample is sealed and imaged using TEM in the native liquid environment.

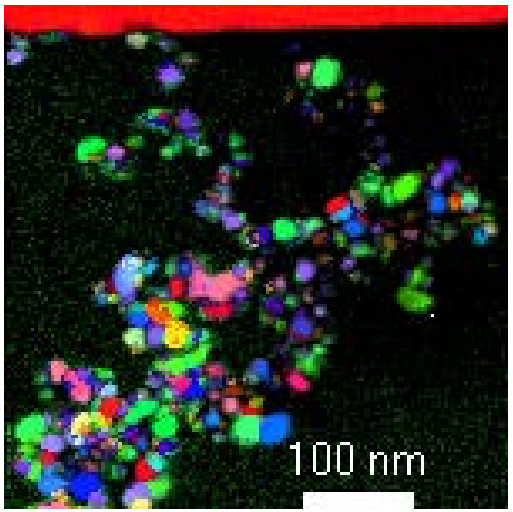
ASTAR : ORIENTATION & PHASE MAP IN LIQUIDS

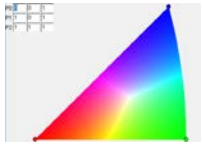


ASTAR Virtual brightfield



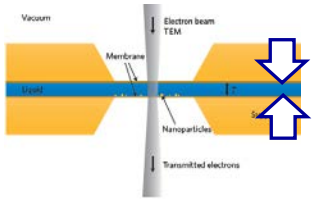
ASTAR Phase Map with index quaility and phase reliability





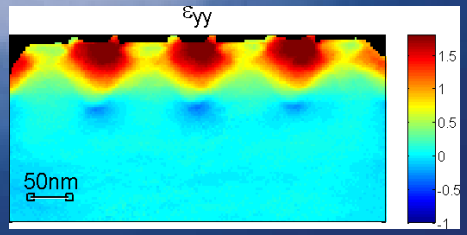
(a) TEM bright field image of gold nanoparticles in water (b) ASTAR phase mapping where shows all crystal are gold and (c) ASTAR orientation map,different colors represent different orientations shown in the stereographic triangle (Courtesy Dr. Muriel Veron CNRS Grenoble France)

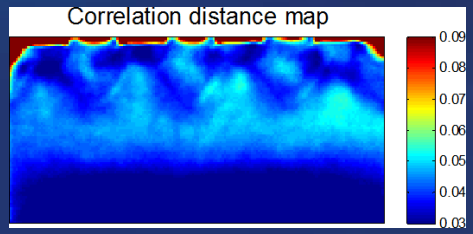
New fronteer

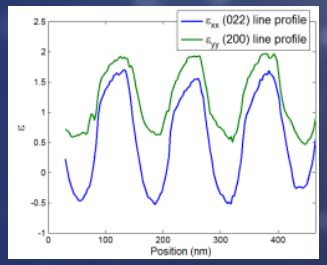


LC spacer 150 nm

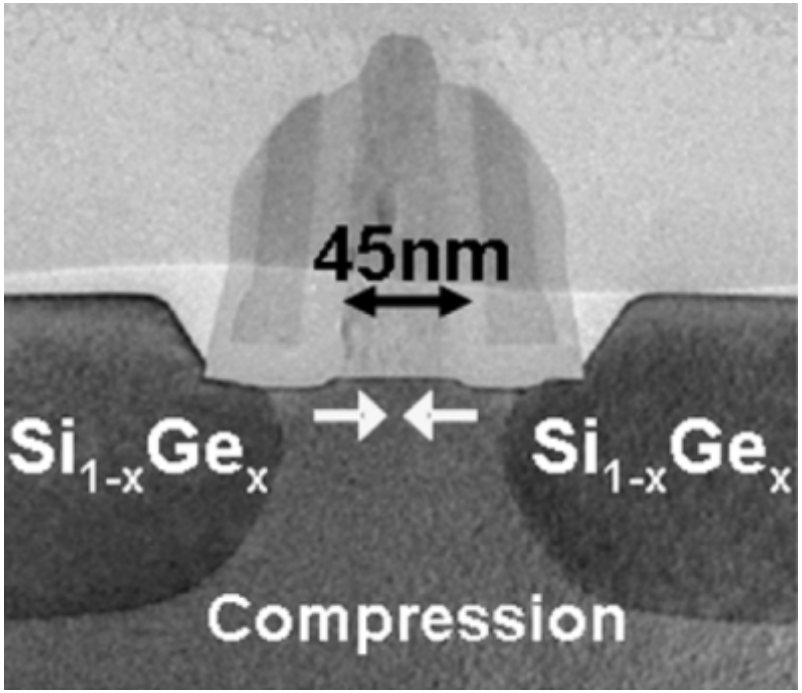
Strain mapping at nm scale





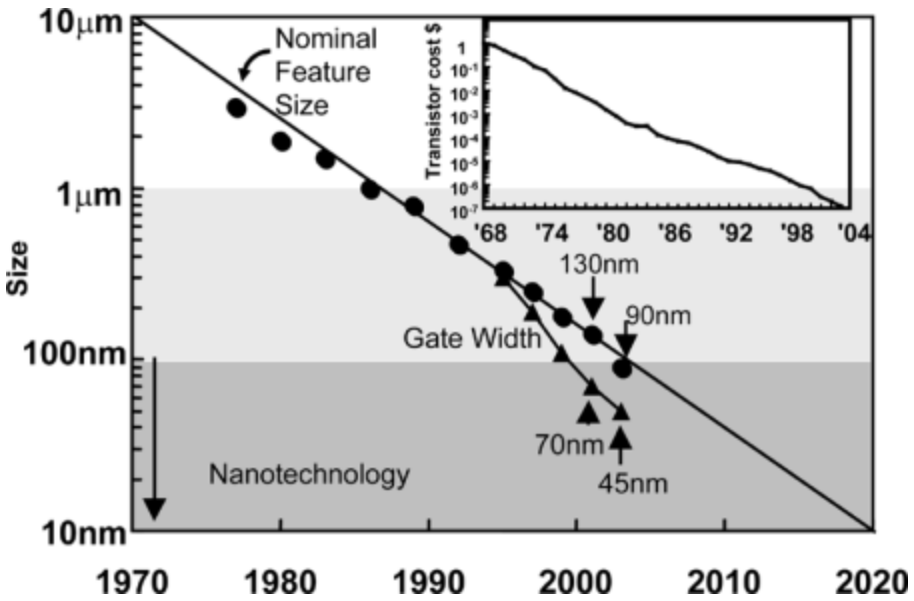


STRAIN ON SEMICONDUCTOR DEVICES



pMOSFET

Thompson et al., IEEE Trans. On Electron Devices, VOL. 51, NO. 11, 2004

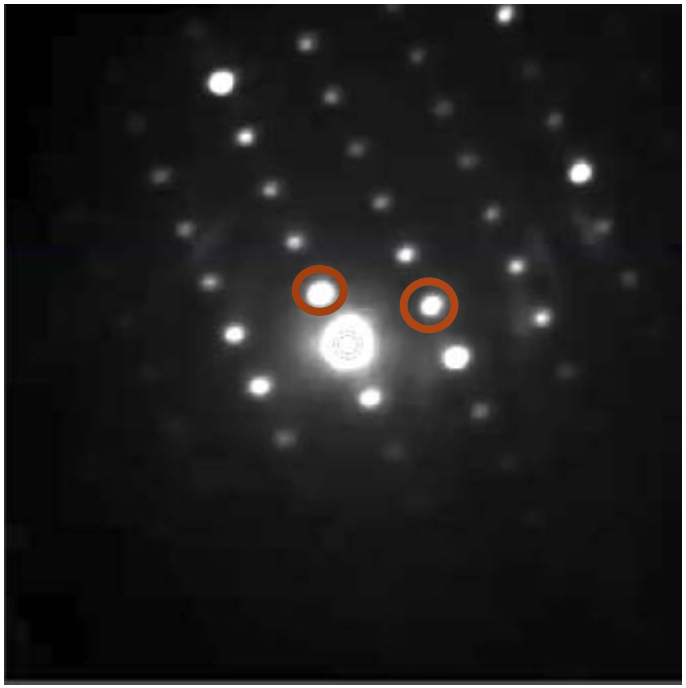


Industry Requirements

- Desired spatial resolution ~ 1 nm
- Strain sensitivity << 0.1%
- Highly automated

Conventional Nano-Beam Diffraction

Strain determined by measuring shift in spot positions



D Cooper et al., Journal of Physics: Conference Series **326** 012025 (2011).

