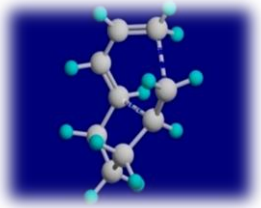
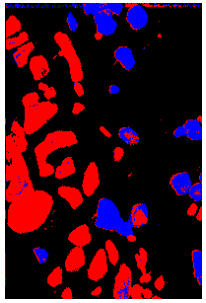
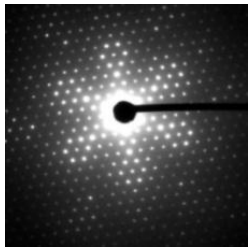
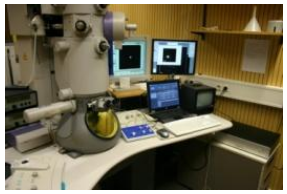
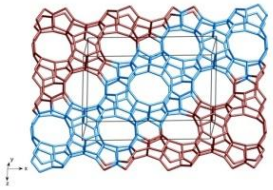
NEW techniques for TEM nanoanalysis

precession electron diffraction for organic – inorganic nanostructures



Dr. Stavros Nicolopoulos
Consultant IUCr Electron Crystallography Comission

This document was presented at PPXRD - Pharmaceutical Powder X-ray Diffraction Symposium

Sponsored by The International Centre for Diffraction Data

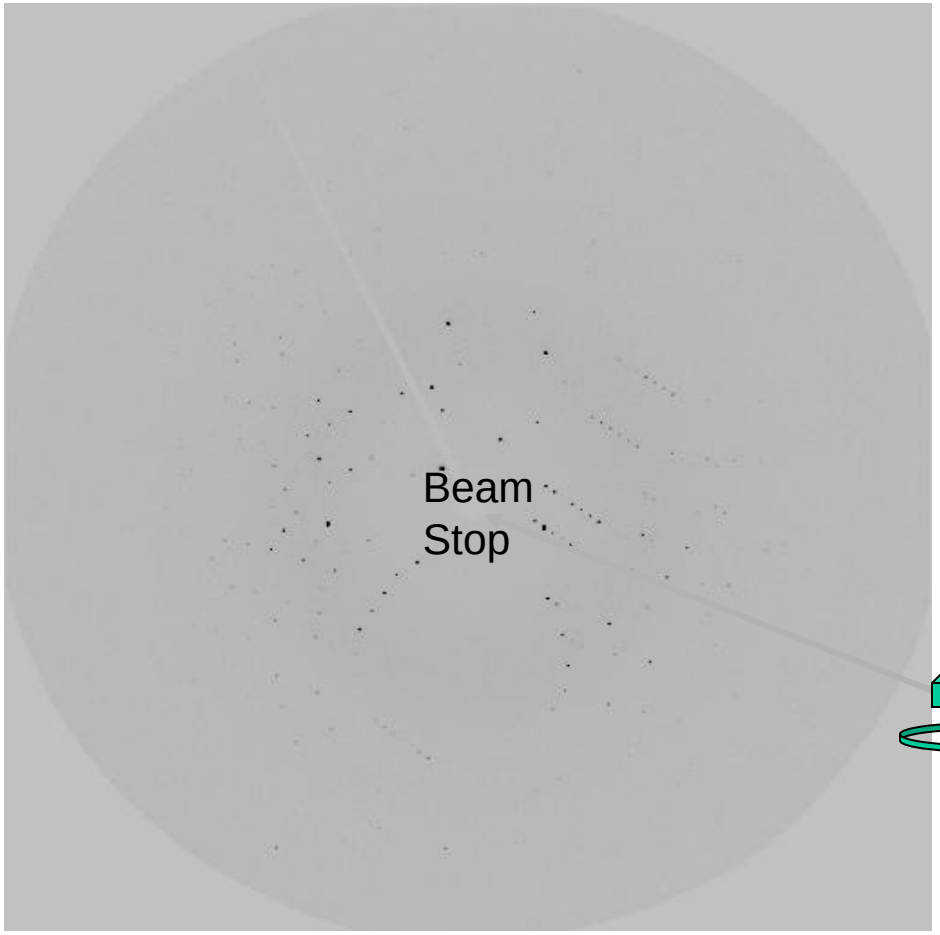
PPXRD Website – www.icdd.com/ppxrd

ICDD Website - www.icdd.com

X-ray Diffraction (single crystal): all info in reciprocal space

Bragg law

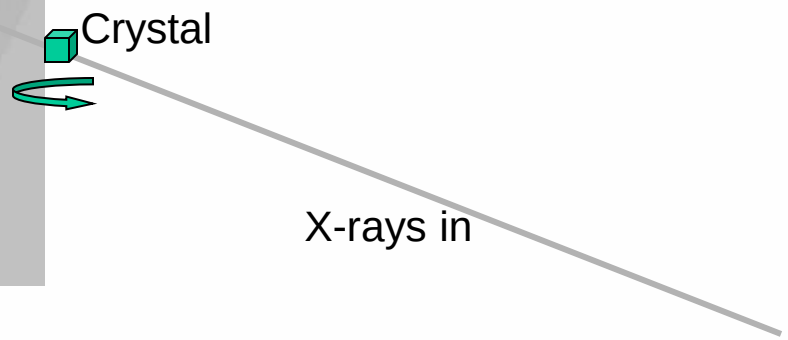
$n\lambda = 2d\sin\theta$



- Single X-Ray diffractometer collects set of 3d HKL reflections

  single crystal dim. about 0.3 mm

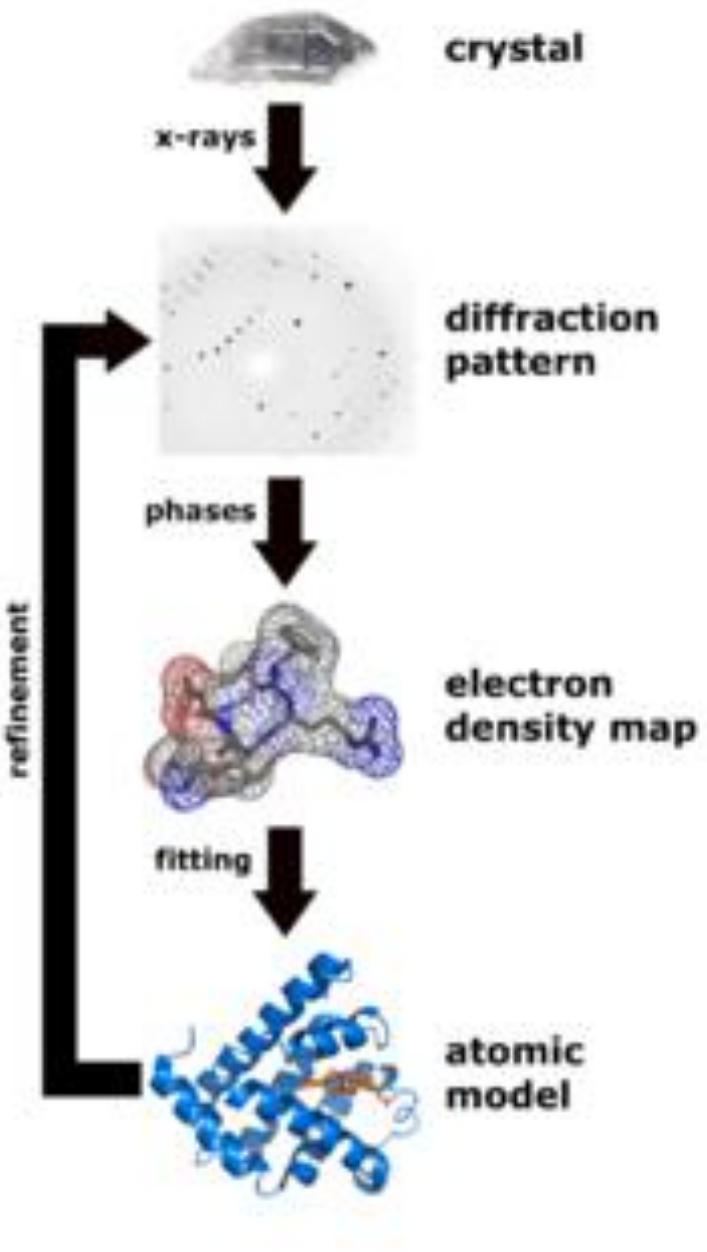
- We measure HKL intensities
- From direct methods (mathem. algoritms) we find directly crystal structure : atomic positions
- **Smallest cystals for str.determination**
  <u>1-5 micron : Synchrotron solution</u>



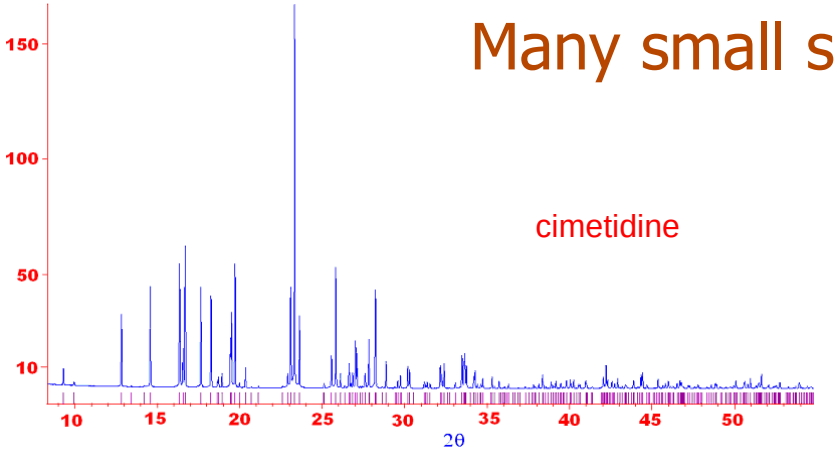
Courtesy I.Margiolaki ESRF Grenonble

X-ray Crystallography

X-ray crystallography is the science of determining the arrangement of atoms within a crystal from the manner in which a beam of X-rays is scattered from the electrons within the crystal. The method produces a three-dimensional picture of the density of electrons within the crystal, from which the mean atomic positions, their chemical bonds, their disorder and sundry other information can be derived.



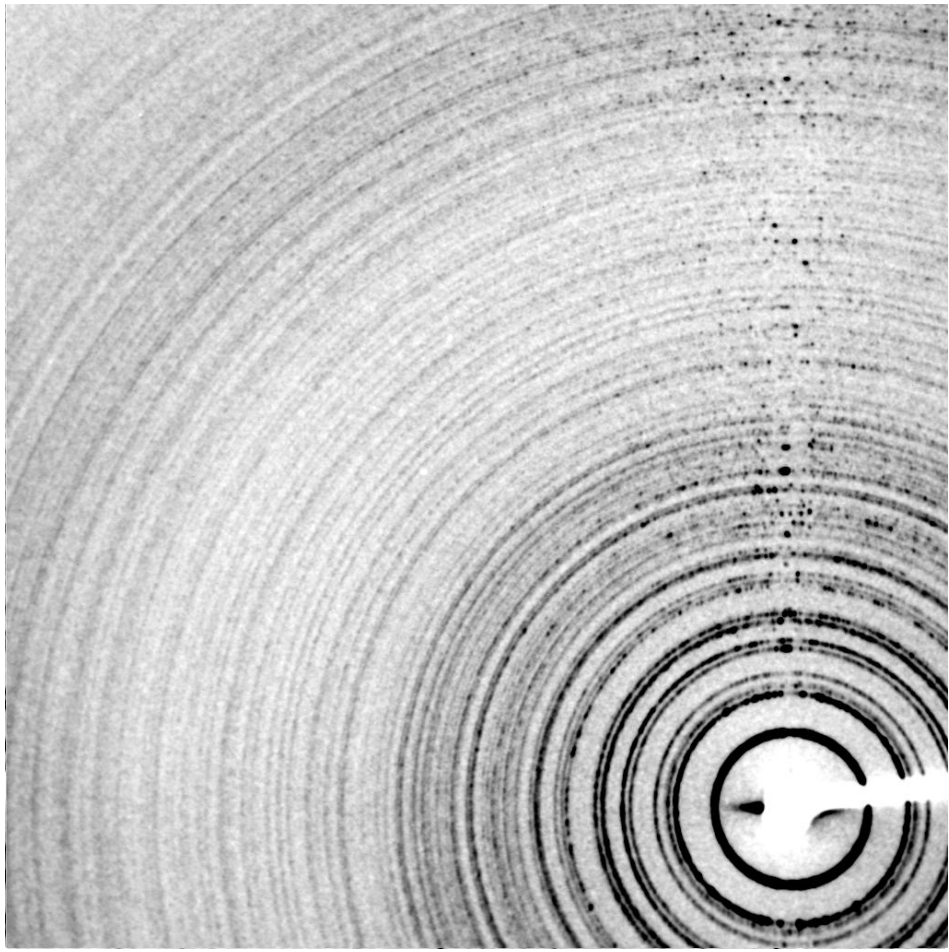
Many small single crystals make a powder



- » 1
- » 2
- » 3
- » 5
- » 10
- » 20
- » 50

- Spots cover spheres in 3D reciprocal space

- 2D area detector takes a slice
- (on Ewald sphere)
- 1D powder scan measures distance from origin



Courtesy I.Margiolaki ESRF Grenonble

X- Ray powder diffraction: limitations

Ovelapping of reflections

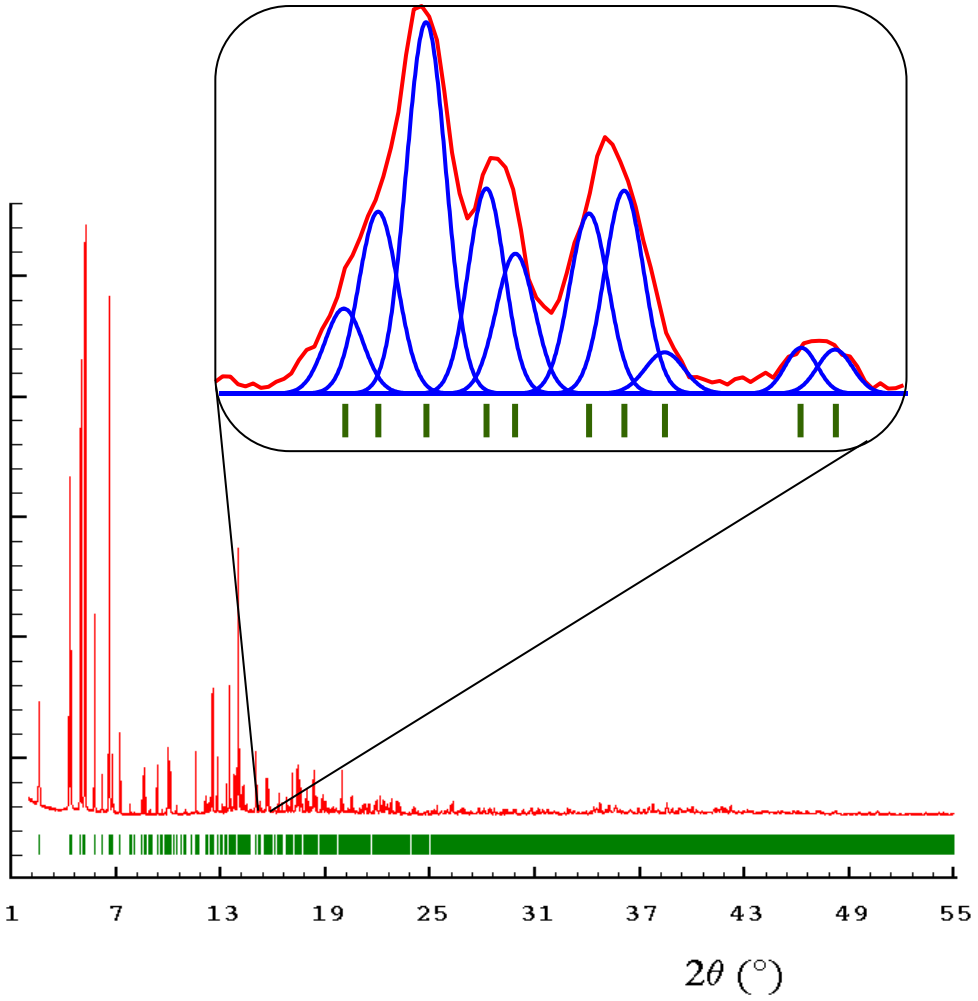
stacking intergrowth

Preferential orientation

Nanocrystals

Impurities

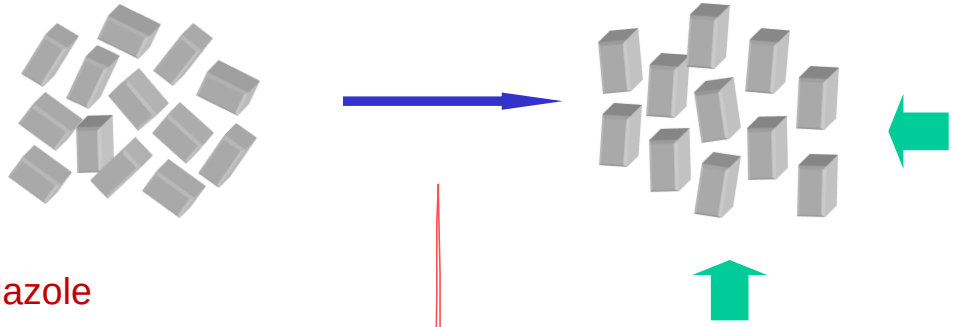
Light atoms (Li, Be)



X- Ray powder diffraction limitations

overlapping

Preferential orientation



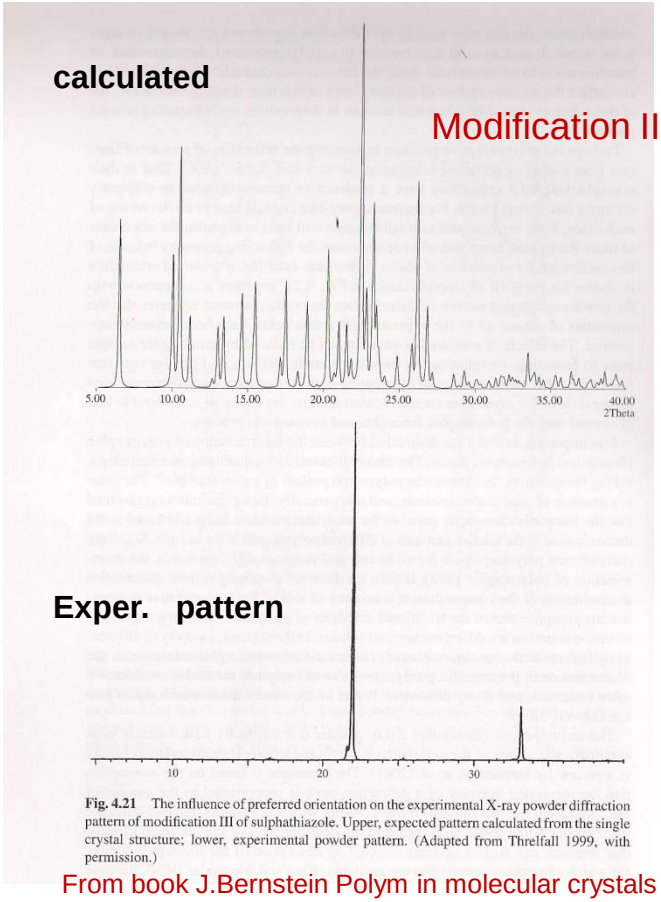
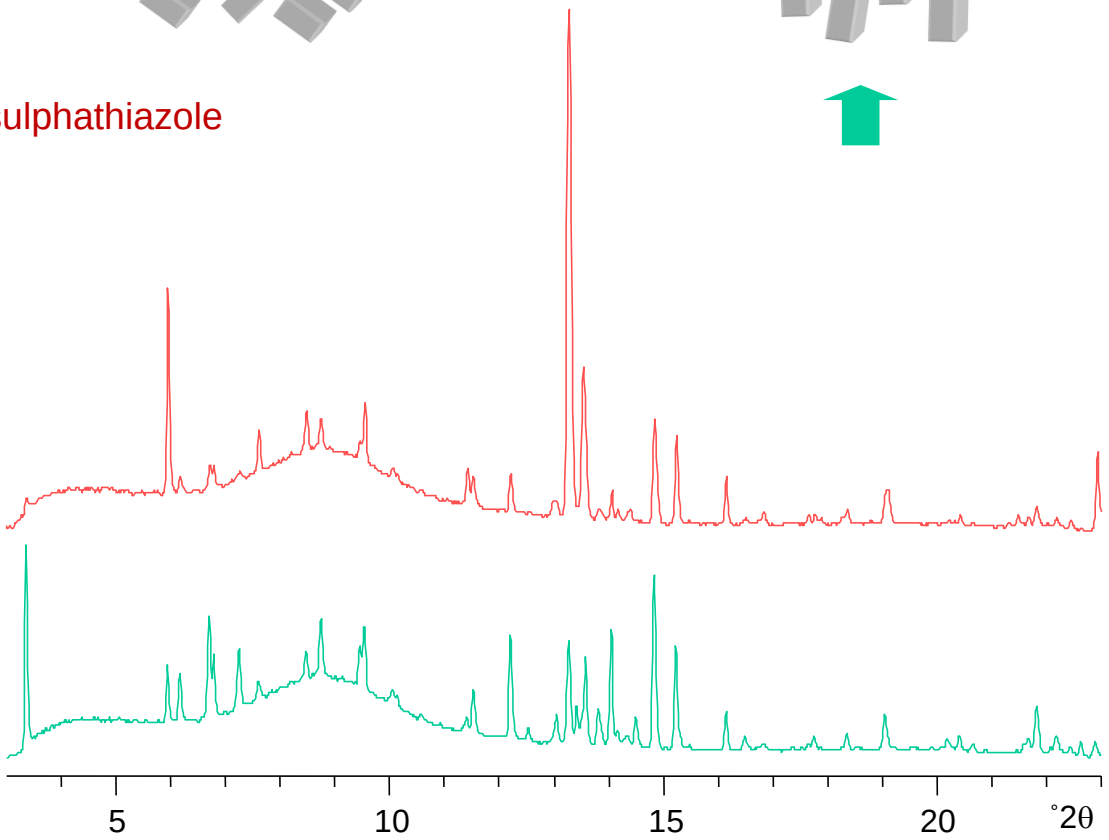


Fig. 4.21 The influence of preferred orientation on the experimental X-ray powder diffraction pattern of modification III of sulphathiazole. Upper, expected pattern calculated from the single crystal structure; lower, experimental powder pattern. (Adapted from Threlfall 1999, with permission.)

Modification III sulphathiazole



From book J.Bernstein Polym in molecular crystals

X- Ray powder diffraction limitations

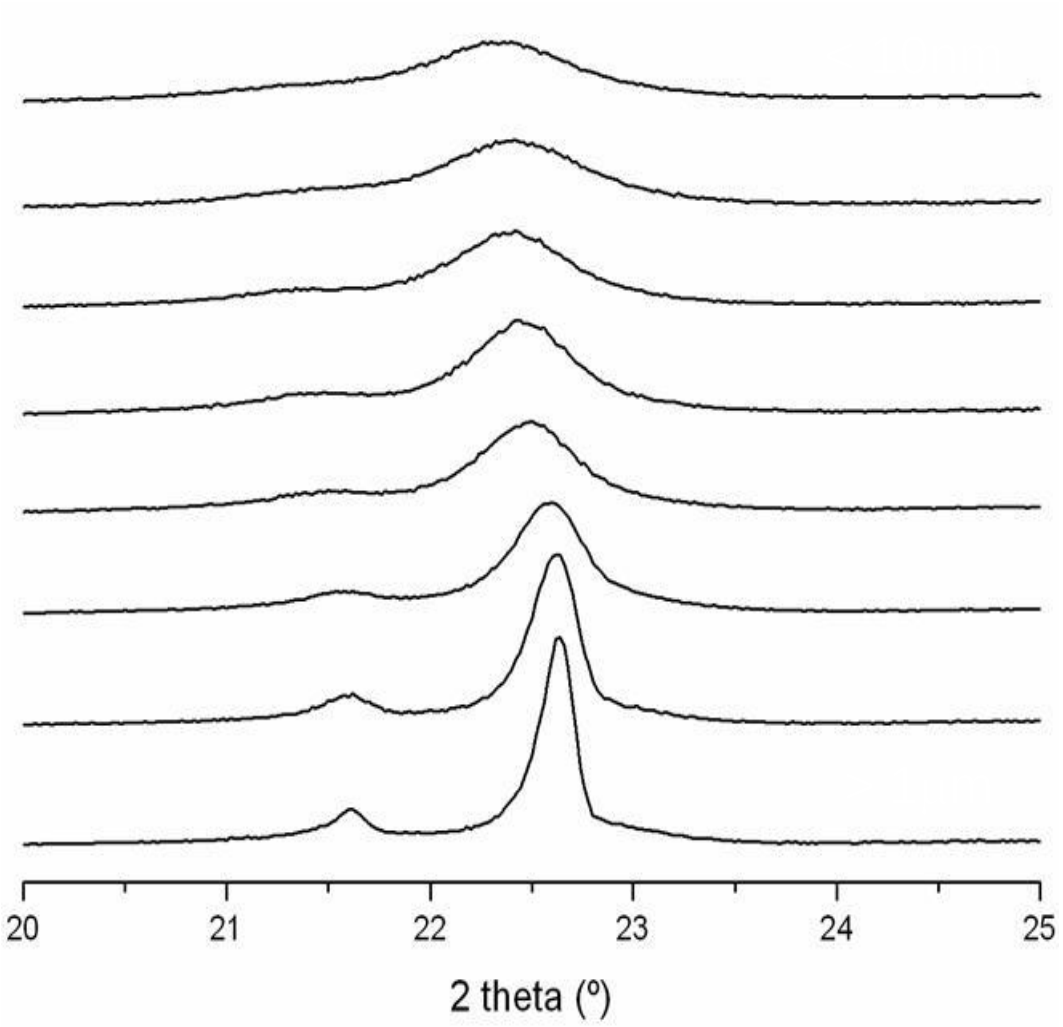
overlapping

Stacking intergrowth

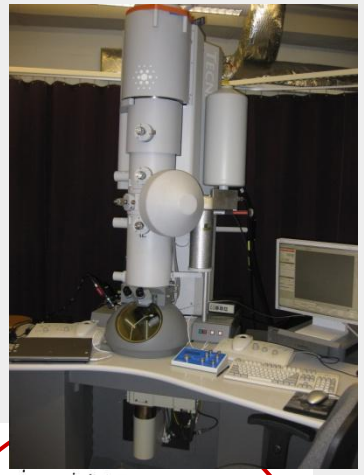
Preferential orientation

Impurities

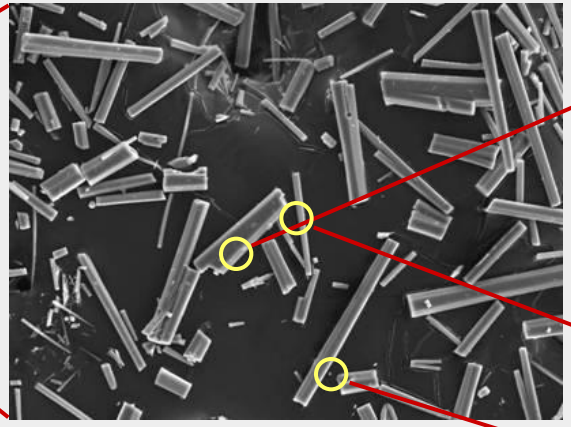
Light atoms (Li, Be)

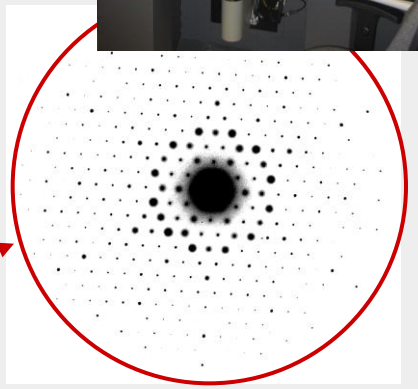


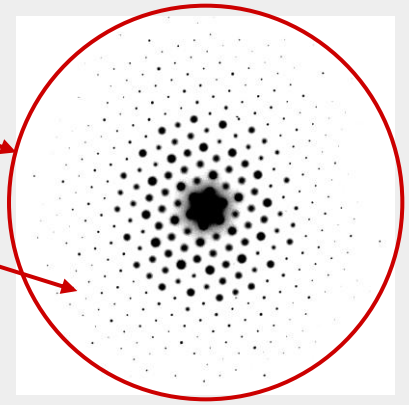
Electron diffraction in transmission electron microscope (TEM)



Powder pattens : sum of individual nanocrystals

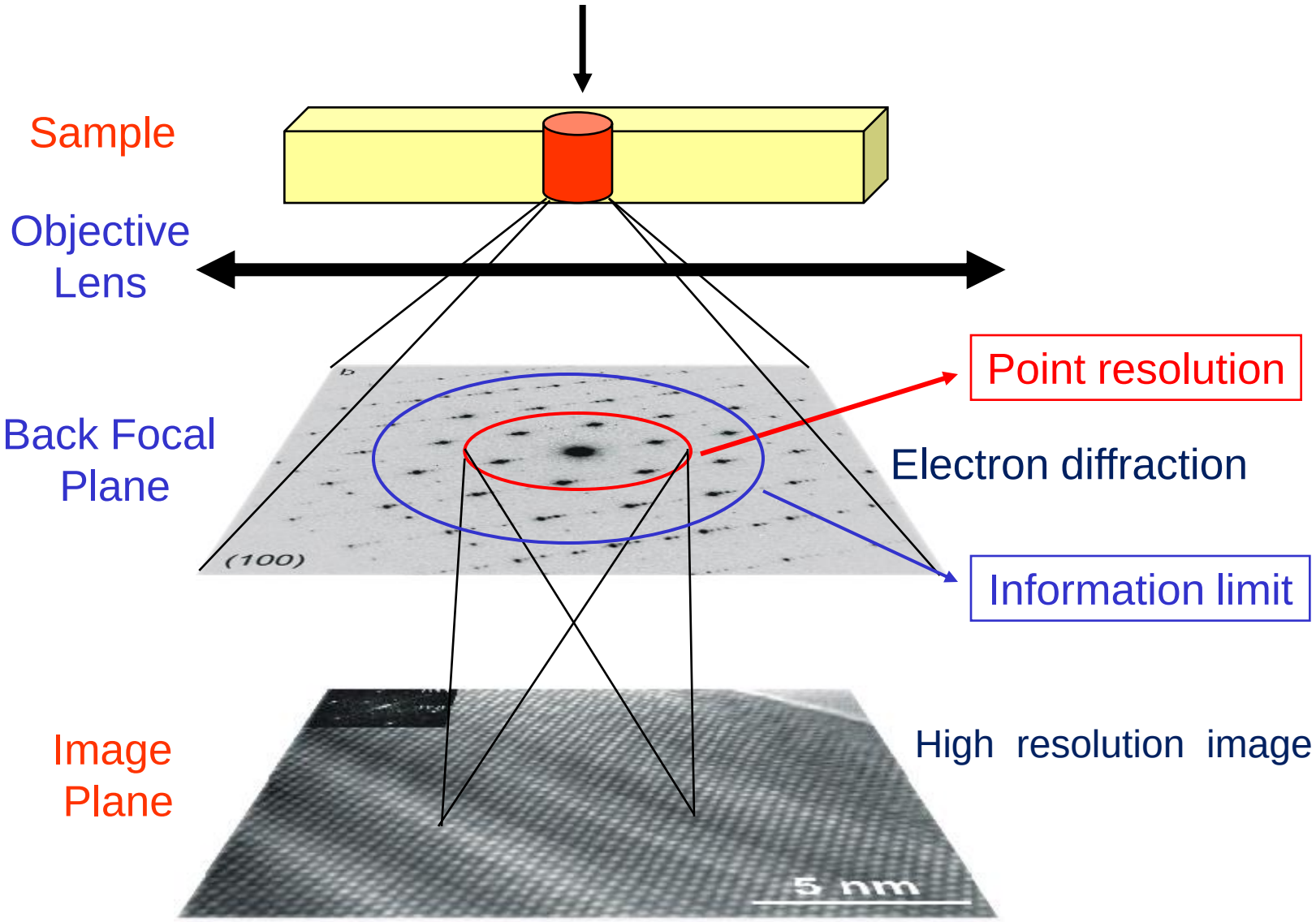






Cell parameter and symmetry determination from nm single crystals

Image formation in TEM



Neutrons, single crystal

X-rays, single crystal
(laboratory diffractometer)

X-rays, single crystal
(synchrotron)

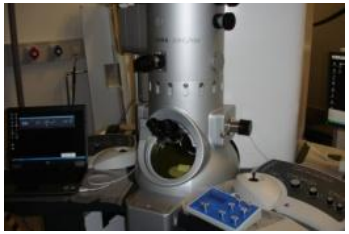
X-rays and neutrons, single phase powder
(laboratory diffractometer)

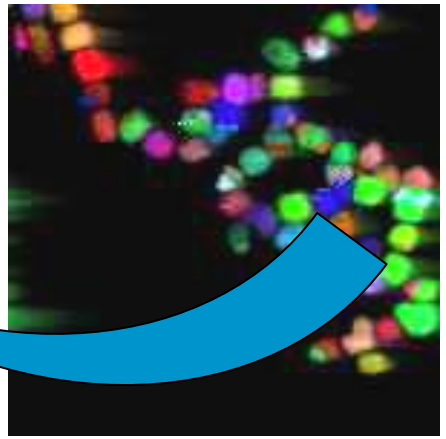
X-rays and neutrons, single phase powder
(synchrotron)

single crystal

10^6 10^5 10^4 10^3 10^2 10 1 nm

3D data 1D data





Fractions of materials with unknown crystal structures.
Data extracted from JCPDS-ICDD Database 1997

NanoMEGAS
Advanced Tools for electron diffraction

With TEM we can analyze nm size crystals

Characterization

for new unknown compound

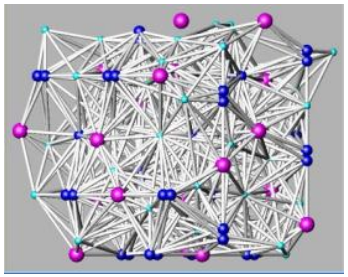
Find crystal cell parameters

Find atomic crystal structure

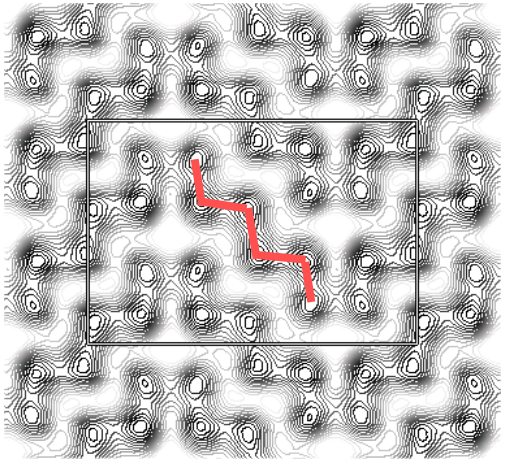
Texture – (multi) phase analysis

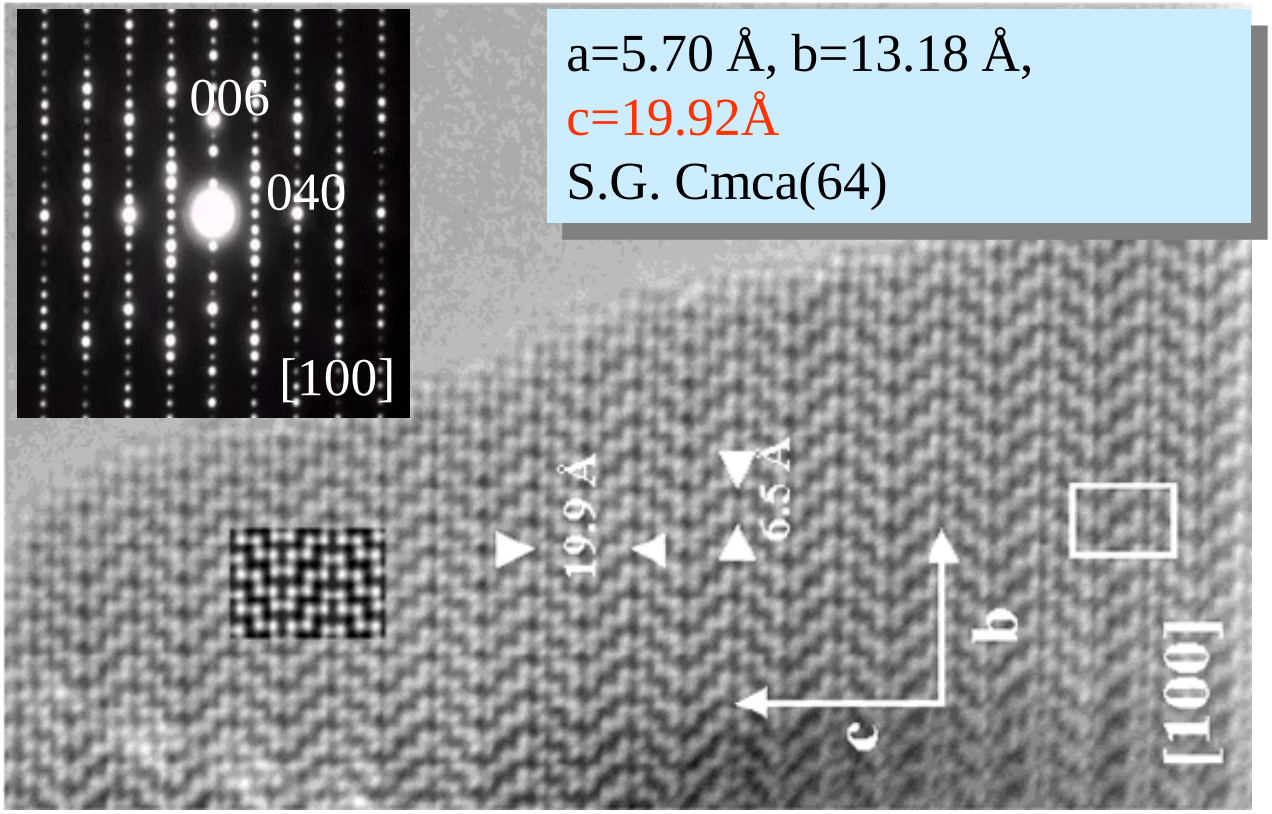
NanoMEGAS
Advanced Tools for electron diffraction