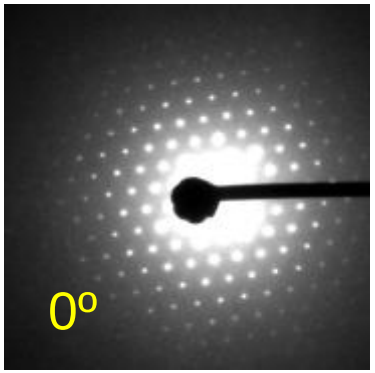
Advantage

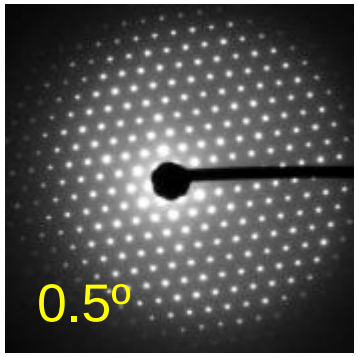
- High spatial resolution - better than 1 nm

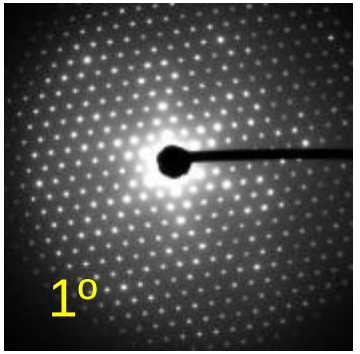
Disadvantage

- Dynamical diffraction -- thickness related effects

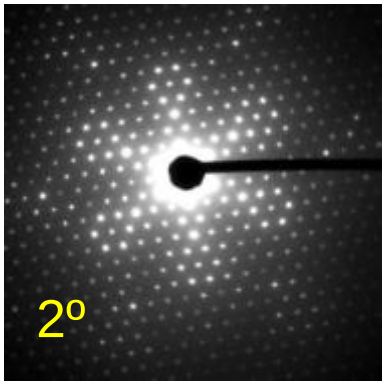
Strain Measurement via NBD with Precession & Automated Analysis

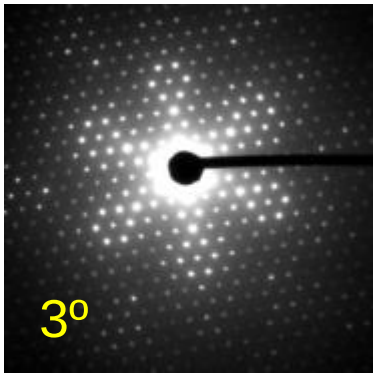






PED is "ideal" (X-Ray like) kinematical pattern
INDEPENDENT of thickness variations !

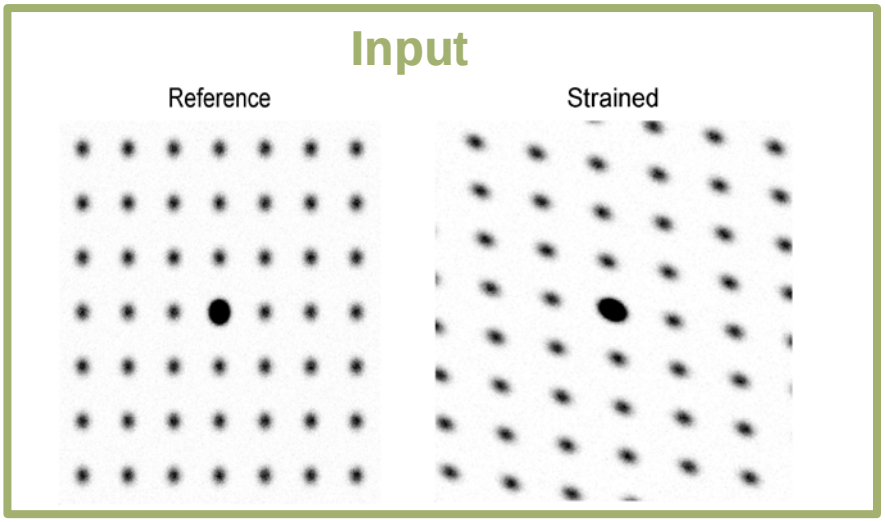


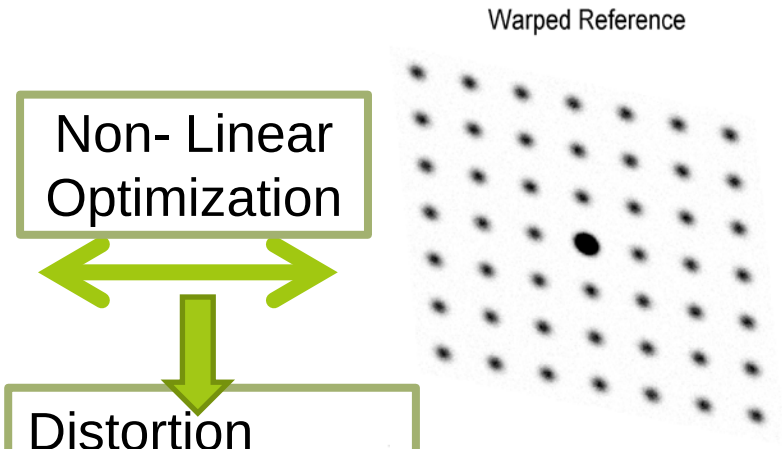


Vincent-Midgley Precession Method

TOPSPIN Strain Measurement Analysis

- Diffraction patterns from strained region are matched against a reference pattern
- **All pixels utilized, not just selected spot centers**



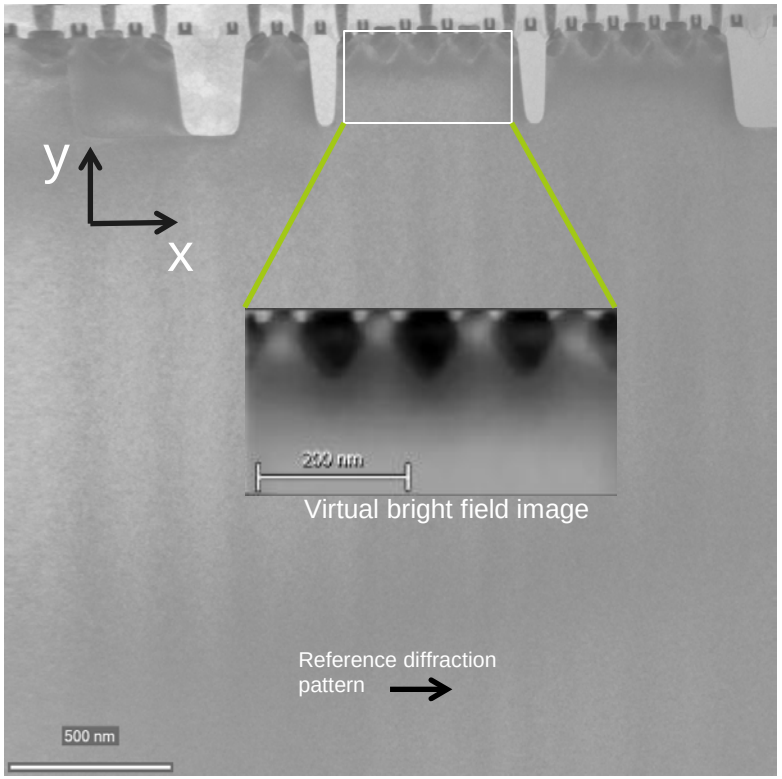


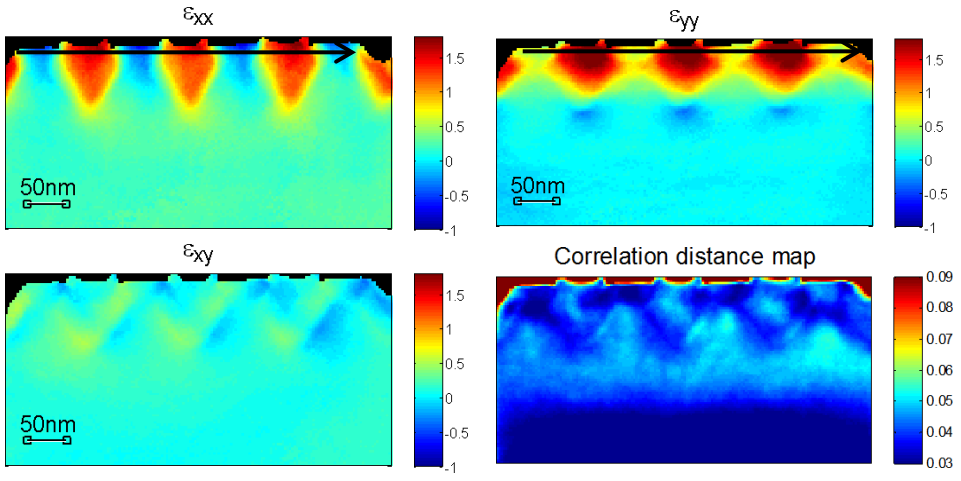
US & EU Patents

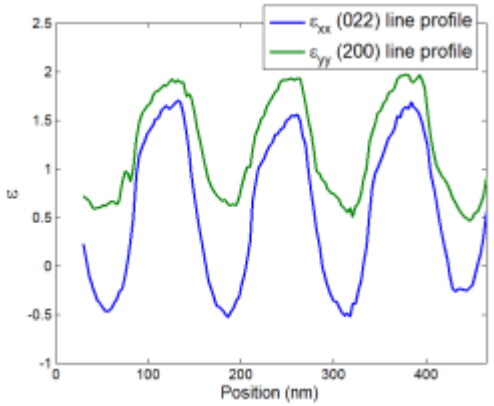
Typical performance of Topspin Strain

- **Practical spatial resolution @ 1 degree precession angle : 1 to 5 nm (FEG TEM)**
- **Sensitivity (precision) @ 1 degree precession angle : 0.1% to 0.01 %**
- Spatial resolution and sensitivity depents on model TEM, beam current, beam convergence and sample quality/thickness
- Fast and automated 1D & 2D Strain Mapping at the nanoscale