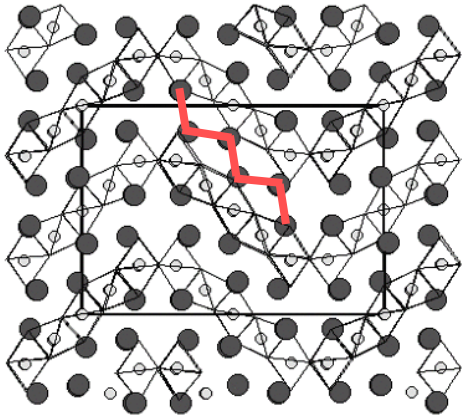
High resolution TEM : only 2D projected atomic structure



NOT possible to get 3D atomic model



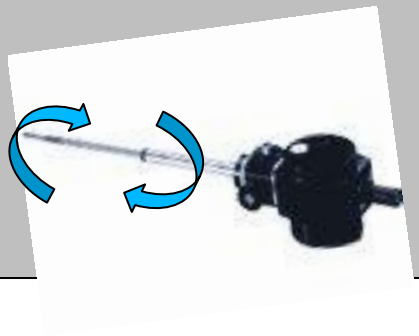


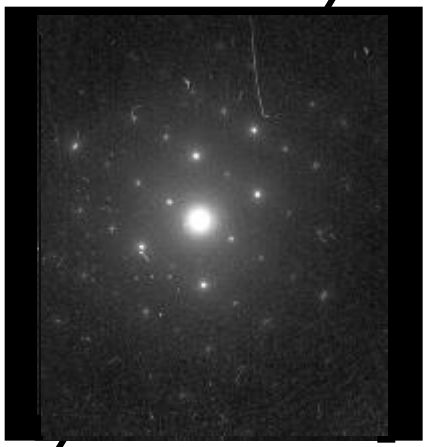


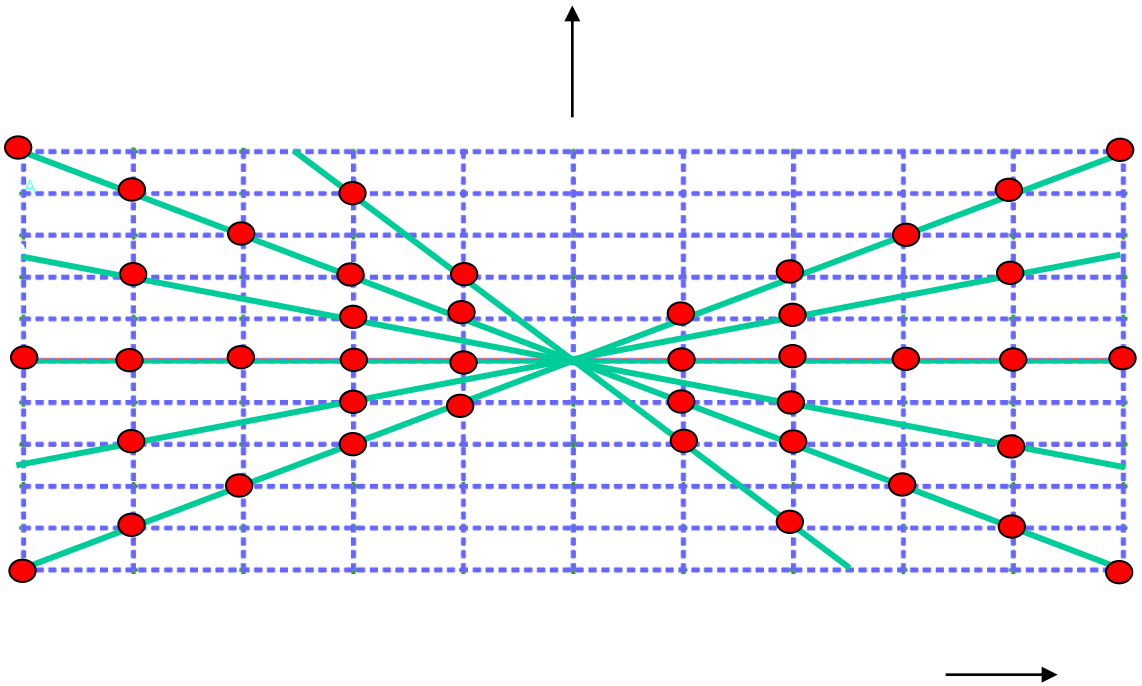
Courtesy K Boulahya Univ Madrid

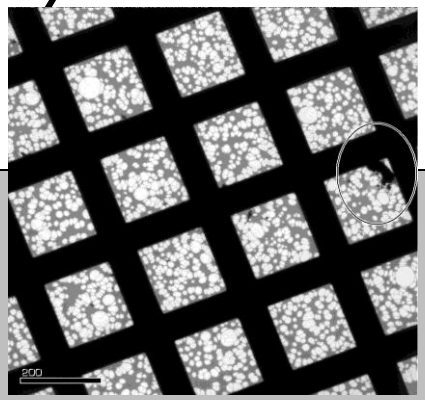
Find crystal cell parameters

TEM : manual tilt series acquisition

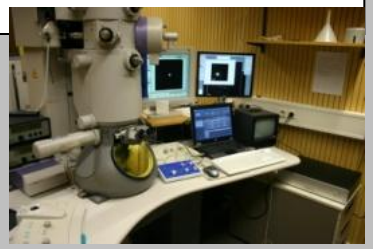




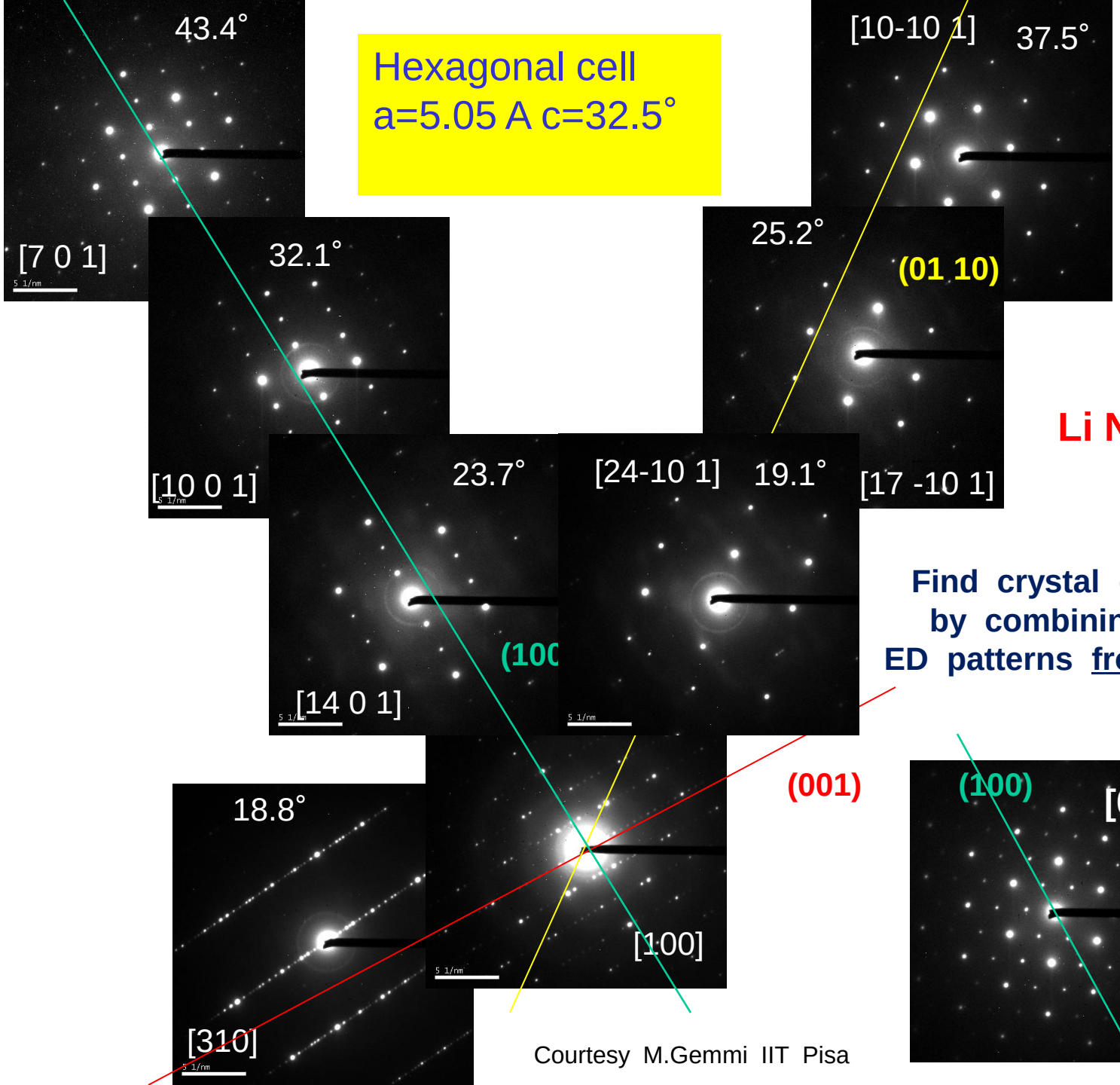




Problem : “missing cone” = lost data



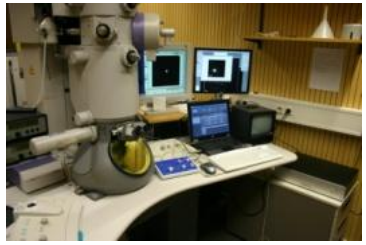
Courtesy : Prof. U Kolb UMainz

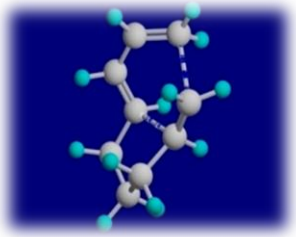

Hexagonal cell
a=5.05 A c=32.5°
43.4°
[7 0 1]
[10-10 1]
37.5°
32.1°
[10 0 1]
25.2°
(01 10)
[17 -10 1]
23.7°
[14 0 1]
[24-10 1]
19.1°
(100)
(001)
18.8°
[310]
[100]
(100)
[001]
Li Ni0.5Ti1.5 O4
Find crystal cell parameters by combining several ZA ED patterns from same crystal
Courtesy M.Gemmi IIT Pisa

ORGANIC crystals : beam sensitive

Only possible to collect several (non ZA oriented ED patterns)

from different crystals

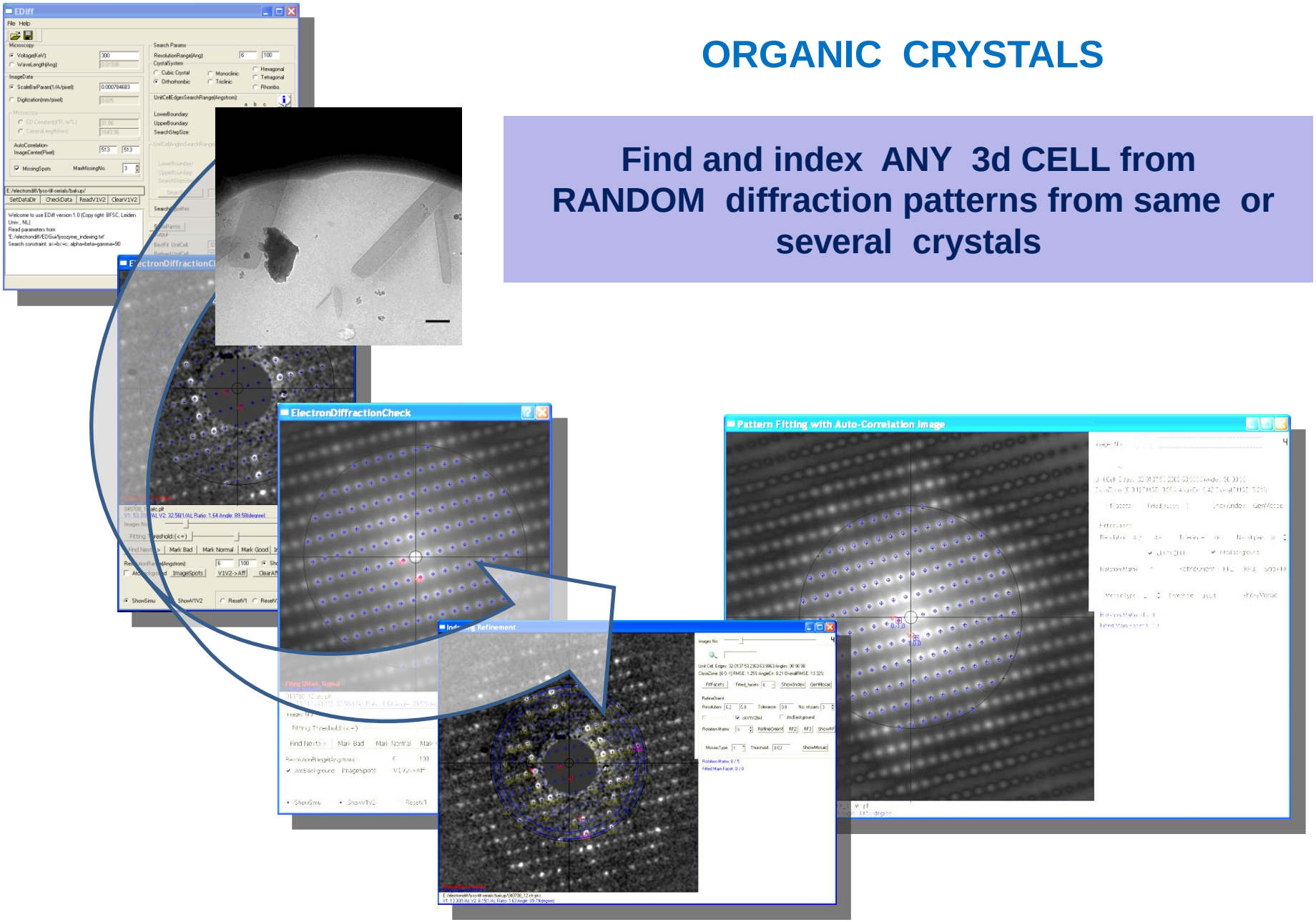




Penicillin G , courtesy Dr.D.Gueorguieva Leiden Univ NL

ORGANIC CRYSTALS

Find and index ANY 3d CELL from RANDOM diffraction patterns from same or several crystals



NanoMEGAS
Advanced Tools for electron diffraction

Courtesy JP Abrahams, D.Georguieva Univ Leiden

Characterization

for new unknown compound

Find crystal cell parameters

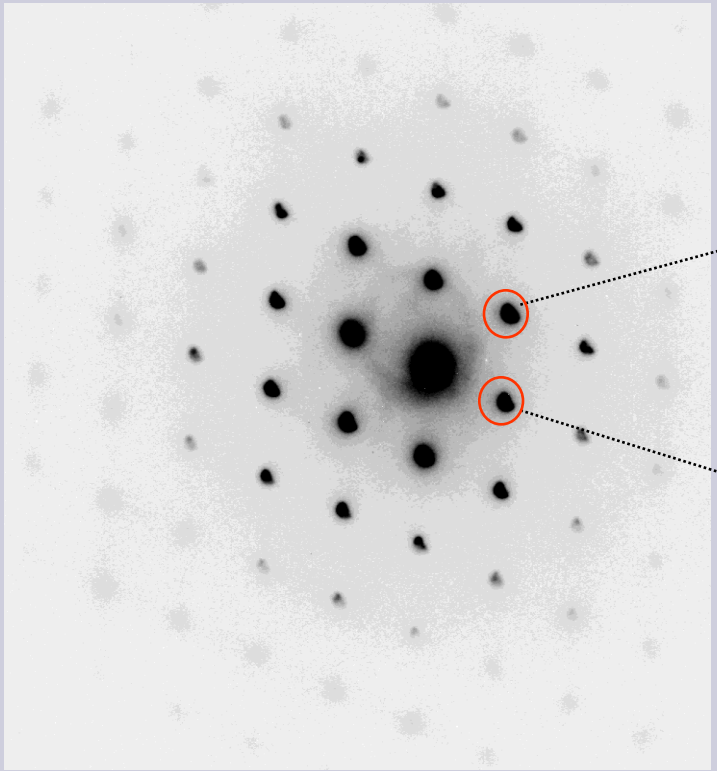
Find atomic crystal structure

Texture – (multi) phase analysis

Electron diffraction

$$I_{exp} \approx \left|F(\vec{h})\right|^2$$

- **Electron diffraction is highly dynamical**



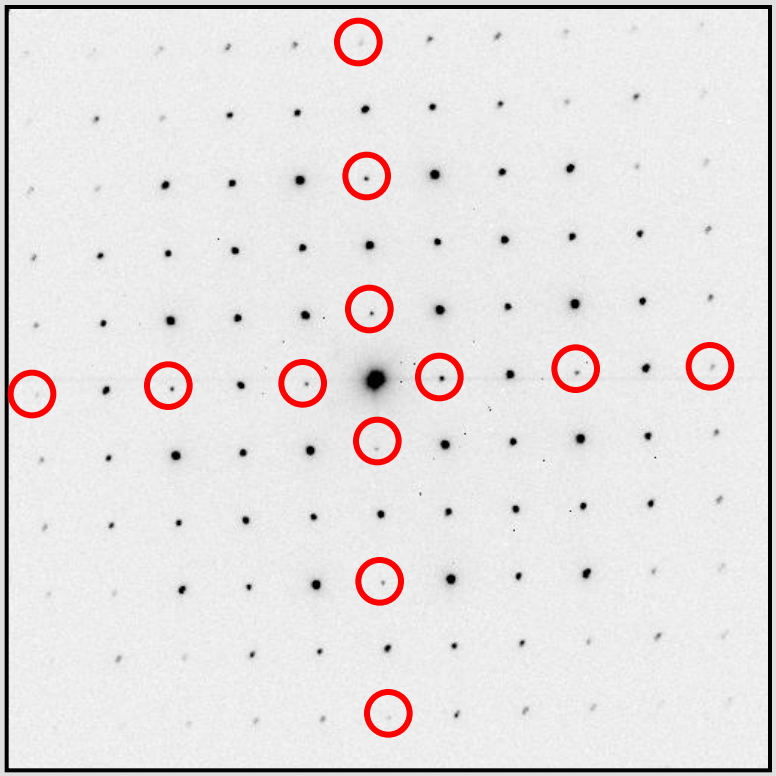
(200)
forbidden

(111)
allowed

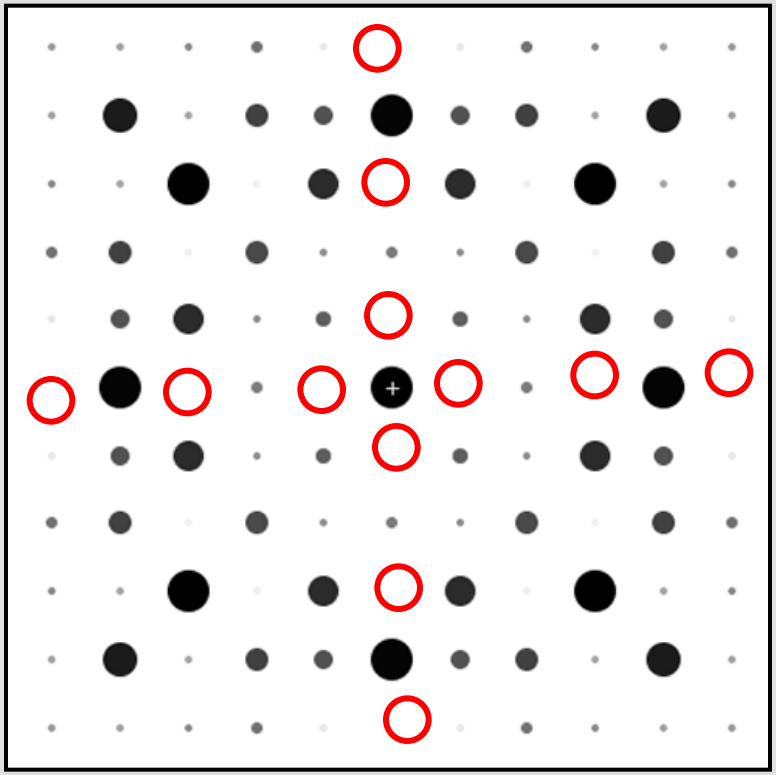
The electron diffraction intensities cannot be used for solving or refining the structure in a straightforward way as X-ray data

Si [011] spg Fd3m

(h00) allowed only if h=4n



Normal electron diffraction pattern
(dynamical) thickness > 10 nm



Ideal kinematic diffraction pattern
(like X-Ray)

Melilite: tetragonal a=b=7.8A c=5.0A

$P\,\bar{4}\,2_1\,m$

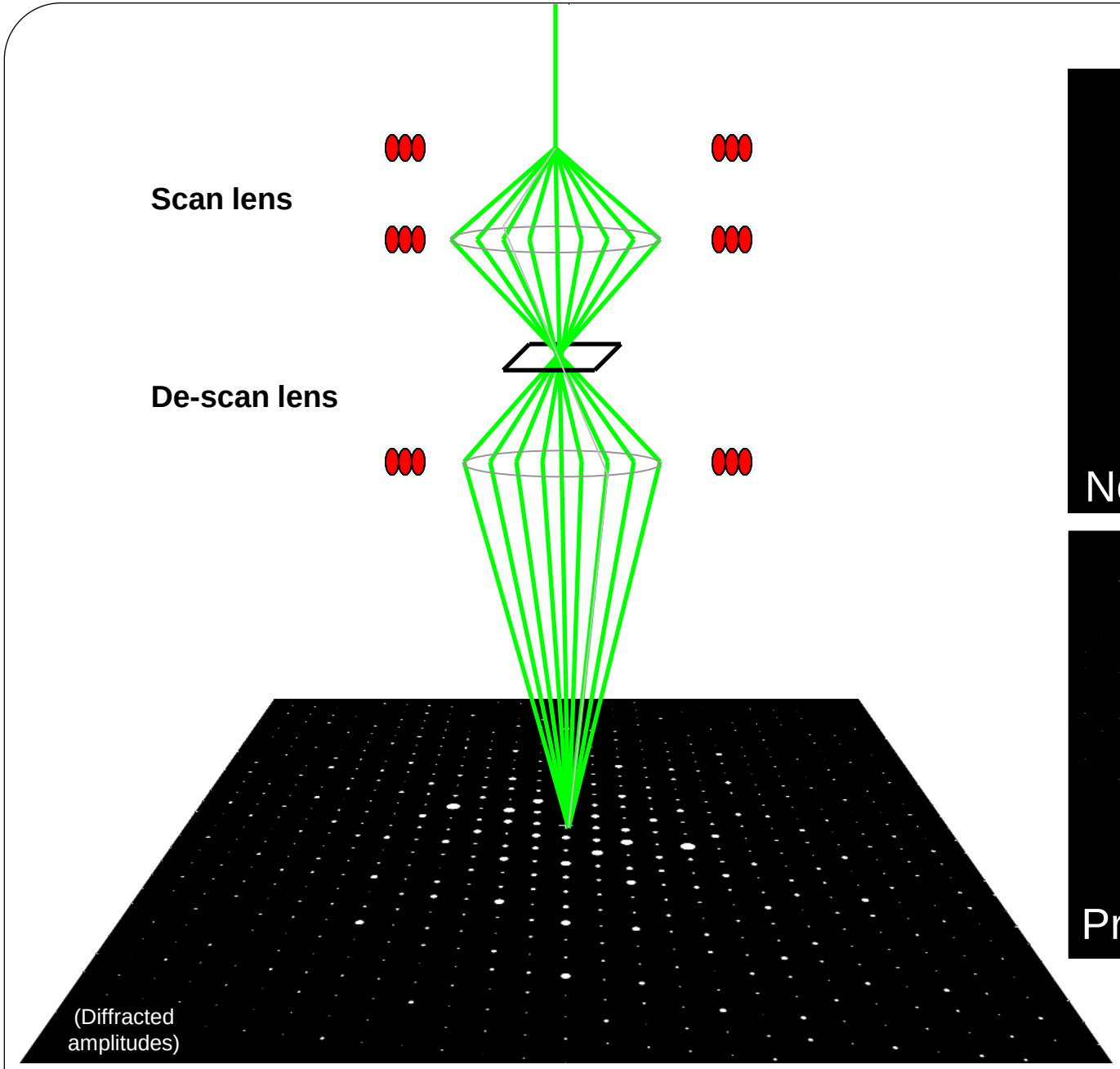
Space group extinction rules :(h00) e (0k0) h=2n, k=2n

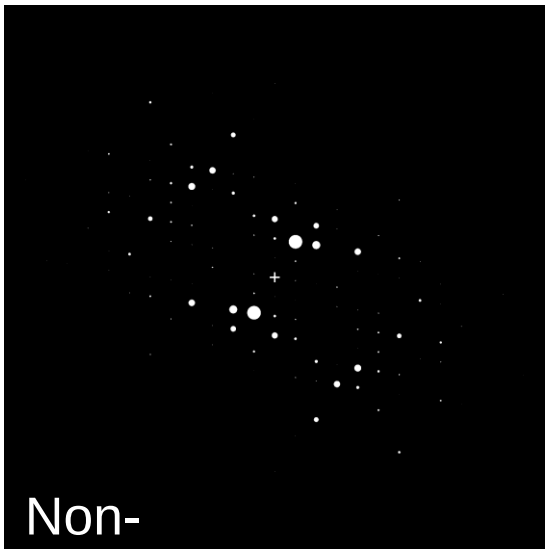
Courtesy M.Gemmi Univ Milano

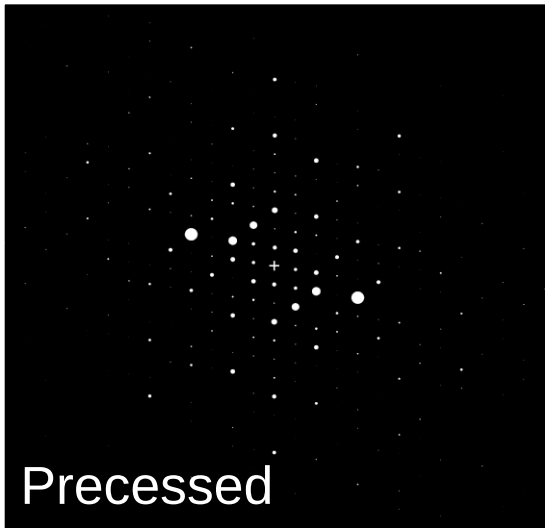
Electron (precession) diffraction : the right way to solve nanostructures in TEM

- **Electron diffraction intensities (usually dynamical) cannot be used (like X-Ray) to solve structures, as they lead in wrong structural models**
- **Precession electron diffraction in TEM has been discovered in Bristol , UK by Vincent and Midgley (1994 , Ultramicroscopy 53, 271)**
- **During beam precession , the beam is tilted and precessed at high frequency though the optical axis on a conical surface : crystal is not moving, but Ewald sphere is precessing aroung the optical axis**
- **Due to precession many HKL intensities far out in reciprocal space appear with intensities integrated over the excitation error**
- **Precession intensities behave much closer to ideal (kinematical) intensities, therore can be used to solve crystal nanostructures (Ultramicroscopy, vol.107, issue 6-7, July 2007)**

Reference : C.Own PhD thesis







Precession…

DigiSTAR digital precession unit

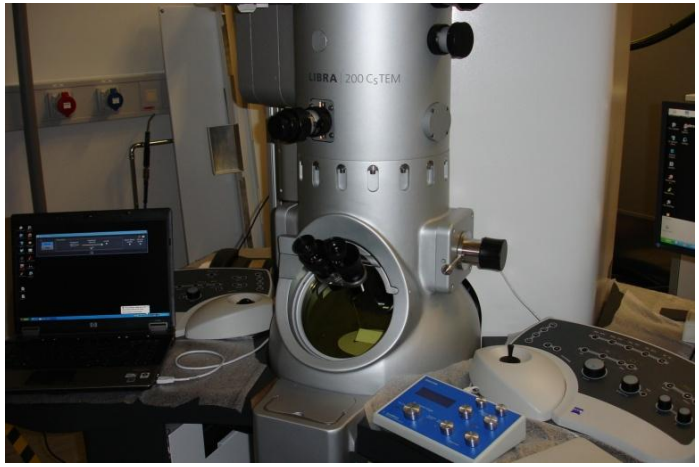
PRECESSION : DISCOVERED IN UK 1996 R.Vincent- P. Midgley

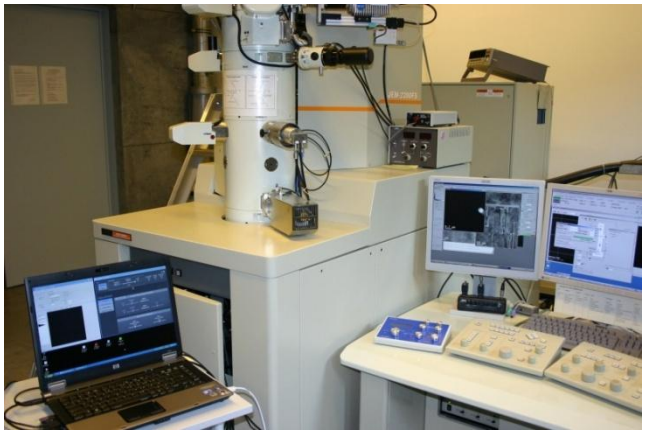
NanoMEGAS : FIRST TEM commercial device

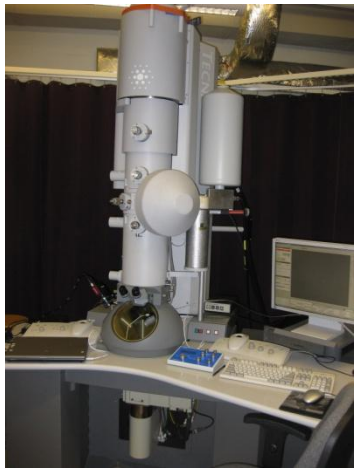
- **MORE THAN 50 ARTICLES SINCE 2004**
- **MORE THAN 60 INSTALLATIONS WORLD-WIDE**

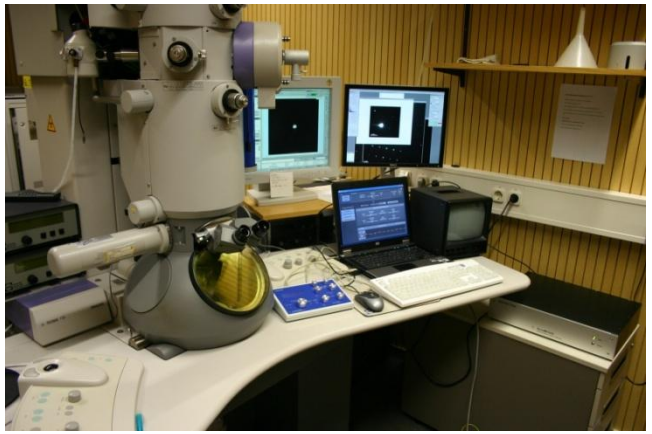
NanoMEGAS
Advanced Tools for electron diffraction

Digital precession interface for advanced TEM





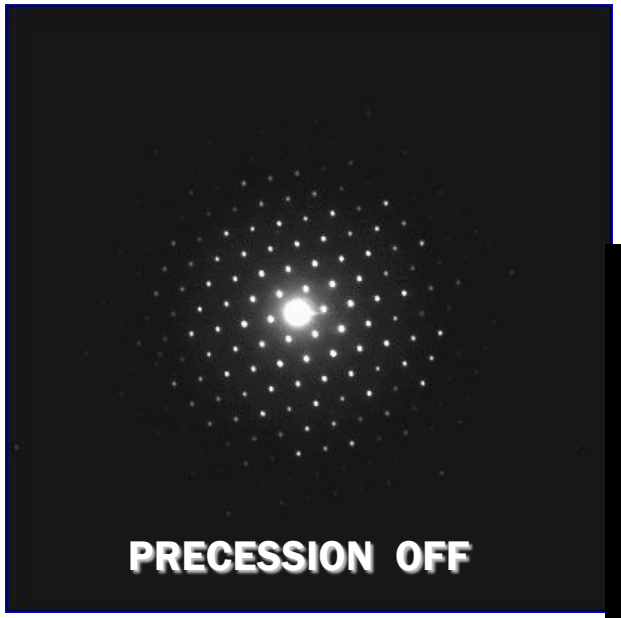


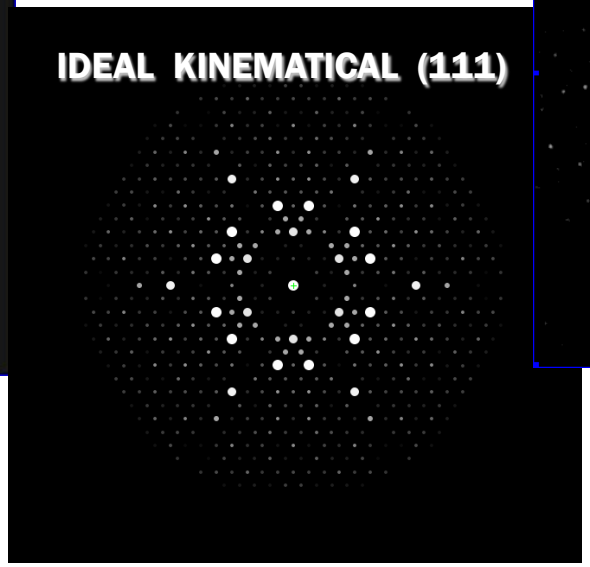


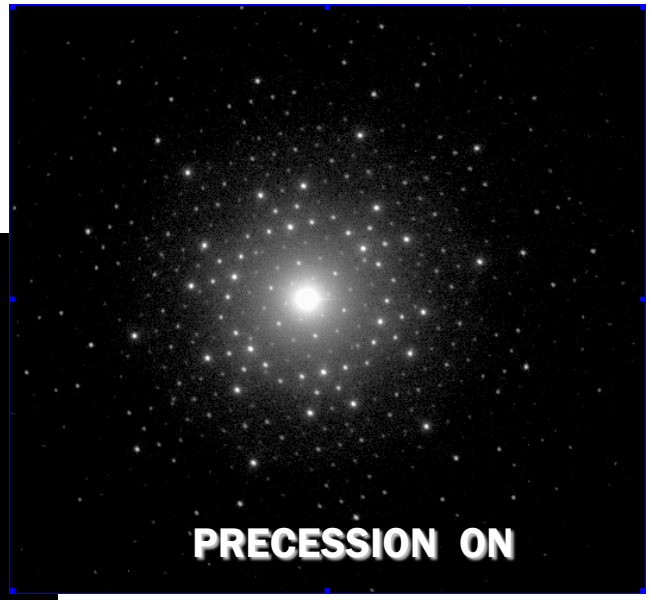
Zeiss Libra 200F Cs corrected **Jeol 2200 FS** **Jeol 2010F**
Tecnai 20F **Tecnai 30F**

NanoMEGAS
Advanced Tools for electron diffraction

PRECESSION : QUASI – KINEMATICAL (X-Ray like) INTENSITIES







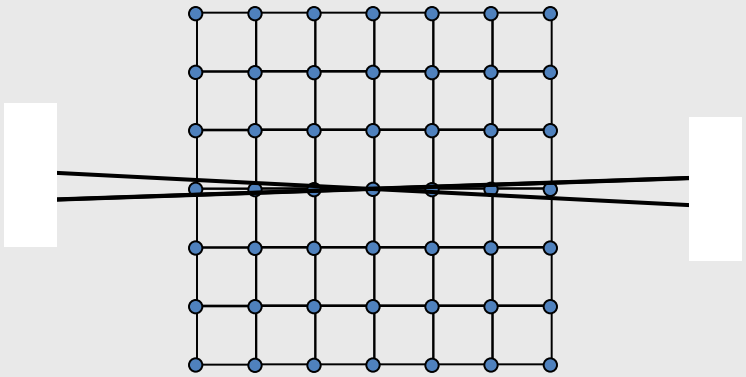
UVAROVITE cubic mineral (111)

When applying precession, dynamical conventional SAED patterns (left) they become very close to kinematical (right) ; compare with simulated kinematical intensities pattern (center).