pMOS Strain Mapping with precession





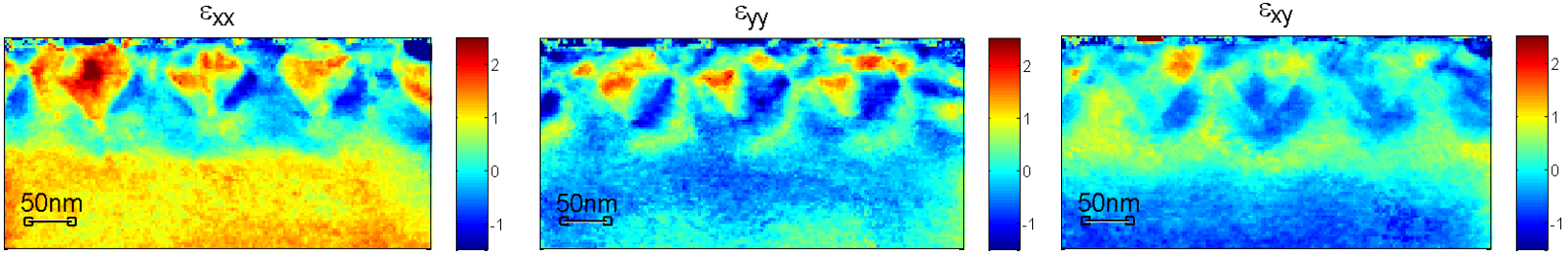


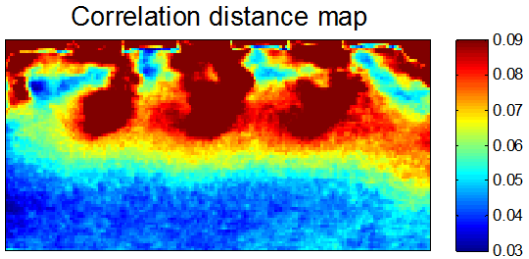
strain values in percent

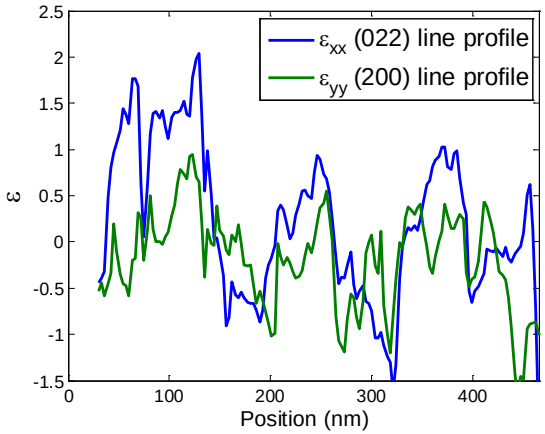
TEM: JEOL ARM200F
Step size: 3 nm
Precession angle: 0.7°

pMOS Strain Mapping without precession

Same pMOS region without precession



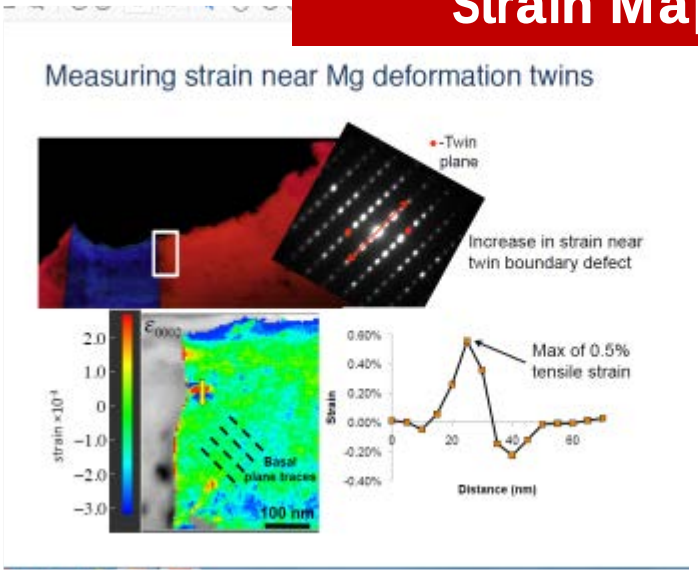


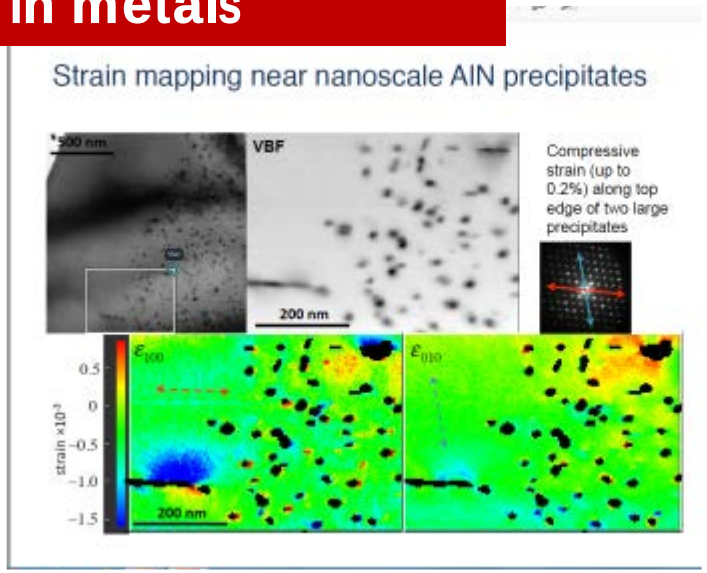


All strain values in percent

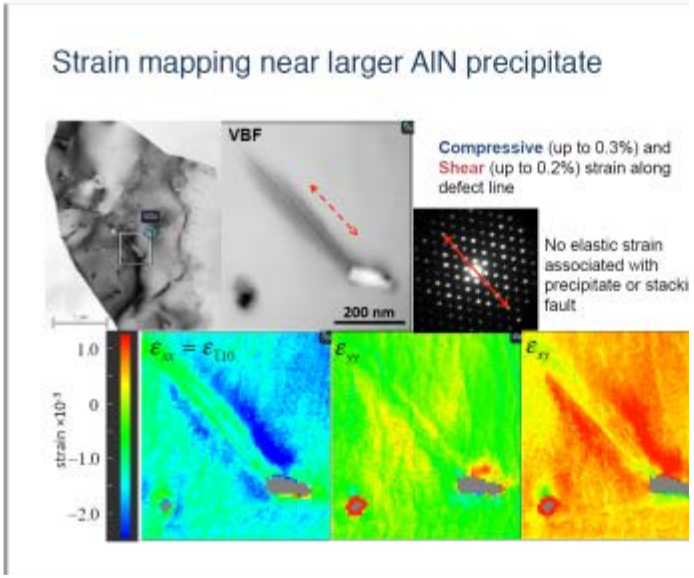
TEM: JEOL ARM200F
Step size: 3 nm
No precession

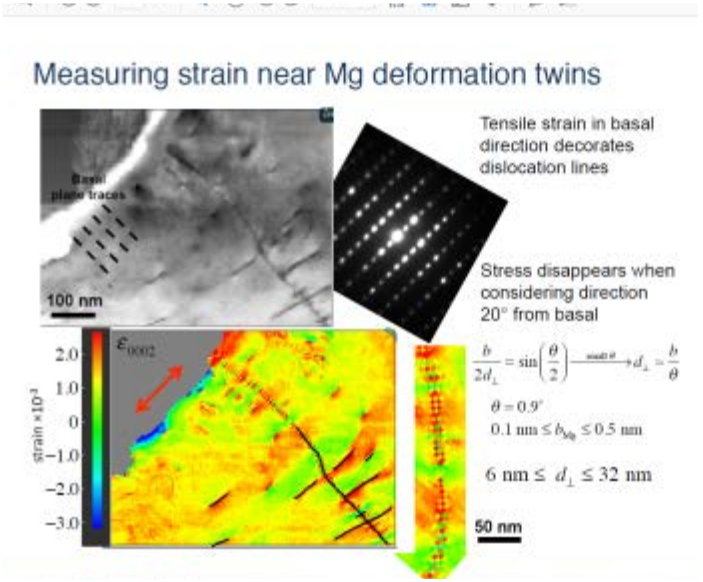
Strain Mapping in metals



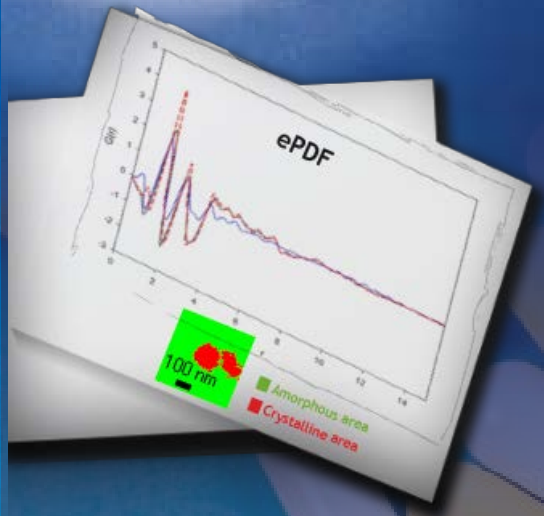


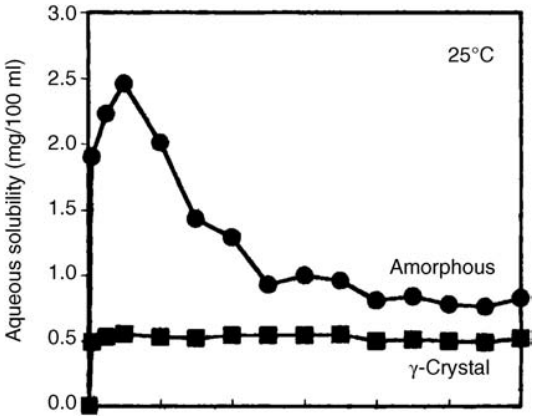
Courtesy Prof. K.Hemker Jons Hopkins University



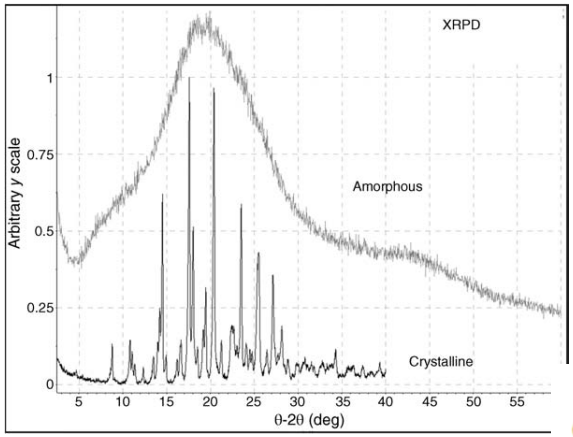


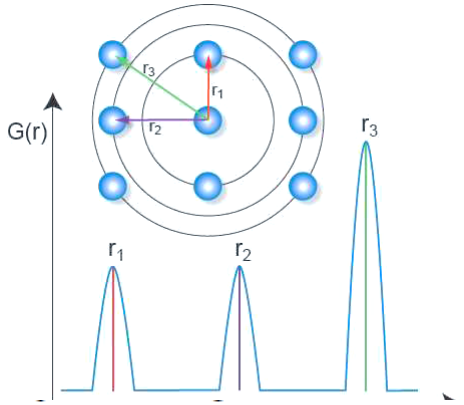
Study Amorphous materials with e-PDF





Solubility vs time for crystalline and amorphous indomethacin in water (Book A.Newman Pharmaceutical ASD Wiley 2015)

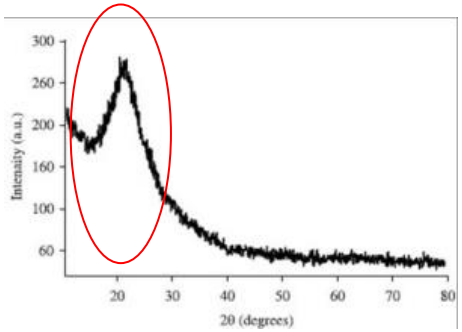


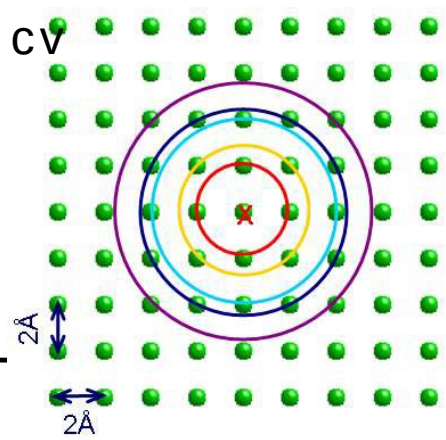


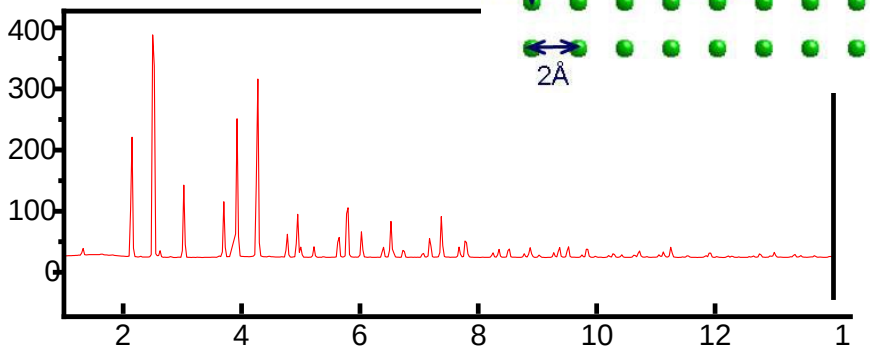
$$G(r) = \frac{2}{\pi}\int_{Q_{min}}^{Q_{max}} Q[S(Q)-1]\sin(Qr)dQ\,.$$

Amorphous /short range order systems can be described by the Pair Distribution Function (PDF) that provides the probability of finding a distance “r” between two atoms in the material

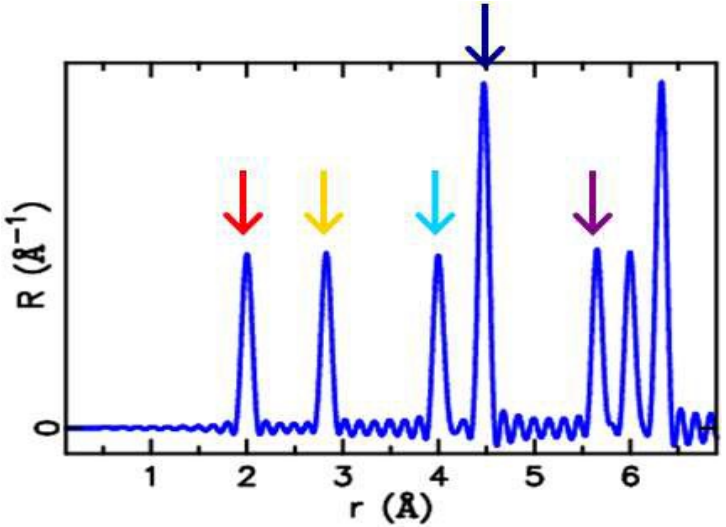
A total pair-distribution function (PDF) is obtained by repeating this process systematically by placing each atom in the origin.







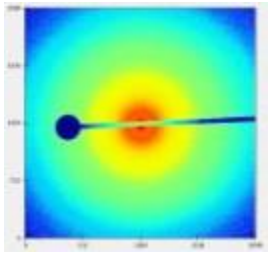
*R refers to radial distribution function



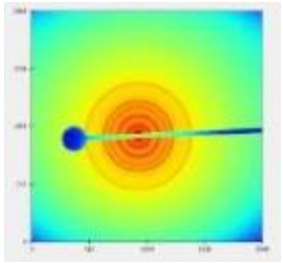
Z. Kristallogr. Supp. 26(2007) 17-26

PDF for amorphous and nanomaterials

amorphous

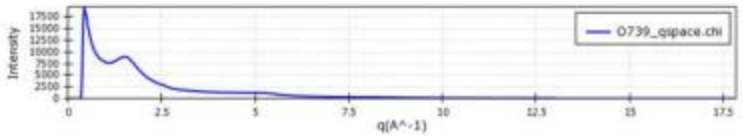


X-Ray diffraction data I(q)

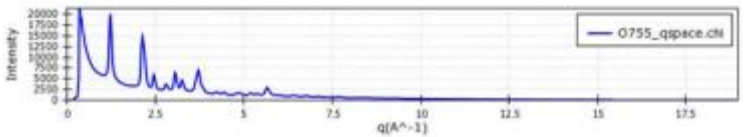


Nanomaterial

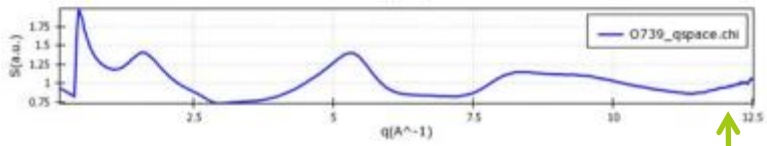
Corrected and Integrated data I(q)



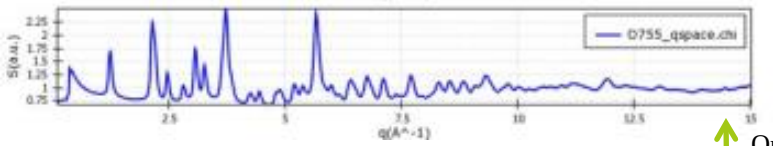
Corrected and Integrated data I(q)



Normalization to calculate S(q)



Normalization to calculate S(q)

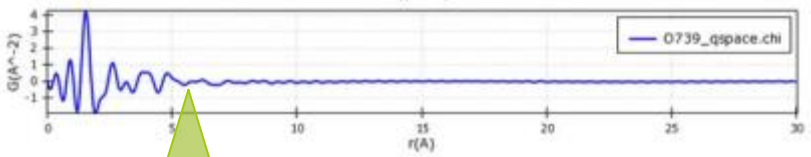


Qmax for FT

Qmax for FT

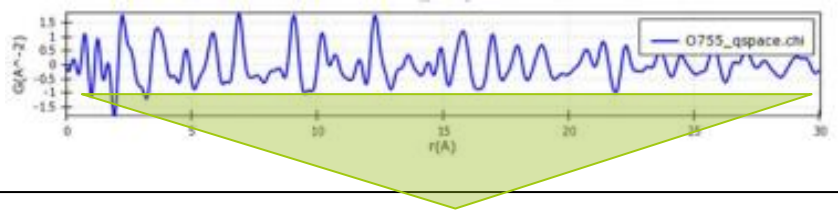
Fourier transformation

PDF



Fourier transformation

PDF

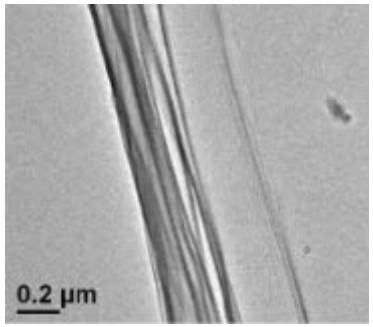


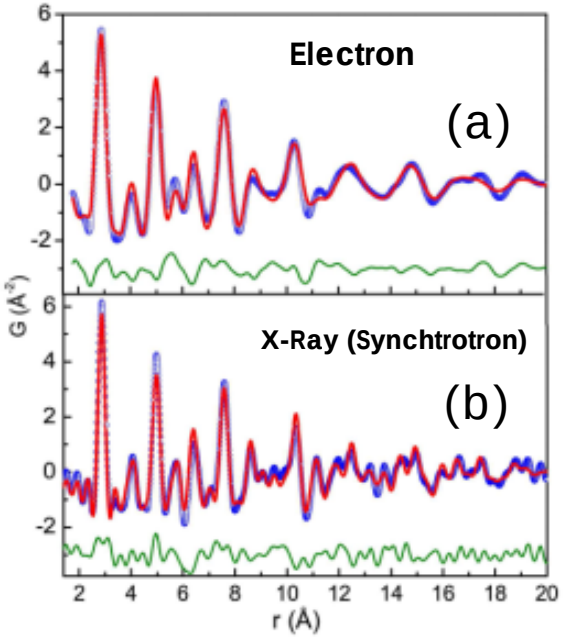
NanoMEGAS
Advanced Tools for electron diffraction