Observe the film of cubic mayenite mineral along 111 ZA , ED pattern how it changes from dynamical to very kinematical at increasing precession angle

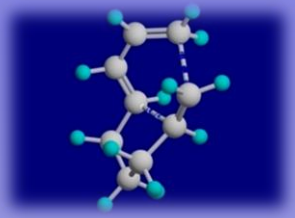
Courtesy M.Gemmi Univ of Milano

Advantages of precession in single exposure data collection



with beam precession,
Ewald sphere
also precess though
the reciprocal space

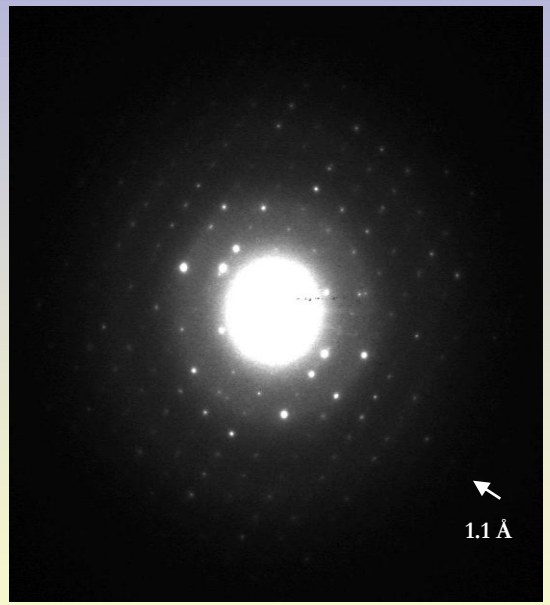
- **More fully recorded reflections**
- **More spots per image**
- **Reduced dynamic effect**



Precession from pharmaceutical nanocrystals

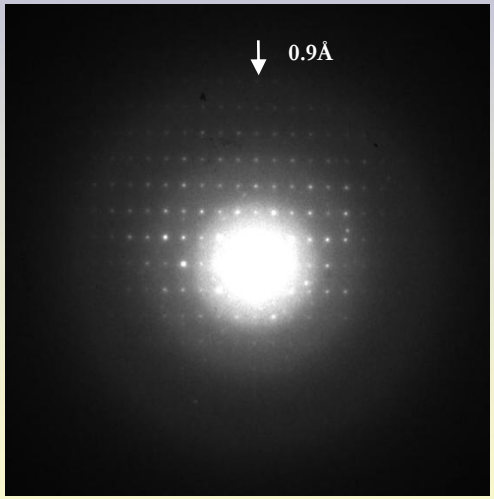
PED patterns in pharmaceutical crystals allow to work with close or with ZA oriented patterns , revealing true crystal symmetry and kinematical intensities good for structure determinations

amoxycillin

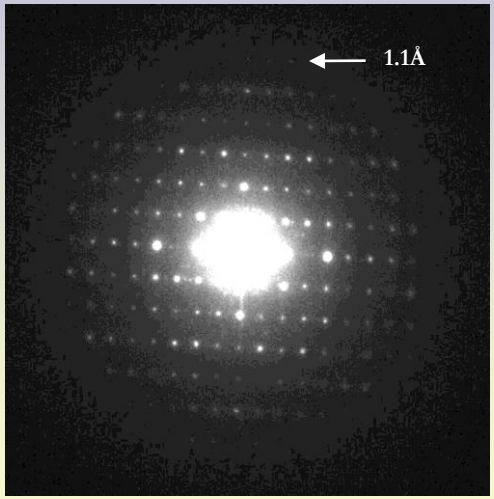


without precession

penicillin G-potassium



without precession



with precession

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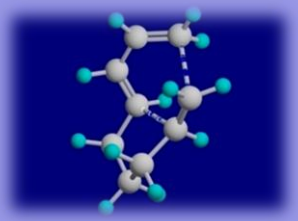
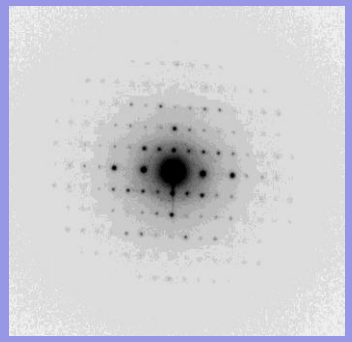
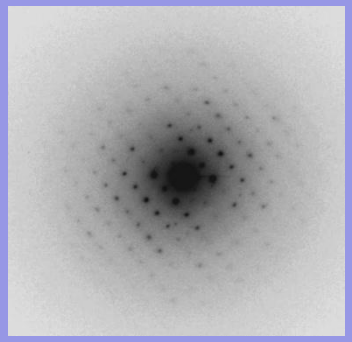
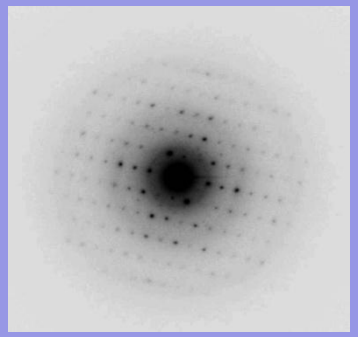
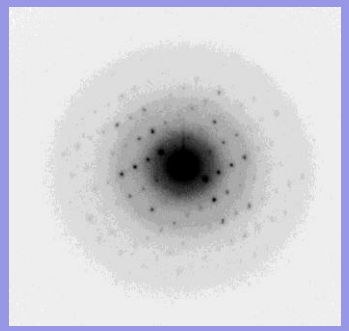
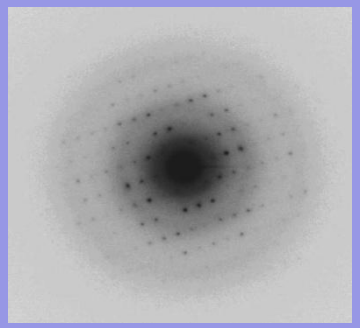
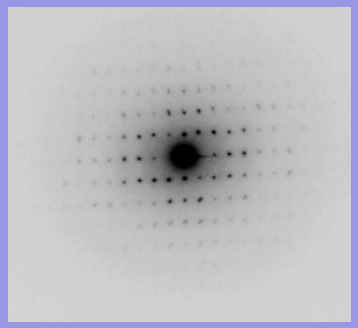
Courtesy JP Abrahams, D.Georgueva Univ Leidenc

Precession electron diffraction (PED) from penicillin G – potassium



oriented PED patterns show Laue class symmetry

Laue class	Zone axes						
CUBIC CRYSTAL SYSTEM							
m-3m	<111>	<001>	<110>	<uv0>	<uuw>	<uvw>	
WP	3m	4mm	2mm	M	m	1	
ZOLZ	(6mm)	(4mm)	(2mm)	(2mm)	(2mm)	(2)	
m-3	<111>	<001>	<uv0>	<uvw>			
WP	3	2mm	m	1			
ZOLZ	(6)	(2mm)	(2mm)	(2)			
HEXAGONAL CRYSTAL SYSTEM							
6/mmm	<0001>	<11-20>	<1-100>	<uv.0>	<uu.w>	<u-u.w>	<uv.w>
WP	6mm	2mm	2mm	m	m	m	1
ZOLZ	(6mm)	(2mm)	(2mm)	(2mm)	(2mm)	(2mm)	(2)
6/m	<0001>	<uv.0>	<uv.w>				
WP	6	m	1				
ZOLZ	(6)	(2mm)	(2)				
TRIGONAL CRYSTAL SYSTEM							
-3m	<0001>	<11-20>	<u-u.w>	<uv.w>			
WP	3m	2	m	1			
ZOLZ	(6mm)	(2)	(2mm)	(2)			
-3	<0001>	<uv.w>					
WP	3	1					
ZOLZ	6	2					
TETRAGONAL CRYSTAL SYSTEM							
4/mmm	<001>	<100>	<110>	<u0w>	<uv0>	<uuw>	<uvw>
WP	4mm	2mm	2mm	m	m	m	1
ZOLZ	(4mm)	(2mm)	(2mm)	(2mm)	(2mm)	(2mm)	(2)
4/m	<001>	<uv0>	<uvw>				
WP	4	m	1				
ZOLZ	(4)	(2mm)	(2)				
ORTHORHOMBIC CRYSTAL SYSTEM							
mmm	<100>	<010>	<001>	<0vw>	<u0w>	<uv0>	<uvw>
WP	2mm	2mm	2mm	m	m	m	1
ZOLZ	(2mm)	(2mm)	(2mm)	(2mm)	(2mm)	(2mm)	(2)
MONOCLINIC CRYSTAL SYSTEM (unique axis b)							
2/m	<010>	<u0w>	<uvw>				
WP	2	m	1				
ZOLZ	(2)	(2mm)	(2)				
TRICLINIC CRYSTAL SYSTEM							
-1	<uvw>						
WP	1						
ZOLZ	(2)						

Easier to find crystal cell parameters from "randomly oriented" PED patterns
Orthorombic a = 6.4 A b = 9.4 A c = 30 A

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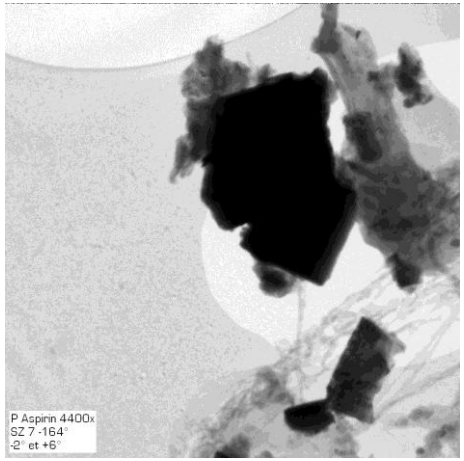
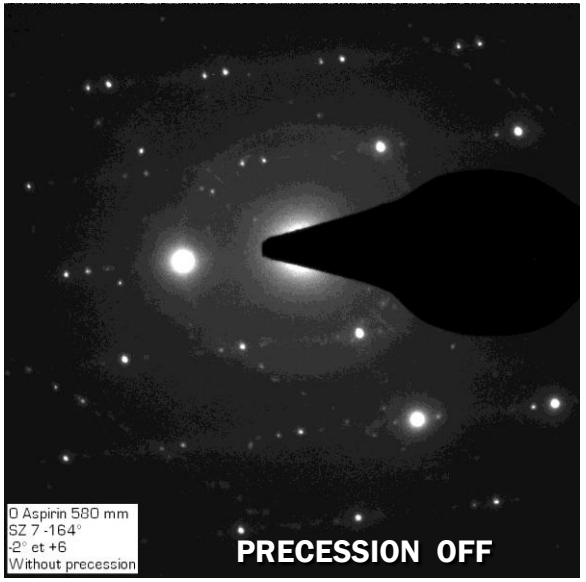
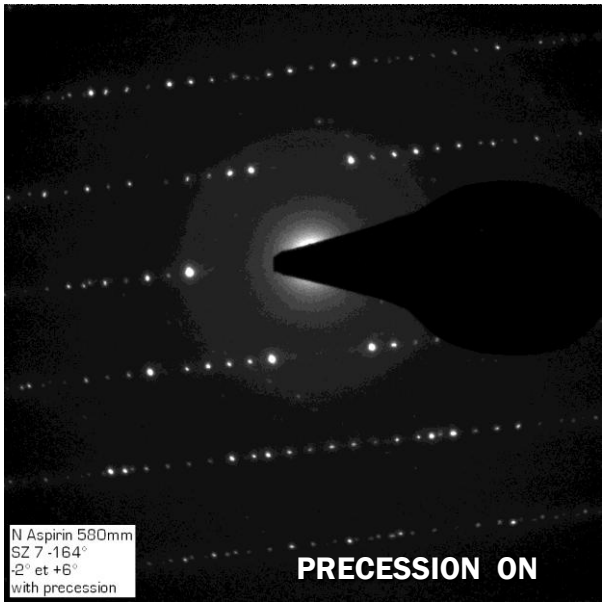
Obtaining « randomly oriented » PED in PHARMACEUTICALS



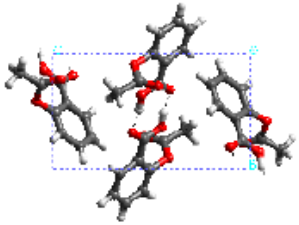
ASPIRIN





Potential Polymorphs of Aspirin

The Polymorph Predictor was used to examine the potential for additional polymorphs of aspirin.



The crystal structure for aspirin. Click on it for a more detailed picture.

Aspirin, also known as acetylsalicylic acid, has numerous pharmaceutical applications. First synthesized in 1897, aspirin is only found experimentally in

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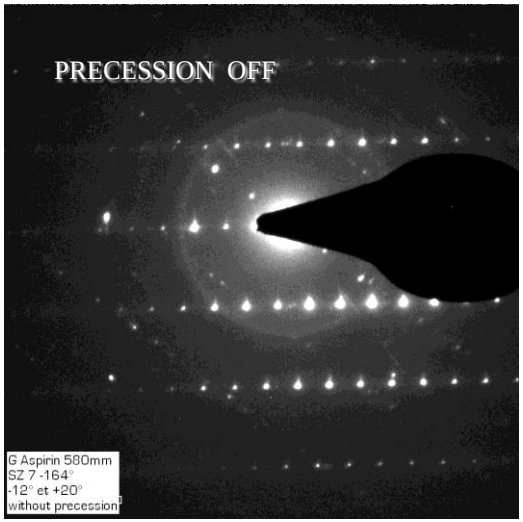
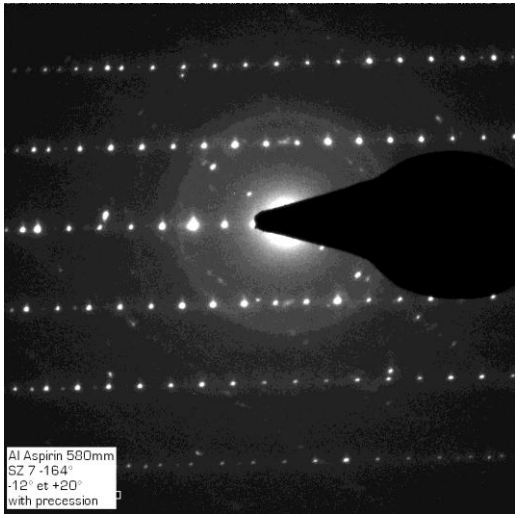
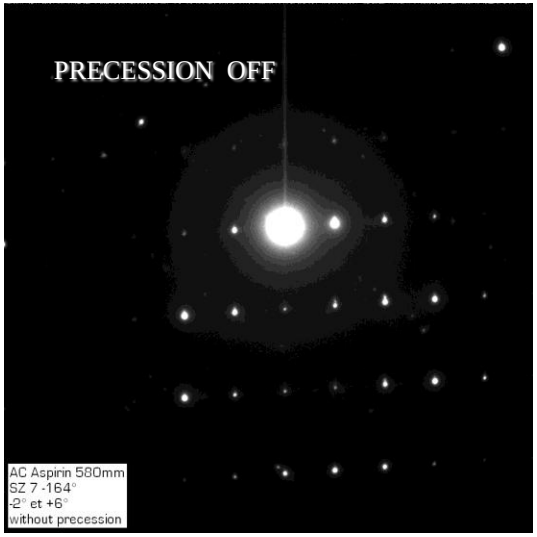
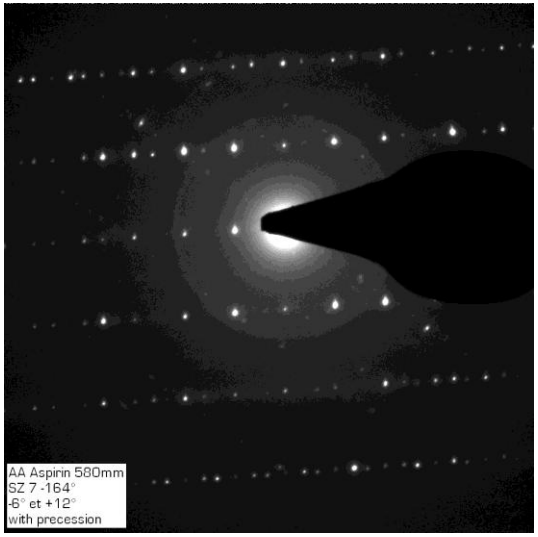
Courtesy JP Morniroli , samples T.Weirich RWTH Aachen





PRECESSION ON





PRECESSION ON

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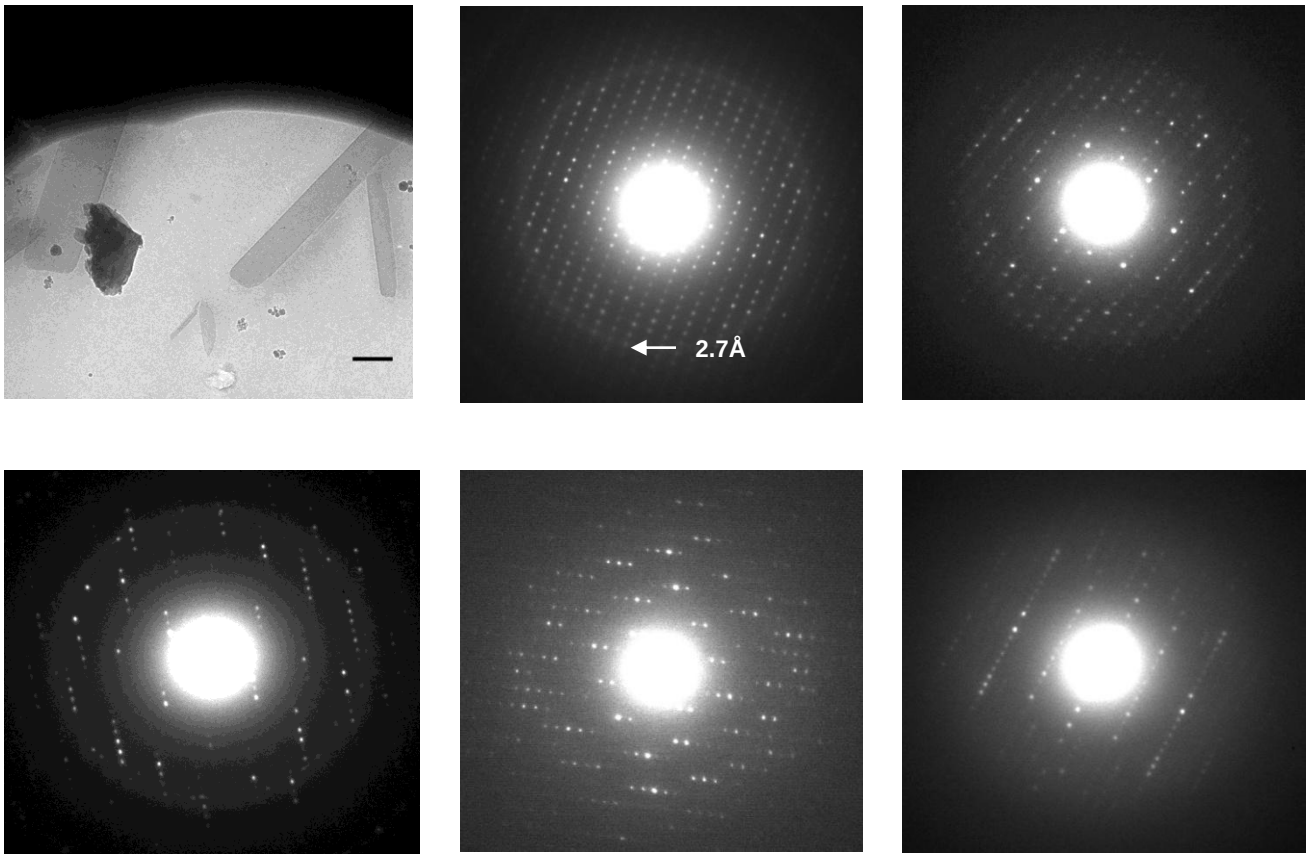
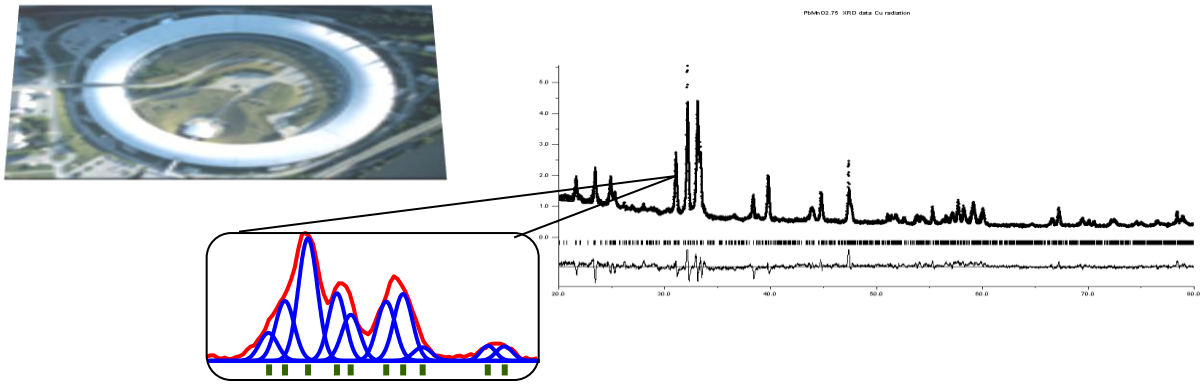
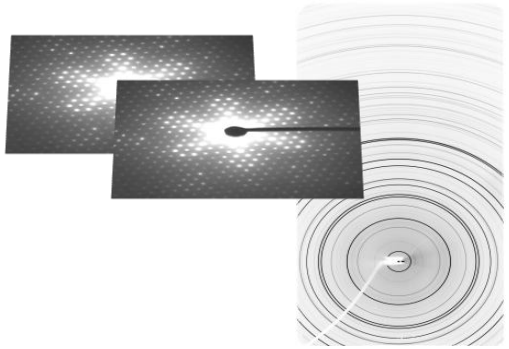
Data collection : precession electron diffraction from lysozyme nanocrystals $P4_32_12$ a=b=79.2 A ,c=38.0 A



Courtesy JP Abrahams, D.Georgieva Univ Leiden

Combine precession electron diffraction - powder X-Ray diffraction to solve complex structures

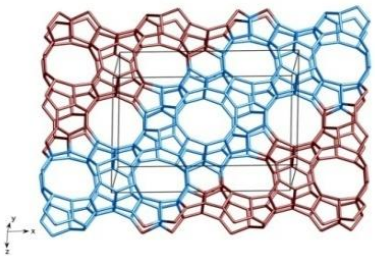


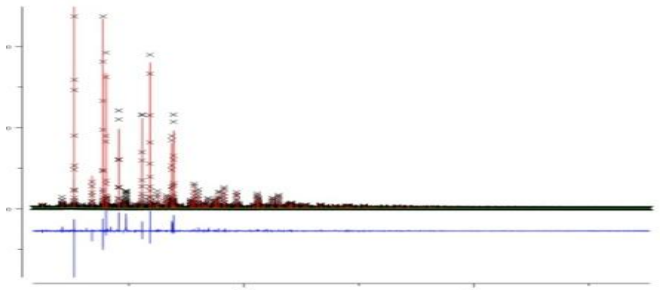


Information from PED can be combined with *hkl reflections from X-Ray* powder diffraction to accurately solve and refine *ab-initio* structures using either *charge-flipping* algorithms or direct methods.

- **technique is useful for poorly crystallized / nm size pollycrystalline materials**
- **useful for solving structures of complex organic and inorganic materials**
- **useful in presence of unknown phases in X-Ray powder pattern**

one of the **most complex known zeolites TNU-9 ($Si_{19}O_{234}$) has been solved by combining Synchrotron X-Ray powder results and data from 5 ZA PED patterns from 300 kV TEM**





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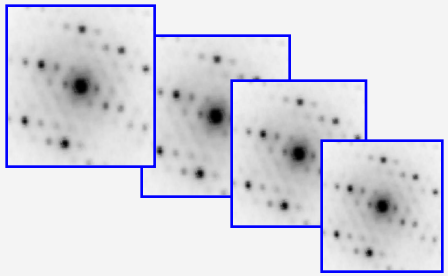
Precession electron diffraction :

ab initio determination of nanostructures

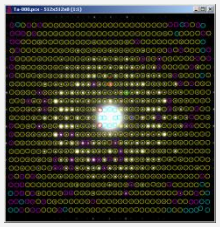
Step 1

TEM crystal experiment
PED patterns collection



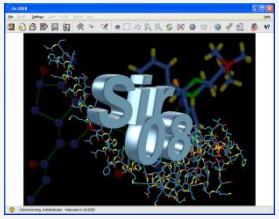
Step 2

ED intensities collection and merging from several zone axis (ELD – Triple)
semi- automatic (off-line)

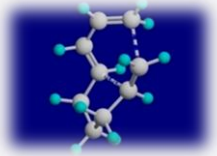


Step 3

STRUCTURE DETERMINATION
(Direct methods)
semi-automatic (SIR software)



Refinement crystal structure



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Precession electron diffraction : steps to solve crystal structure

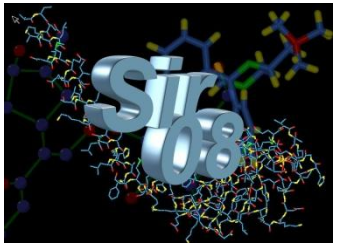
STEP 1 : collect precession diffraction patterns from oriented ZA; for symmetrical crystals (cubic, tetragonal) a few 3-4 patterns may be enough ; collection can be done with films (less precise method as films are easily saturated in intensity , image plates , CCD or our electron diffraction dedicated electron diffractometer)

STEP 2 : extract electron diffraction intensities automatically by software; merging intensities from different ZA by comparing and establish scale factor between common row intensities

STEP 3 : after reducing intensities , considering possible space group symmetry , imput HKL and intensities at direct methods software using electrion diffraction scattering factors (example SIR2008 , SHELX etc..) to solve structure

STEP 4 : all atomic positions and atomic type will appear as one of the most probable solutions; heavy atoms are usually all placed in correct positions, while lighter atoms (eg oxygen appear displaced from ideal positions).

R crystallographic residual from PED intensities is usually between 10-25 % as structure solution by electron diffraction is less precise than X-Ray solution where R is 3-5%



Electron diffraction intensities are measured automatically

FROM

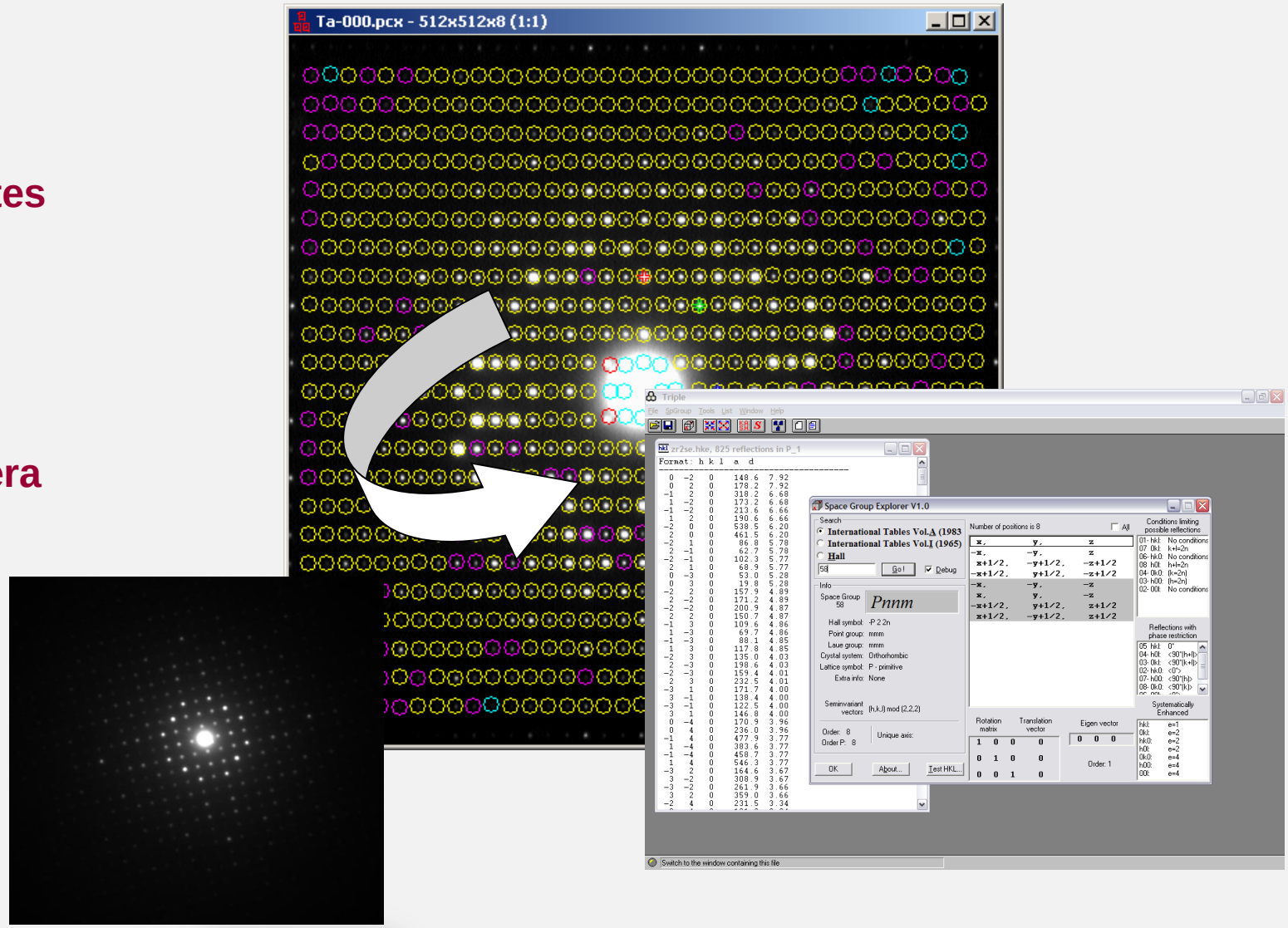
Image plates

Photo film

OR

CCD camera

- 1k x 1k
- 2k x 2k
- 4k x 4k



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TVIPS
Tietz Video and Image Processing Systems

Use Direct methods, charge flipping (like X-Ray) to solve crystal structures

DIRECT METHODS (electron scattering)

SIR 96, SIR 2007, SIR 2008, FOX ,….

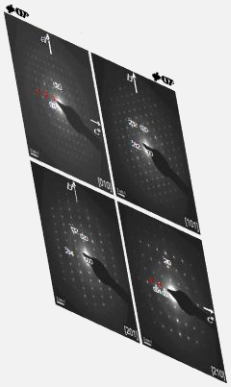
Structure solution with direct methods: SIR2008

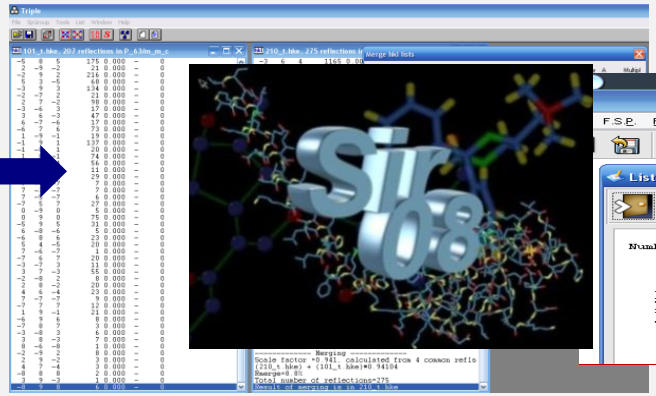
http://www.ic.cnr.it/registration_form.php

FullProf suite : **http://www.ill.eu/sites/fullprof/**

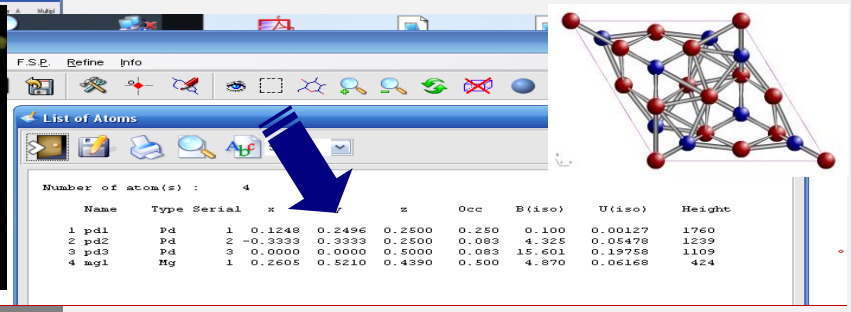
Use precession diffraction intensities to solve crystal structures

In this example PED intensities from 5 zone axis (ZA) from **Mg_5Pd_2 nanocrystal** have been collected with a 100 kV TEM. Use of **SIR2008** direct methods software allowed direct calculation of all the (Mg,Pd) atomic positions.

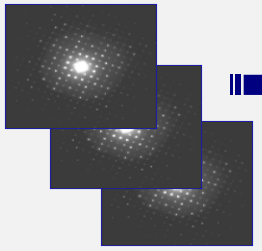




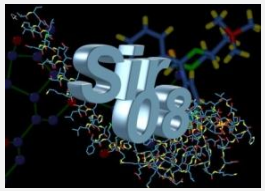
P 6_3/mmc, a=0.867 nm c= 0.816 nm

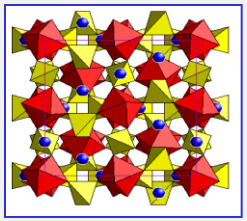


Collection of **3 ZA ([0 0 1], [1 0 1] ,[1 0 2]) PED intensities** with a 200KV TEM from **uvarovite mineral $Ca_3Cr_2(SiO_4)_3$ cubic Ia-3d a=1.2nm** and the use of SIR2008 revealed precise atomic structure (see table) ***calculated atomic positions are very close to X-Ray*** 3D refined atomic model



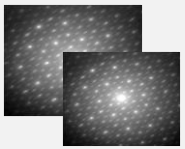
h	k	l	F (hkl)
0	6	0	6031
3	5	0	5981
5	1	0	5570
5	2	0	4751
2	7	0	4262
4	0	0	4189
3	6	0	3782
5	3	0	3705
5	4	0	3315
2	6	0	3285
3	4	0	2958
4	5	0	2763
4	3	0	2657
6	0	0	2278
1	8	0	2111
4	4	0	1868
4	2	0	1607
3	2	0	1512

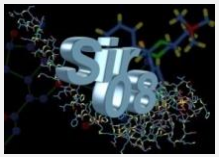




Atom	X(Sir)	Y(Sir)	Z(Sir)	X(Pub)	Y(Pub)	Z(Pub)	Distance
Cr	0.000	0.000	0.500	0.500	0.000	0.500	0.00000
Ca	0.000	0.750	0.375	0.750	0.125	0.500	0.00000
Si	0.000	0.750	0.625	0.750	-0.125	0.500	0.00000
O	0.654	0.963	0.455	0.039	0.047	0.653	0.02687

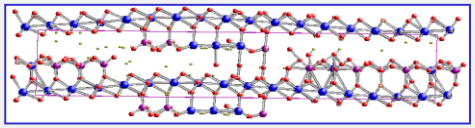
Using set of simulated PED intensities from 2 ZA of complex commensurate structure of **antigorite mineral ~$Mg_3Si_2O_5(OH)_4$** and solving with direct methods (SIR2008), **most of the atomic positions are revealed**