Long range order

www.nanomegas.com

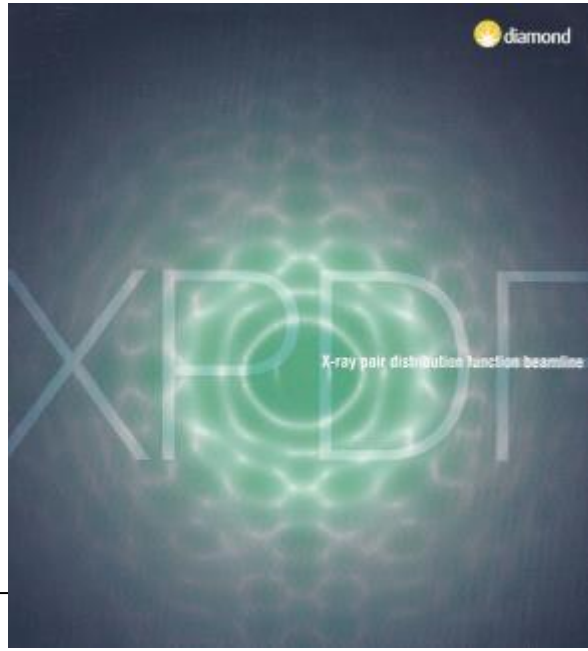
Comparison e- PDF vs Synchtrotron X-Ray PDF Au nanoparticles





Fitting of Au structure model with PDF

(a) e- PDF calculated from ED Data
(b) PDF calculated from X-Ray data



PDF obtained from election diffraction data and PDF obtained from X-ray are fully comparable , using e-PDF very small amorphous areas can be studied

Reference: Billinge *et al.* Condensed Material 2012

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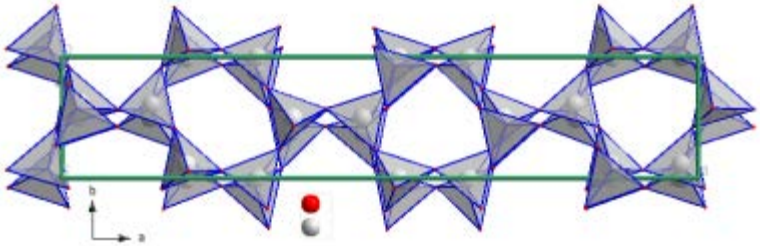
Honduras Opal: Understanding the Local Structure

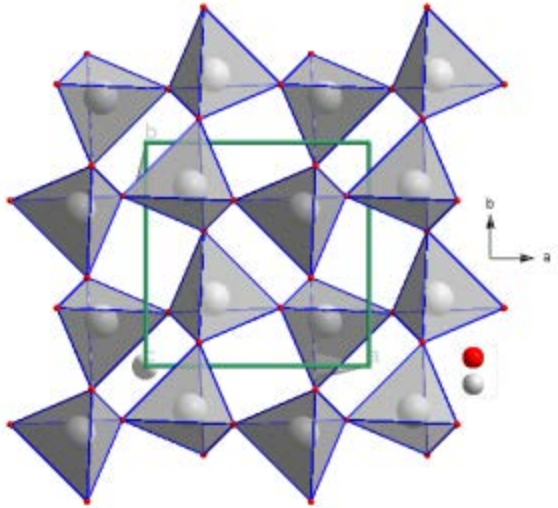
Opal is hydrated silicon dioxide

Can be Microcrystalline, Nano Crystalline or Amorphous

Microcrystalline opal are stacking of cristobalite and tridymite over very short range scale

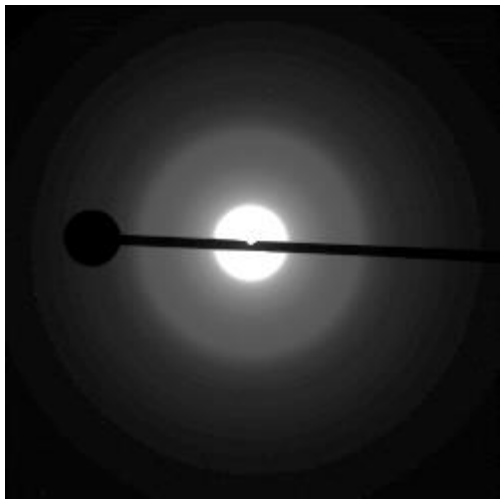


Structure of tridymite

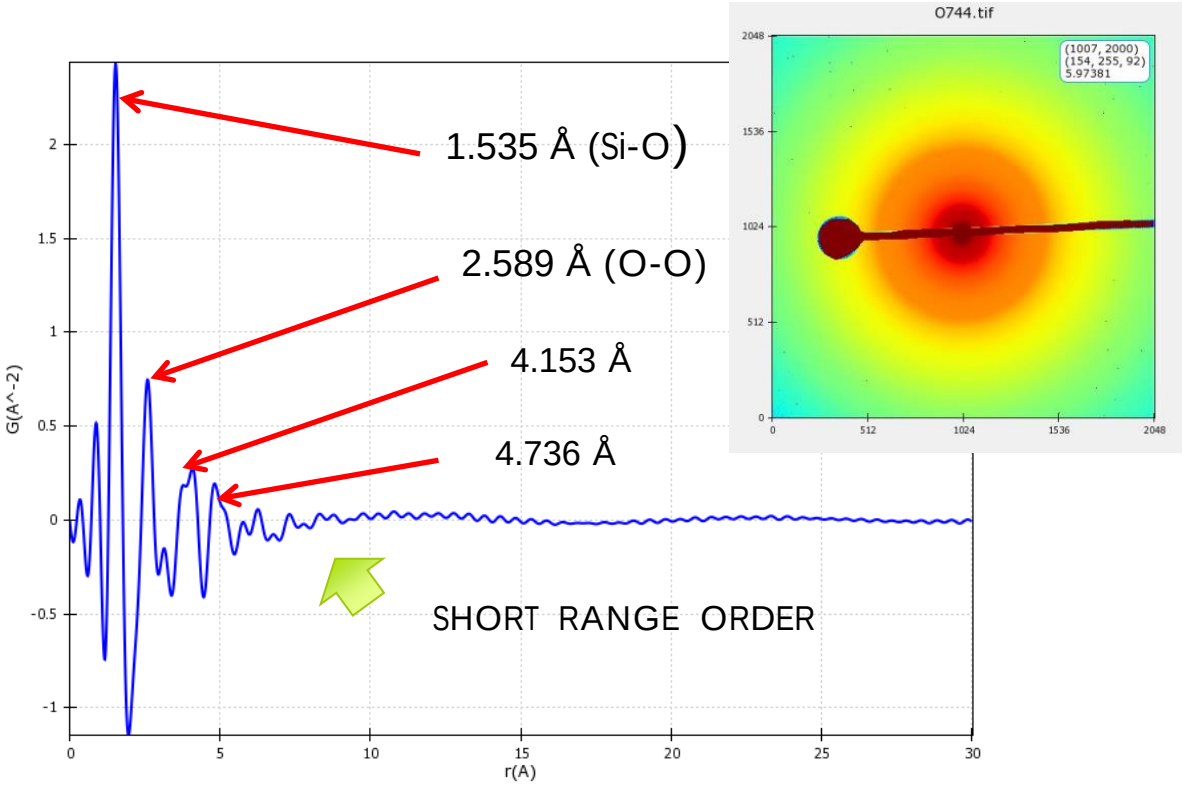


Local Structure of Opal Type C (α-Cristobalite)

Honduras Opal



Data Collected on Zeiss 120 KV

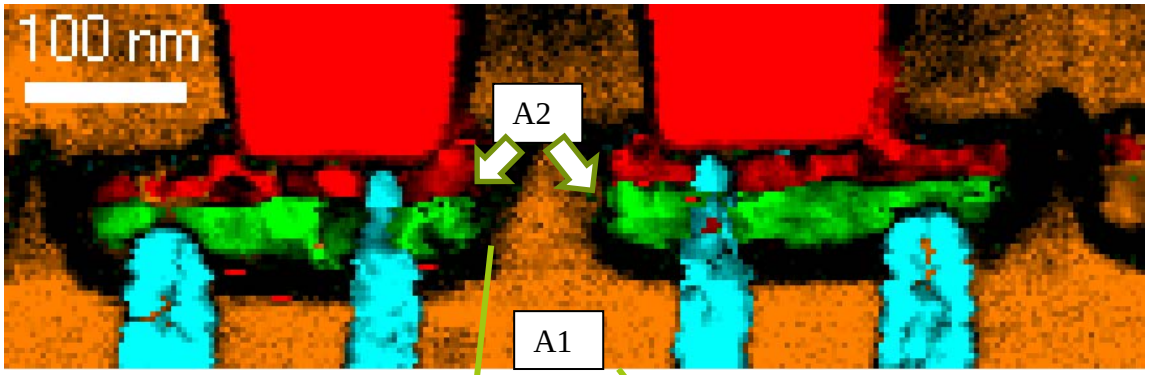


PDF Plot from raw data and Peak Positions below 5 Å

Mineral: Crystobalite SiO_2
a=7.12 Å (cubic)