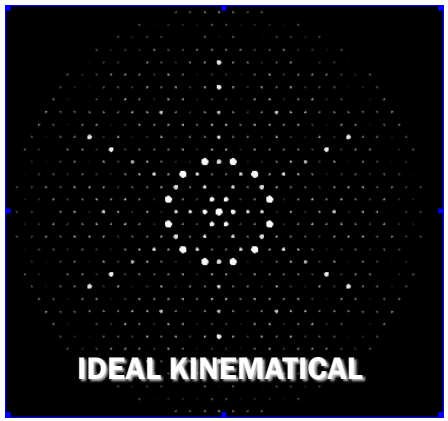


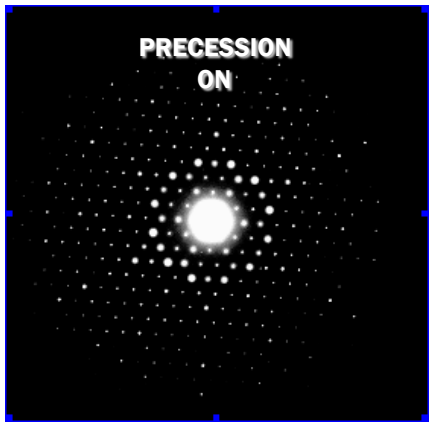
Model after SIR2008 procedure

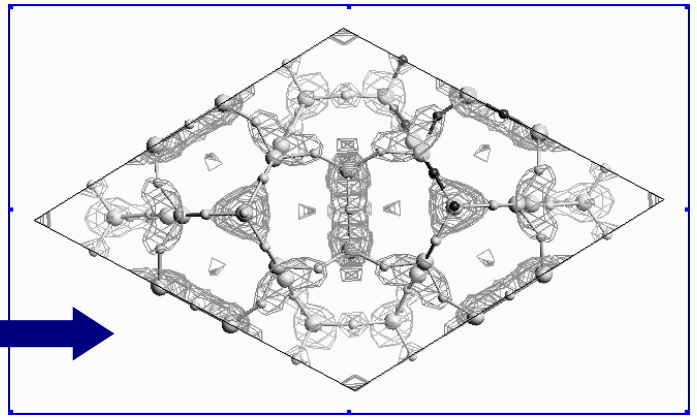
132/147 atoms found

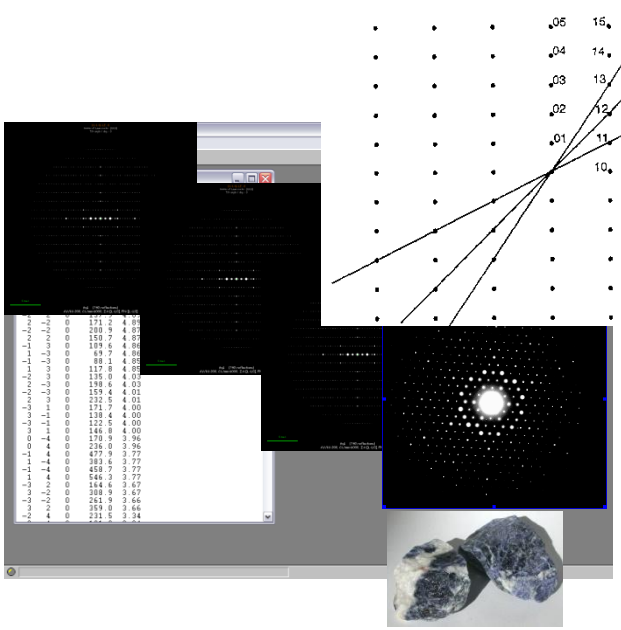


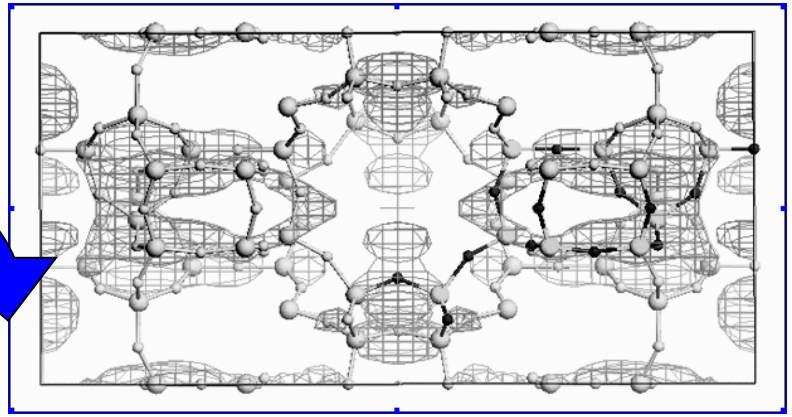
Ab initio determination of MCM-22 (ITQ-1) zeolite framework





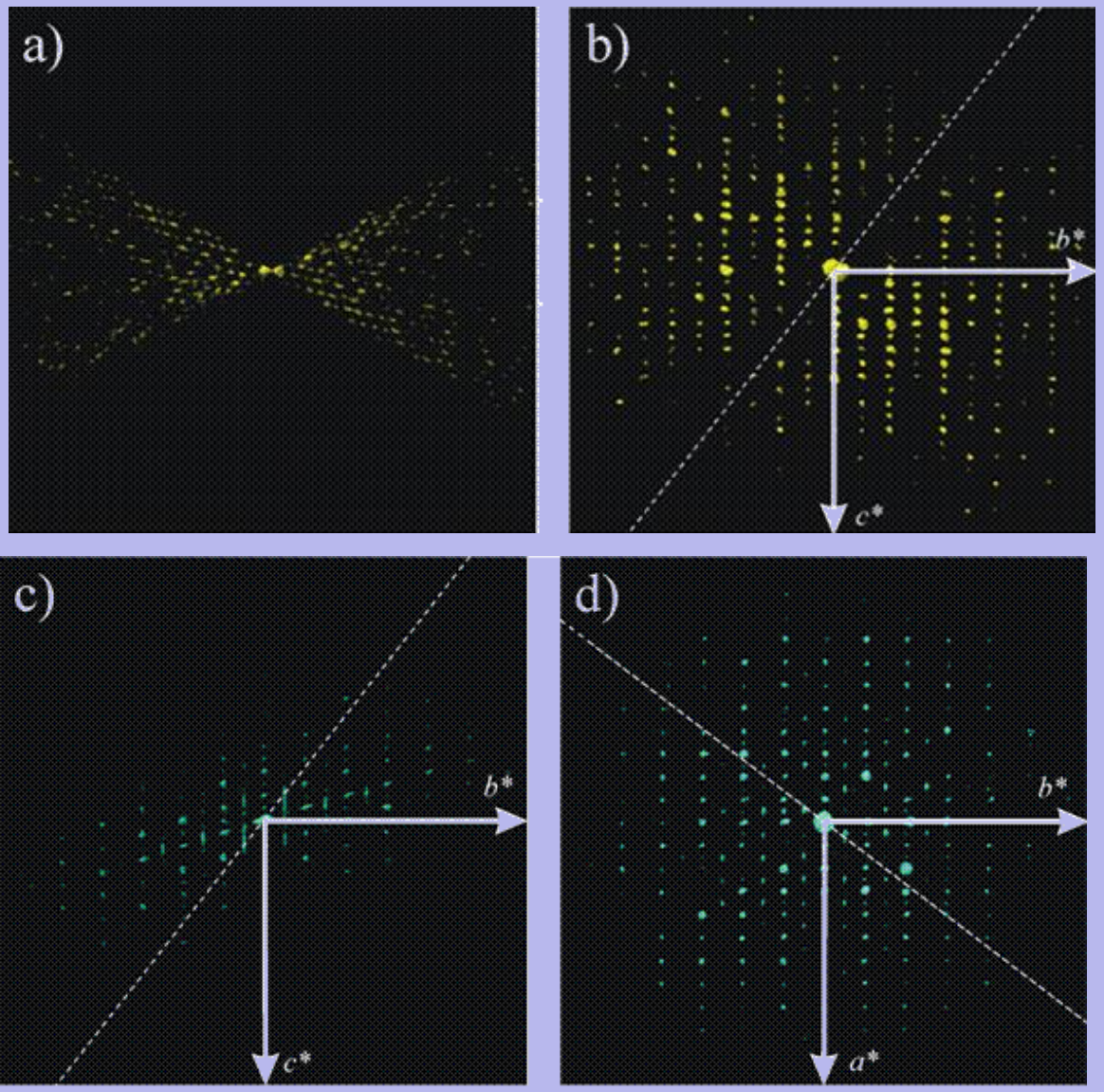




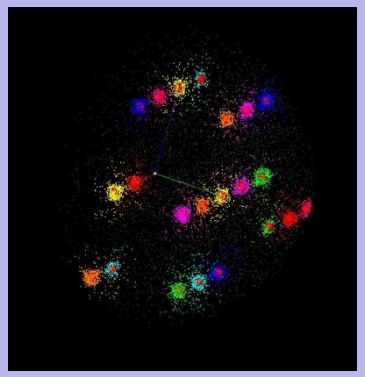


3D frameworks can be revealed by collecting and combining quasi-kinematical precession electron diffraction intensities from different zone axis to one 3D electron diffraction data set (image courtesy Douglas Dorset USA)

3D precession electron diffraction tomography (ADT)
3D visualization - Detection of disorder



Cell parameter determination
on single
nanoparticle



Conference by Dr. Gorelik

Courtesy : Prof. U Kolb UMainz

Characterization

for new unknown compound

Find crystal cell parameters

Find atomic crystal structure

Texture – (multi) phase analysis

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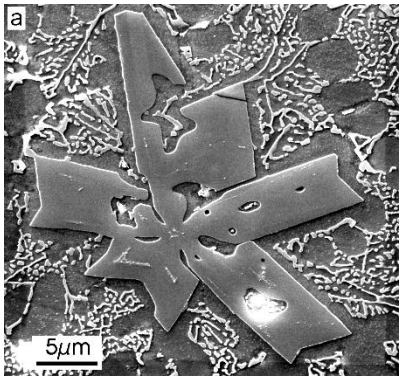
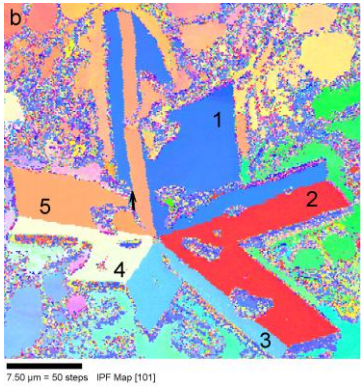
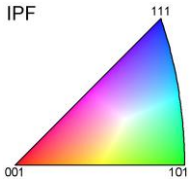
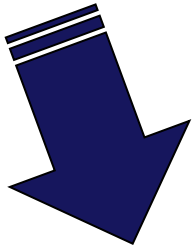
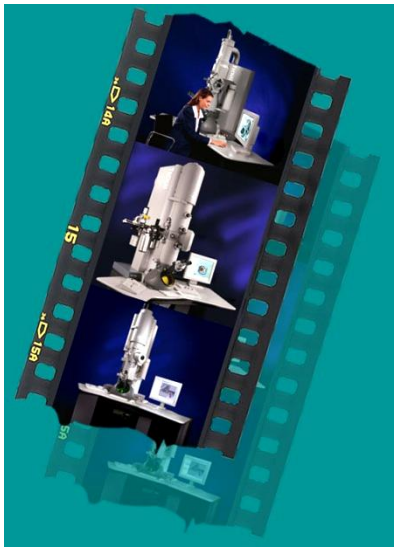


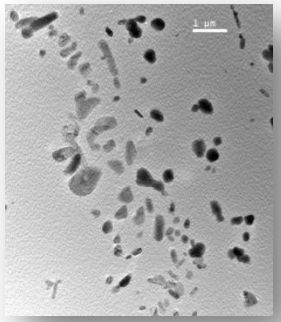


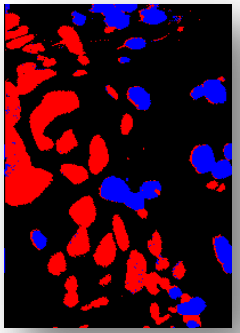


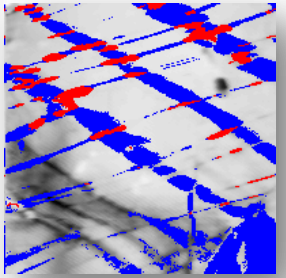


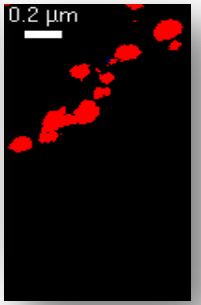
NEW precession application
“EBSD” – TEM











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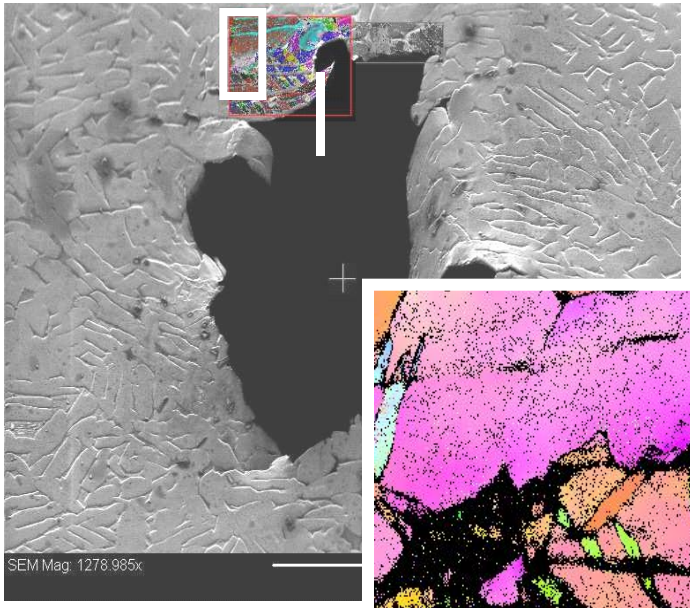
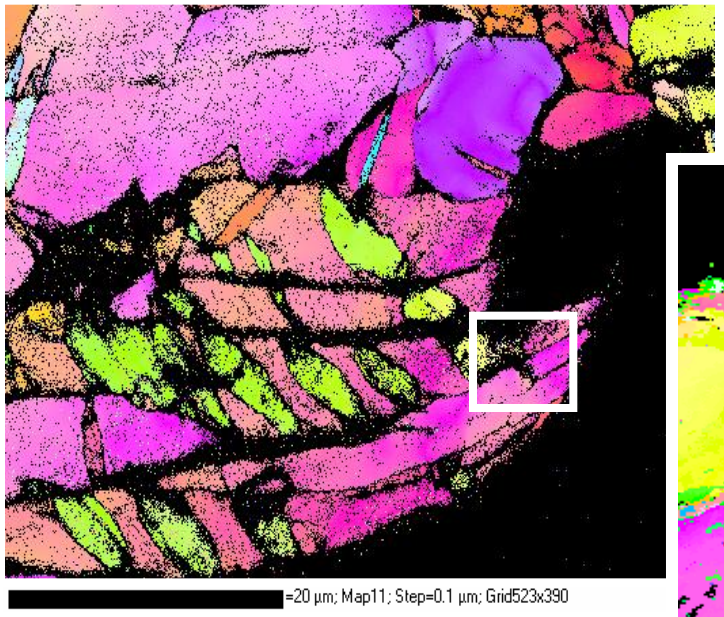
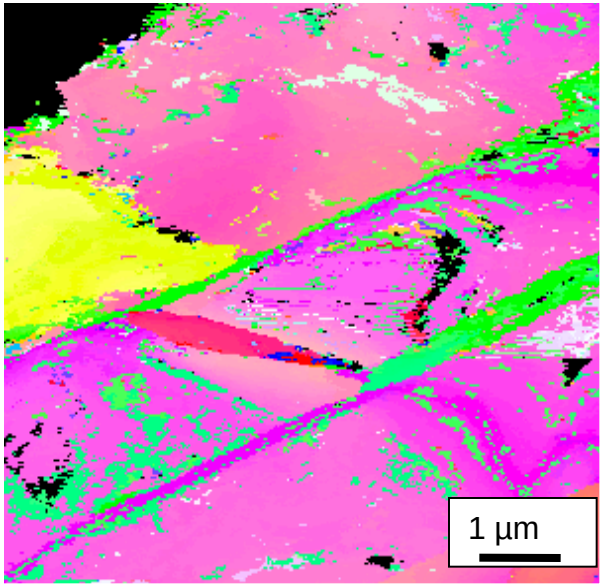
Comparison SEM-(EBSD) vs TEM spatial resolution



SEM orientation map
deformed Ta_6V alloy



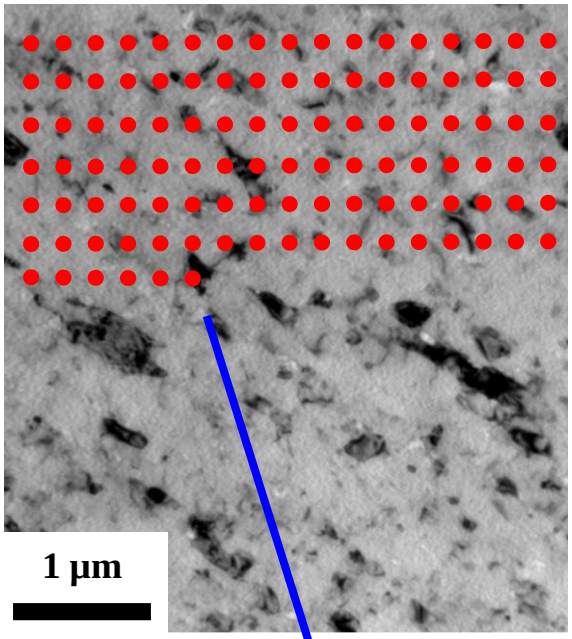
TEM orientation map
(1-10 nm stepsize)

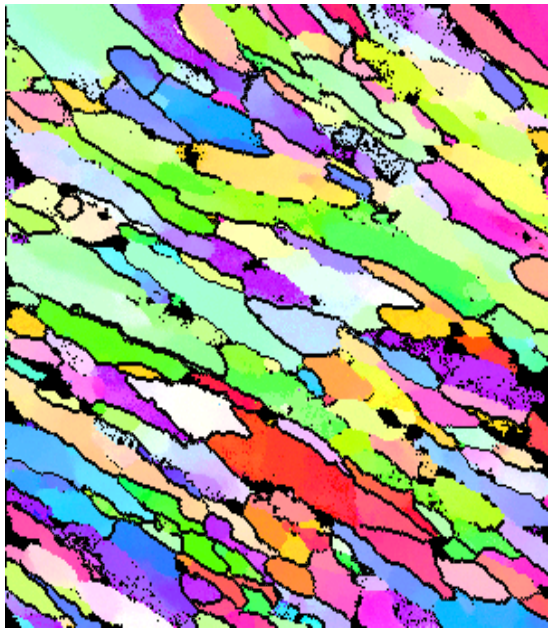


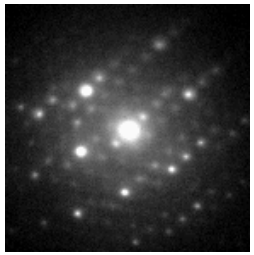
EBSD-SEM map (50 nm resolution)

Electron Backscattering Diffraction (EBSD) orientation maps in SEM have usually poor resolution in comparison with TEM maps showing detailed nanostructure