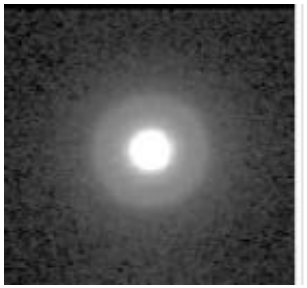
Bond Distances Below 5 Å
Si – O : 1.5415 Å
O – O : 2.5173 Å
Si – Si : 3.0831 Å

e-PDF analysis on amorphous semiconductors



Bank_200kV_[Si]_50_0.5_r3.5
Bank_200kV_[NiSi_Rabadanov]_100_1_r3.5

Bank_200kV_[Tungsten]_100_1_r3.5
Bank_200kV_[]_amorphous_1_r1.2

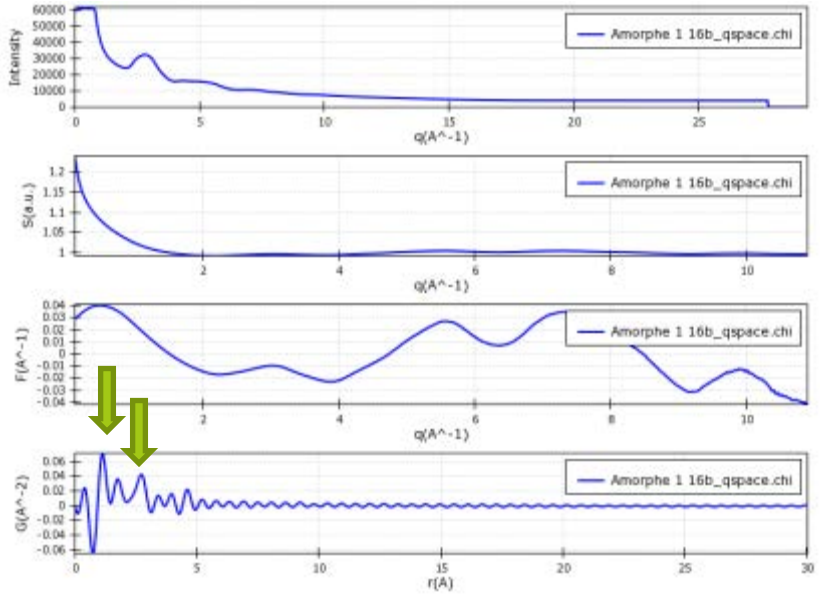


A1 region SiO2 amorphous
A2 (black) region Si3N4 amorphous

Image courtesy E.Rauch and SIMAP Grenoble, ST Microelectreonics

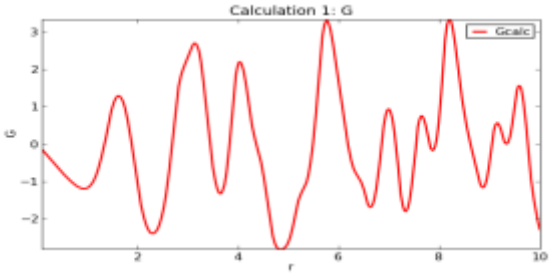
e-PDF analysis on amorphous semiconductors

Gatan CCD 2kx 2k Qmax 10 Å-1



Distances found from PDF analysis match Si3N4 amorphous

1.10 Å
1.747 Å
2.75 Å



Si3N4

Image courtesy E.Rauch and SIMAP Grenoble, ST Microelectreonics

NanoMEGAS
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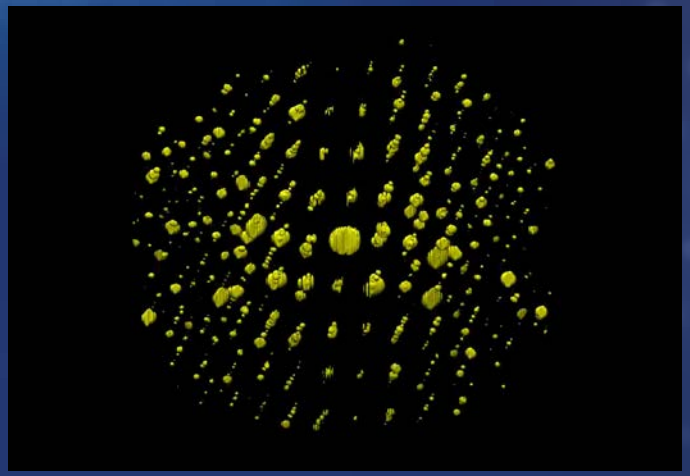
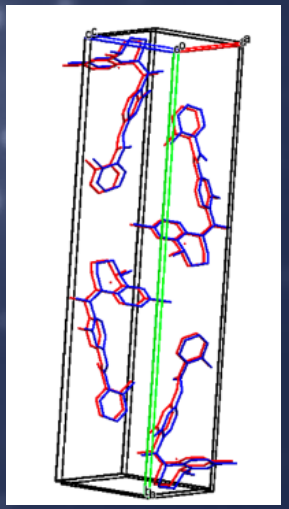
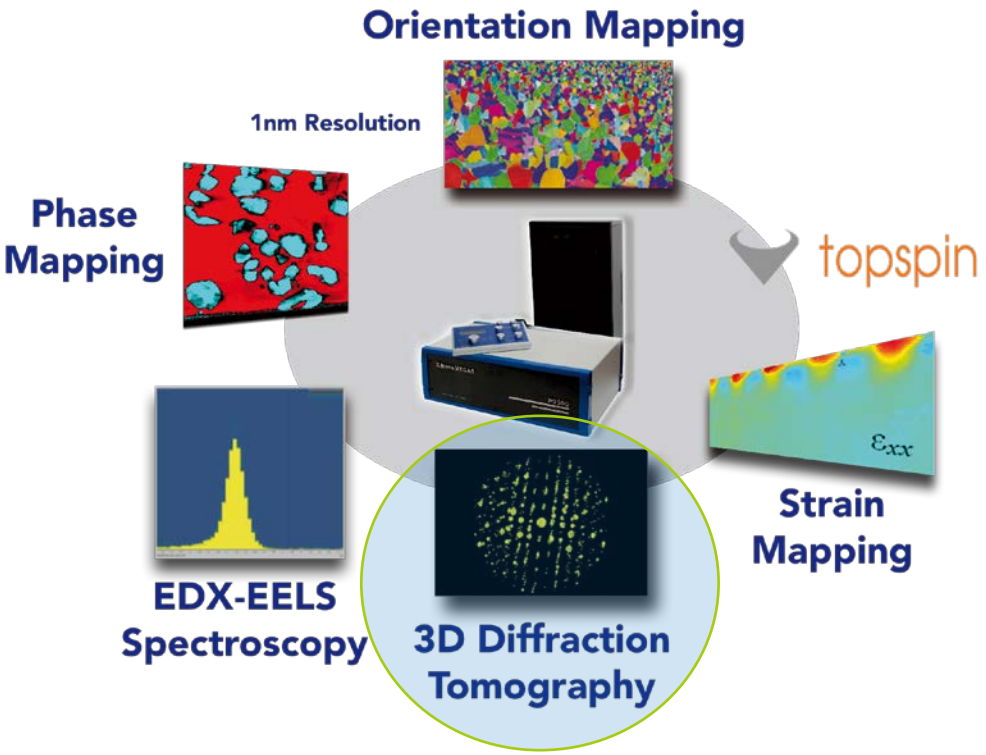
EPDFSUITE V1.0

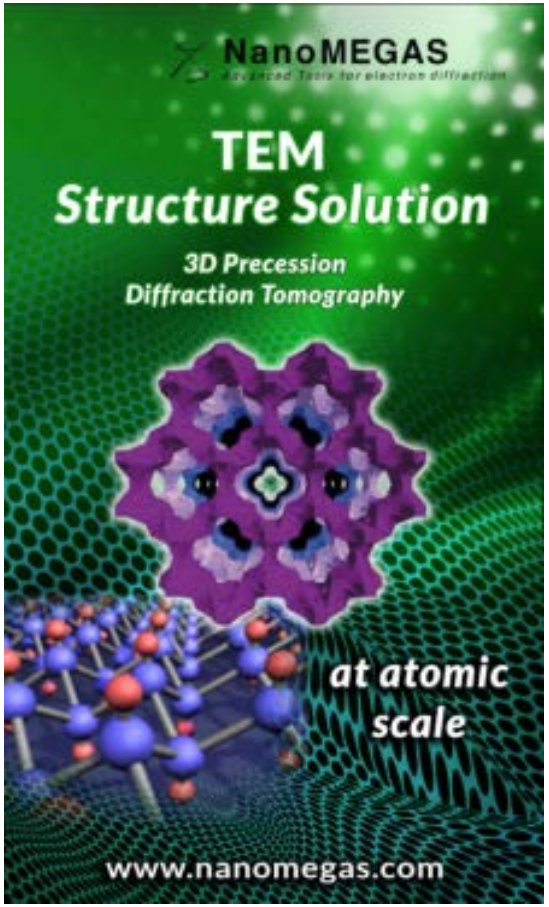
3D Diffraction Tomography





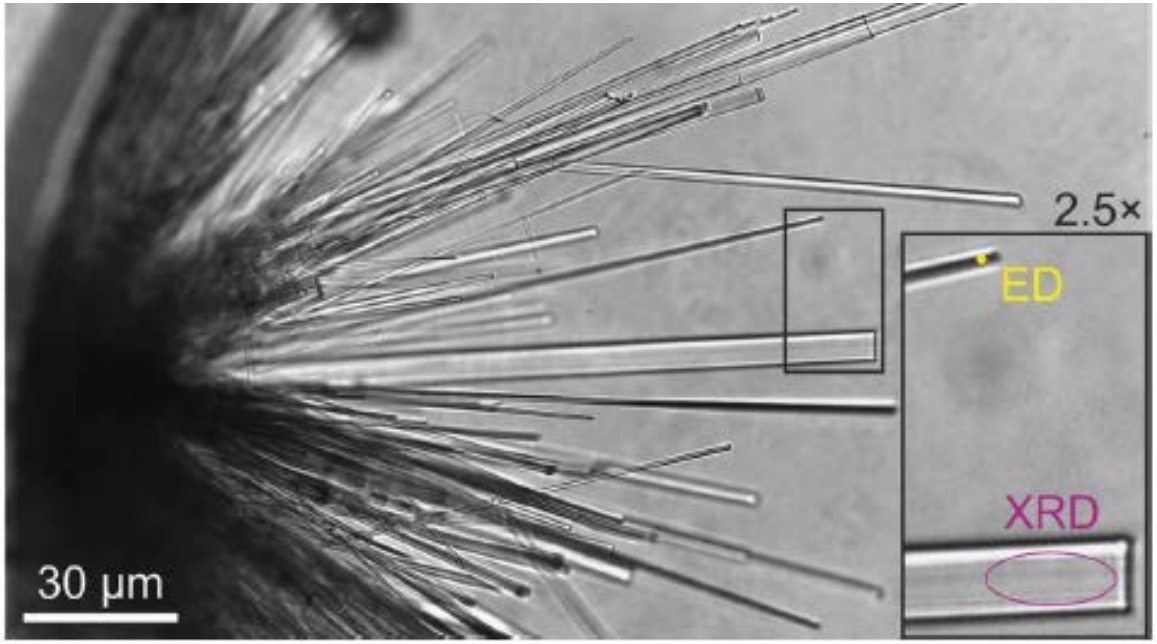
3D Diffraction Tomography
TEM Precession Electron Diffraction



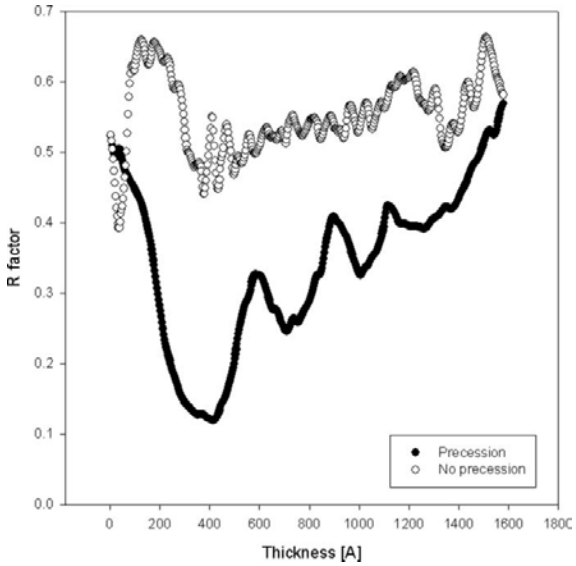


SOLVING CRYSTAL STRUCTURES WITH PED

Own et al. (2006), Acta Cryst. A62



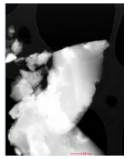
SYNCHTROTRON



HIGH PRECESSION ANGLE
IMPROVES CRYSTAL STUCTURE DETERMINATION

3D Diffraction Tomography

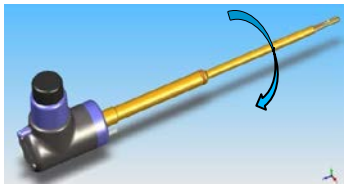
3D TEM diffraction tomography : 3D reconstruction of reciprocal space

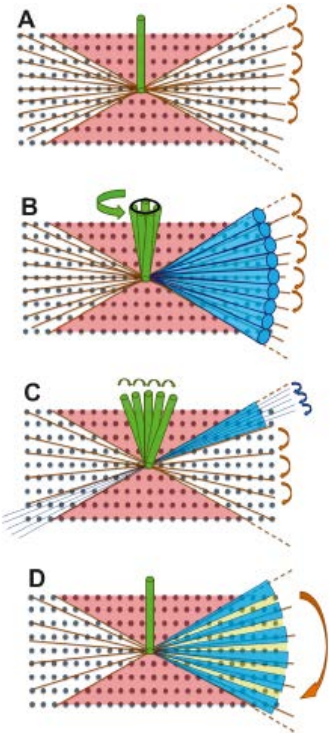


1° Tilt
(total +- 60°)

Crystal tracking

Electron diffraction acquisition

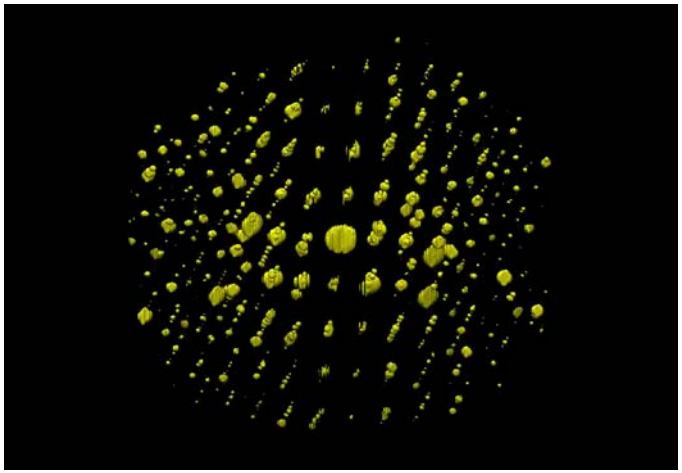


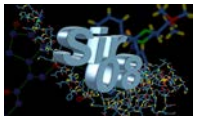


- ✓ complete or almost complete diffraction data to **extract unit cell and crystal symmetry**
- ✓ conceptually simple, data can be taken **with any CCD camera**
- ✓ solution of structures by direct methods or simulated annealing

R close to 15-35 % : reveal all 3D atomic positions with 5-30 pm precision !

3D TEM Diffraction Tomography for 3D atomic structure solution



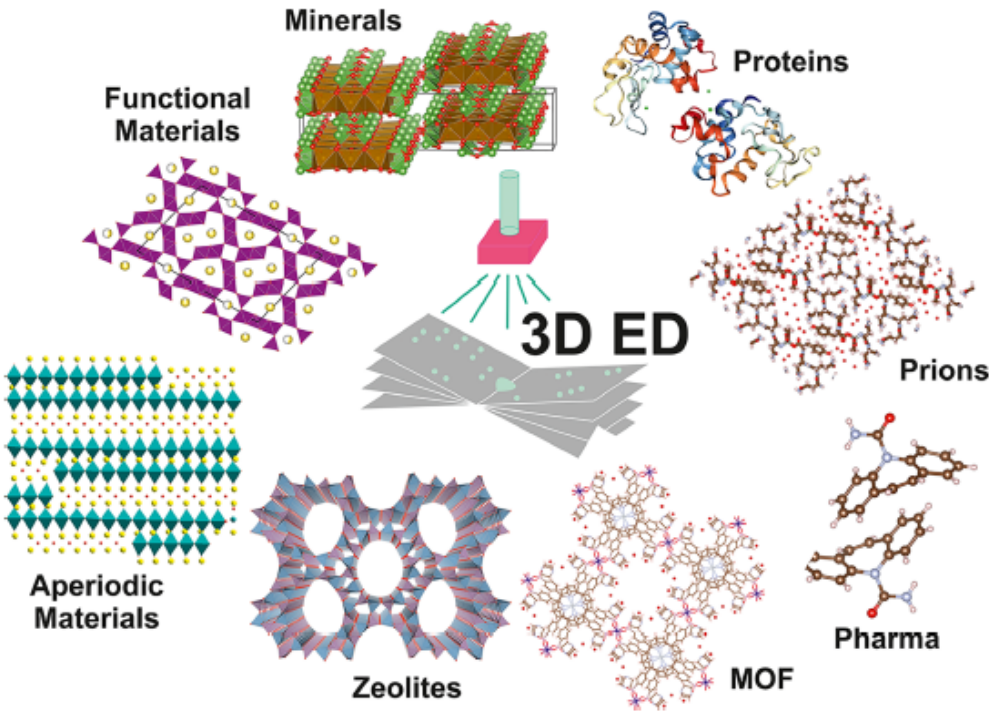


Hemimorphite		**Reference structure (X-ray and neutron diffraction)**			**3D precession diffraction Tomography**			
Atoms	**Label**	**X**	**Y**	**Z**	**X**	**Y**	**Z**	**Δ(Å)**
Zn	Zn	0.2047(1)	0.1613(1)	0	0.205	0.160	0	0.02
Si	Si	0	0.1465(2)	0.5076(5)	0	0.141	0.529	0.12
O	O1	0.1604(8)	0.2055(1)	0.6363(4)	0.152	0.217	0.657	0.18
O	O2	0	0.1669(2)	0.1938(4)	0	0.156	0.204	0.12
OH	O3	0.3050(2)	0	0.0410(6)	0.289	0	0.073	0.21
O	O4	0	0	0.5912(6)	0	0	0.601	0.05
H_2O	O5	1/2	0	0.5195(13)	1/2	0	0.491	0.15
Mayenite		**Reference structure**			**Electron**			
Atoms	**Label**	**X**	**Y**	**Z**	**X**	**Y**	**Z**	**Δ(Å)**
Ca	Ca	0.89096(5)	0	3/4	0.902	0	3/4	0.14
Al	Al1	0.01866(3)	0.01866(3)	0.01866(3)	0.018	0.018	0.018	<0.02
Al	Al2	¼	7/8	0	¼	7/8	0	-
O	O1	0.18556(3)	0.18556(3)	0.18556(3)	0.184	0.184	0.184	0.03
O	O2	0.44182(4)	0.15035(3)	0.03677(4)	0.439	0.148	0.041	0.06
$Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$		**Reference structure**			**Electron**			
Atoms	**Label**	**X**	**Y**	**Z**	**X**	**Y**	**Z**	**Δ(Å)**
Ba	Ba	0.5	0.5	0.1850(2)	0.5	0.5	0.1874	0.05
Y/Pr	Y	0.5	0.5	0.5	0.5	0.5	0.5	-
Cu	Cu1	0	0	0	0	0	0	-
Cu	Cu2	0	0	0.3565(5)	0	0	0.355	<0.02
O	O1	0	0.5	0	0	0.5	0	-
O	O2	0	0	0.1566(23)	0	0	0.160	<0.02
O	O3	0.5	0	0.3776(21)	0.5	0	0.382	0.06
O	O4	0	0.5	0.3765(21)	0	0.5	0.383	0.06

Kinematical refinement : Find all 3D atomic positions with 2-15 pm accuracy !

NanoMEGAS
Advanced Tools for electron diffraction

> 300 structures solved with ED (2004 - 2019)



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Cite This: ACS Cent. Sci. XXXX, XXX, XXX−XXX

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3D Electron Diffraction: The Nanocrystallography Revolution

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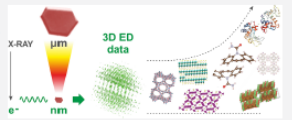
ABSTRACT: Crystallography of nanocrystalline materials has witnessed a true revolution in the past 10 years, thanks to the introduction of protocols for 3D acquisition and analysis of electron diffraction data. This method provides single-crystal data of structure solution and refinement quality, allowing the atomic structure determination of those materials that remained hitherto unknown because of their limited crystallinity. Several experimental protocols exist, which share the common idea of sampling a sequence of diffraction patterns while the crystal is tilted around a noncrystallographic axis, namely, the goniometer axis of the transmission electron microscope sample stage. This Outlook reviews most important 3D electron diffraction applications for different kinds of samples and problematics, related with both materials and life sciences. Structure refinement including dynamical scattering is also briefly discussed.



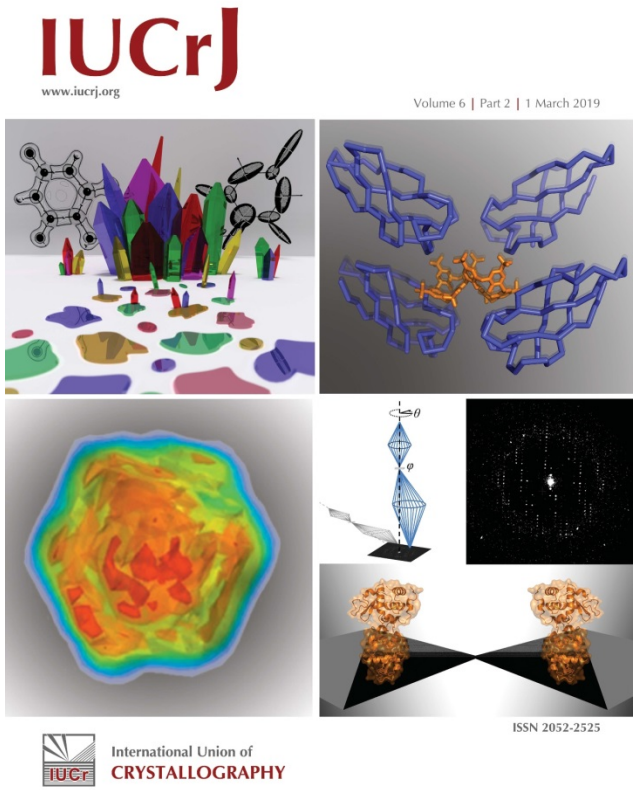
1. INTRODUCTION

Accelerated electrons have been long considered the less promising among the radiation types used in crystallography for attaining diffraction data suitable for atomic structure determination. In fact, the large majority of structural models deposited in crystallographic databases[1−5] have been obtained by means of X-ray diffraction, and most of what is left has been derived from neutron diffraction or spectroscopic methods. Although still limited, the use of electron diffraction has grown rapidly over the past decade, mostly due to the introduction of 3D methods for the systematic acquisition and analysis of diffracted intensities. Here, we would like to examine how the use of parallel beam electron diffraction for structure determination has evolved from a mostly qualitative technique, used only by few specialists, to a quantitative approach accessible to a much larger community.

To understand the full picture of this (r)evolution, it is important to focus on the strengths of accelerated electrons for crystallography. First, the possibility to have parallel electron probes with a size of a few nanometers allows collecting diffraction data from sample volumes 2 or 3 orders of magnitude smaller than the ones suitable for synchrotron microfocused X-ray beams. Second, the ability to deliver both diffraction and imaging from the same nanovolume allows the combination of reciprocal and direct space information and the experimental determination of crystallographic phases. Third, the strong Coulomb interaction between electrons and matter allows a good signal-to-noise ratio even from very thin samples and an easier identification of light atoms, like lithium and hydrogen, when compared with X-rays.

However, the strong scattering of electrons is also the reason why electron diffraction (ED) was disregarded for many years for structure analysis. The occurrence of multiple scattering

Received: April 17, 2019



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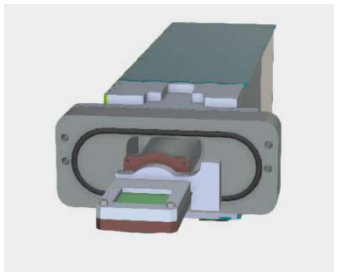
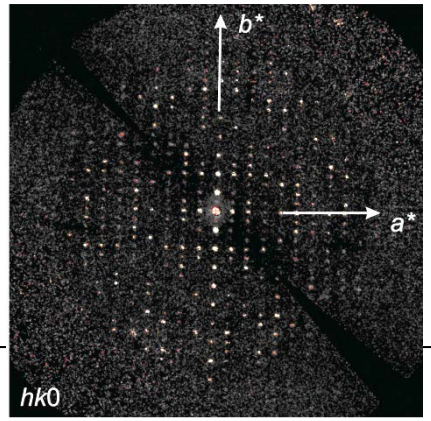
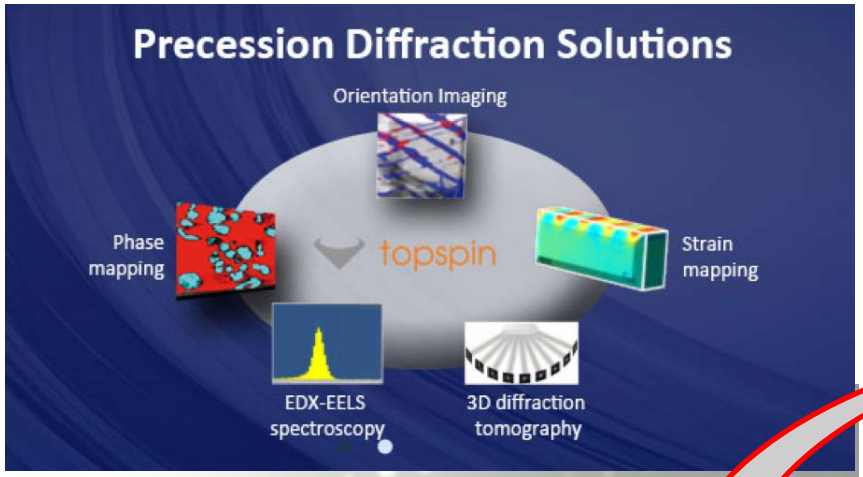
Protein 3D Tomography (Micro-ED)





4D STEM ELECTRON DIFFRACTION AND PIXELATED DETECTORS

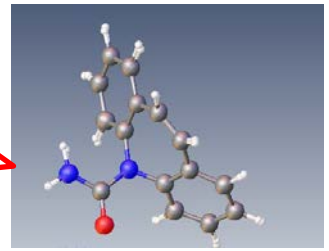


Accurate orientation/phase maps

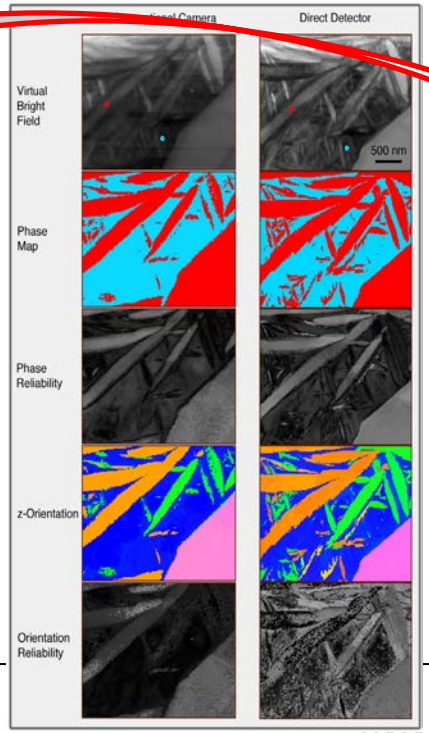
More accurate structures with ED

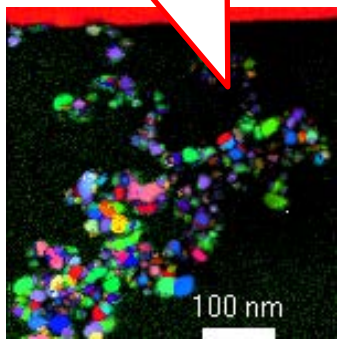
Low dose sensitive materials

Dynamic phenomena in LC



New fronteers





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Merci pour votre attention !

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