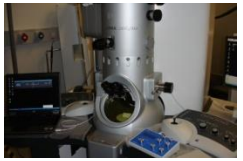
ASTAR : diffraction pattern adquisition







Example :Severely deformed 7075 Aluminium Alloy



Any TEM –FEG/LaB6 may work with ASTAR

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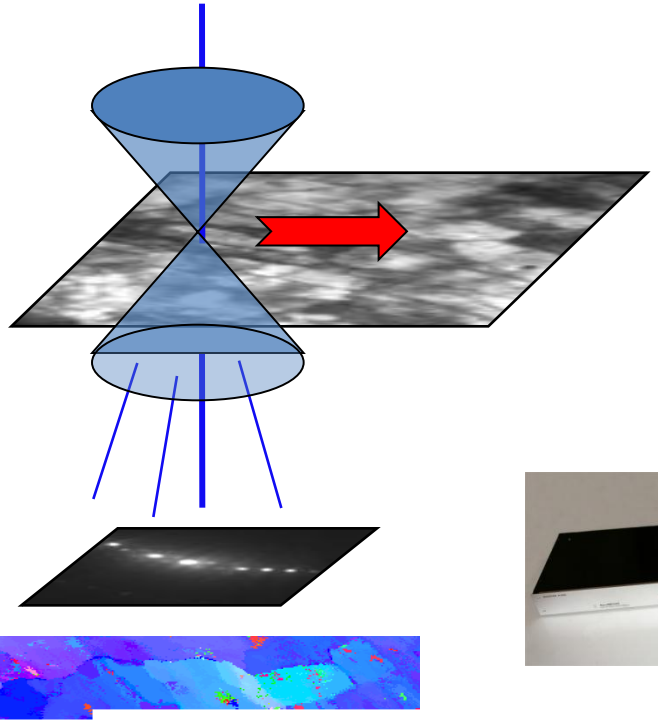
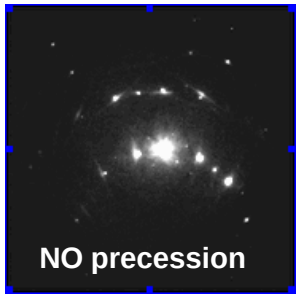
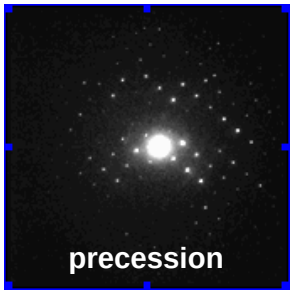
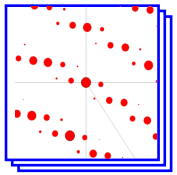
ASTAR (EBSD-TEM like procedure)



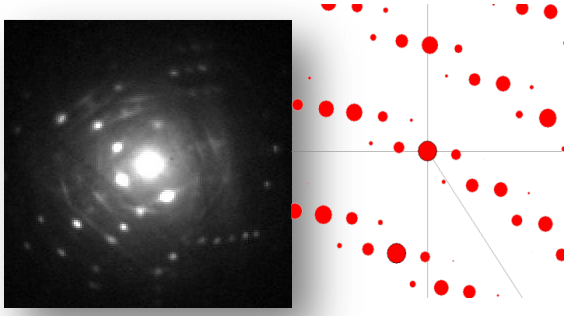
Orientation map

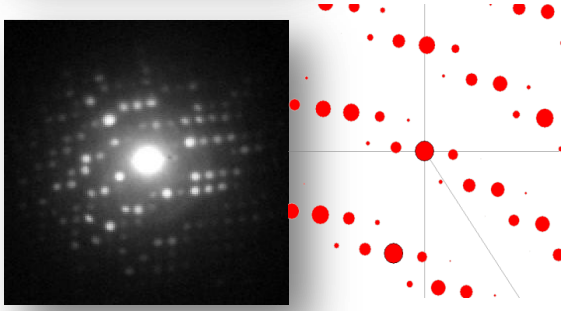






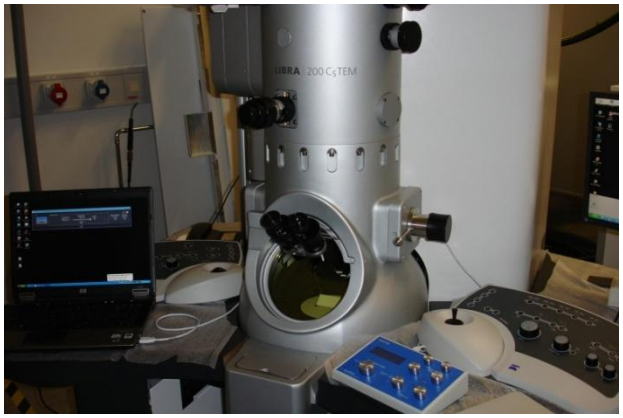
Using precession diffraction the number of ED spots observed increases (almost double) ; correlation index map becomes much more reliable when compared with templates

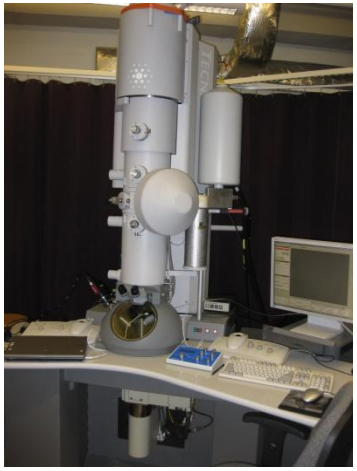


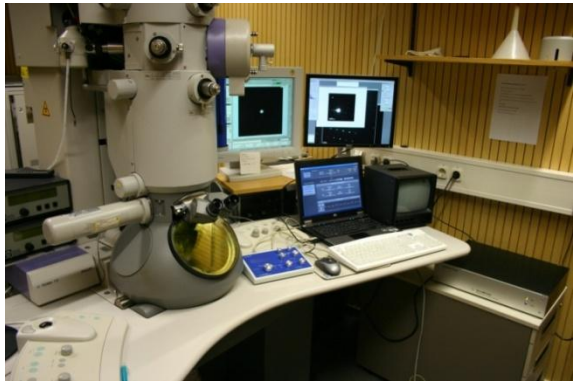


In this example (right) a metal particle gives wrong correlation index without precession due to presence of Kikuchi lines; after applying precession (right lower image), index gets correct value as ED quality improves and Kikuchi lines dissapear

ASTAR phase –orientation mapping for advanced TEM







Zeiss LilBRA 200F Cs corr TECNAI 20F TECNAI 30F

JEOL 2200 FS JEOL 2010F

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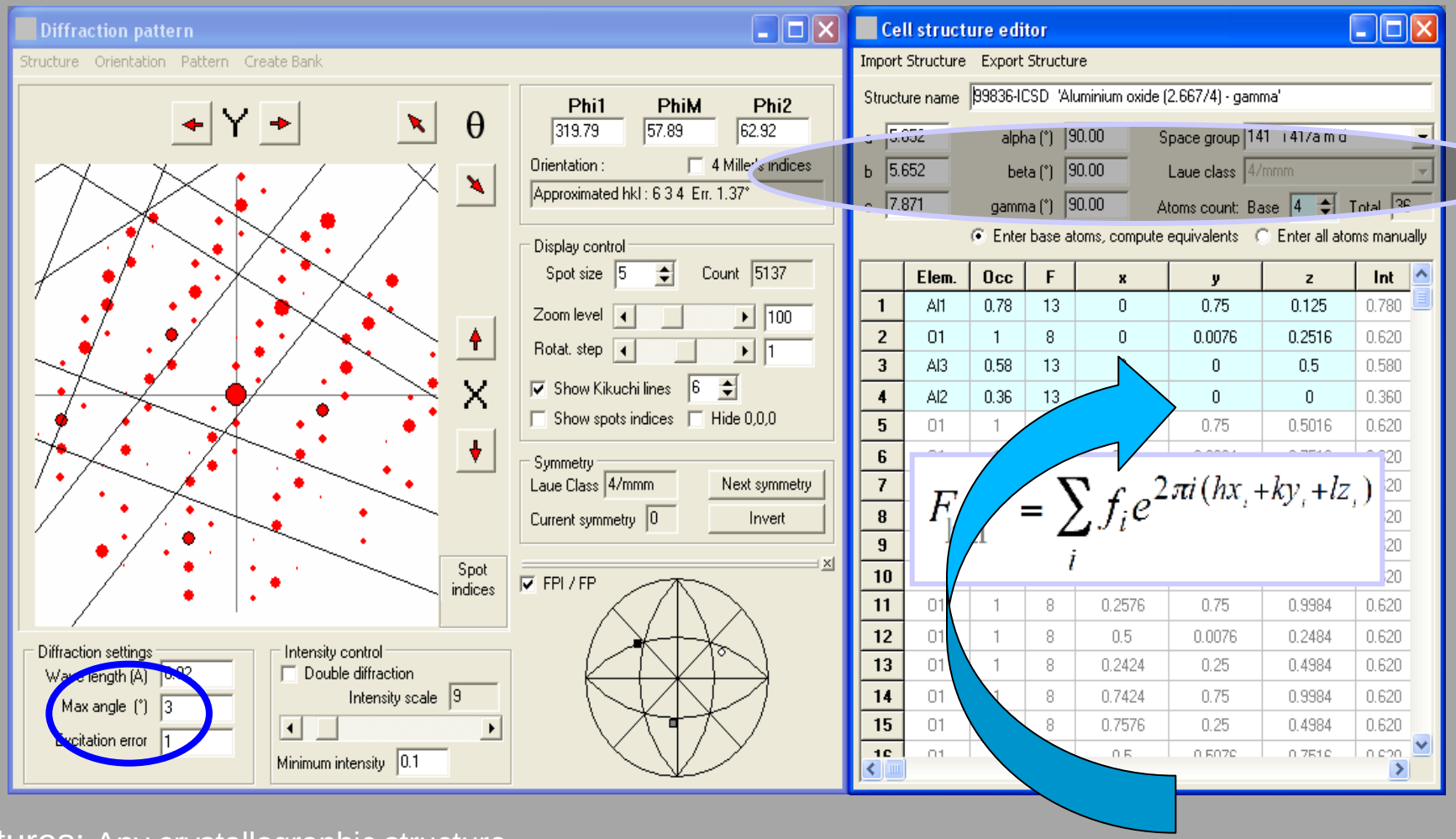
DiffGen : Template generator



Features: Any crystallographic structure
Laue class adapted to the space group
Structure generator (space group, structure factor equ.)

input from ICDD database

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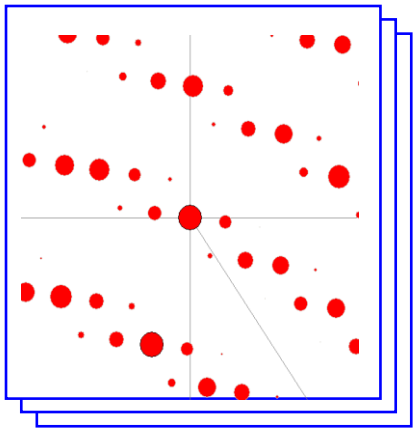
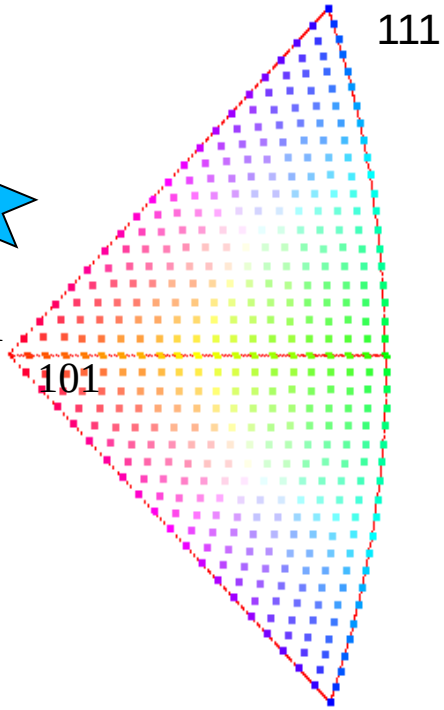
ASTAR : crystallographic orientation identification

Pre-calculated templates



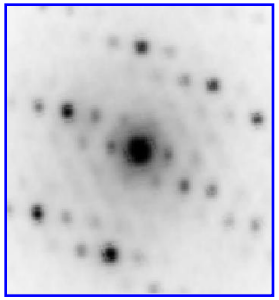
Template generation of all possible simulated orientations (every1º) within stereographic triangle for given crystal lattice(s) and symmetry



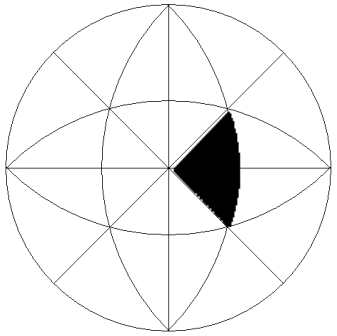
Stereographic projection

$$Q(i) \sim \sum_{j=1}^{m} P(x_j,y_j)\, T_i(x_j,y_j)$$

Correlation index



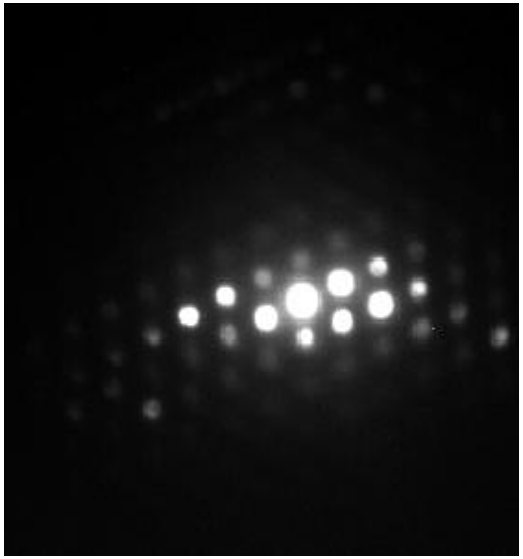
Acquired pattern



Degree of matching between experimental patterns and simulated templates is given by a correlation index ; highest value corresponds to the adequate orientation/phase

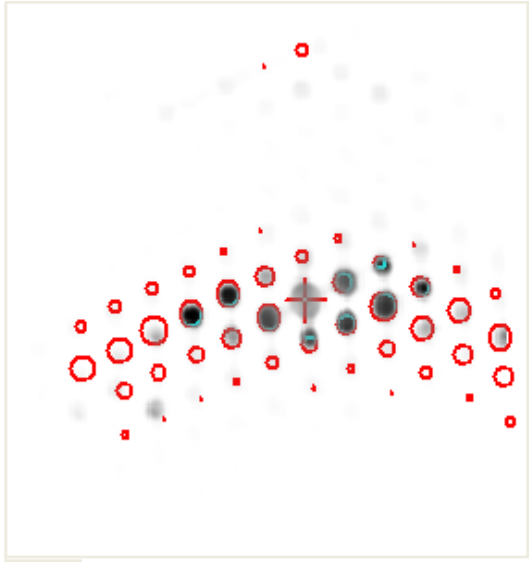
(example ,cubic)~ **2000 simulated patterns**

ASTAR identification example : nanocrystalline Cu

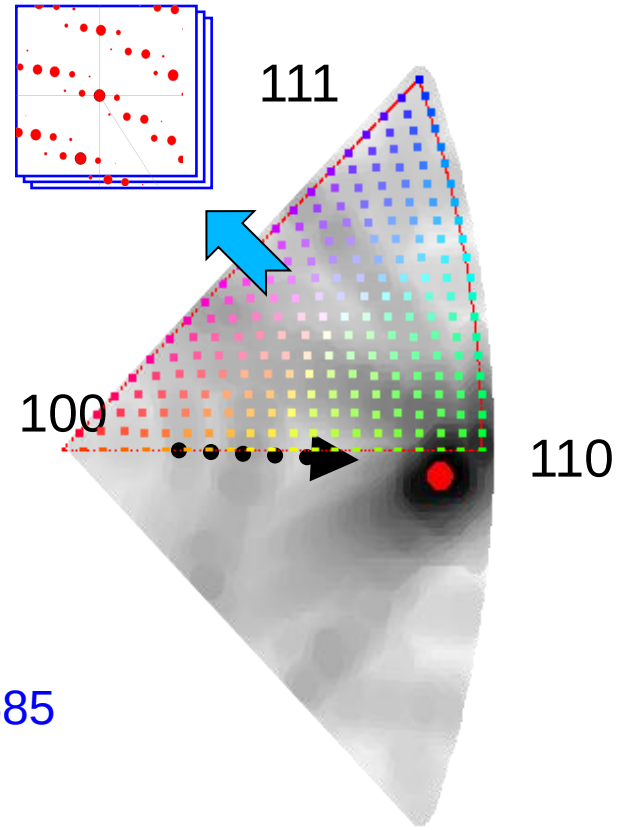


Diffraction pattern

(nanocrystalline cubic copper)



correlation index = 585



Correlation index map

For a given ED pattern, the correlation index map is calculated for all possible template orientations and plotted on a map that represents a portion of the stereographic projection (reduced to a double standard triangle). That resulting map reveals the most probable orientation for every experimental spot ED pattern (in this case ED pattern is found to be close to 110 ZA orientation)

ASTAR : ultra-fast TEM orientation map

Sample : severely deformed copper

Orientation map

250 x 200 pixel data adquisition

5-10 min

Typical software data analysis time (for cubic)

5-15 min

(hexagonal , tetragonal)

x 3- 4 more time

Map resolution equals beam size resolution

NBD step 20 nm (LaB6)

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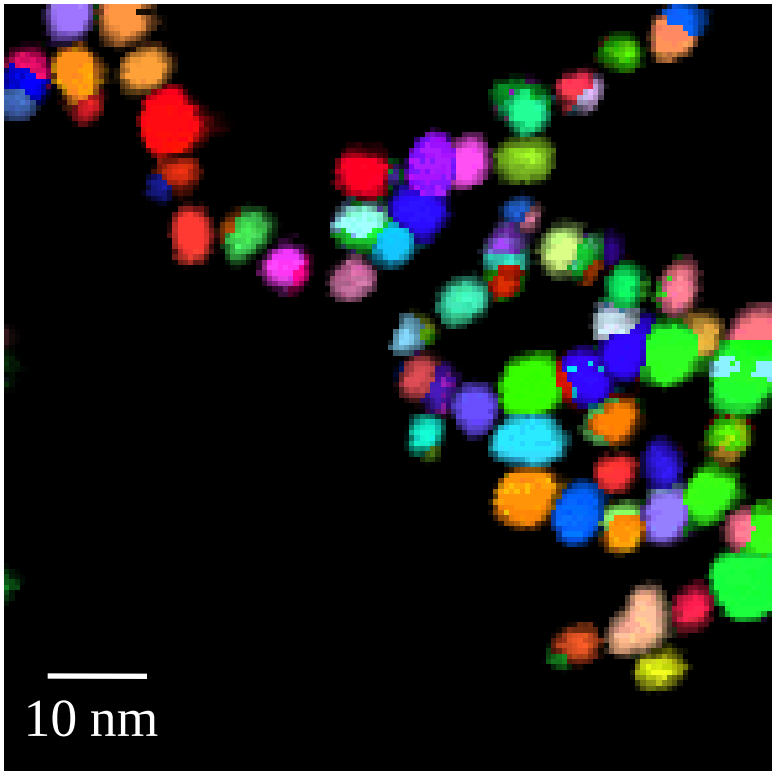
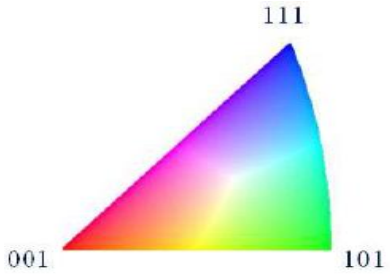
Power of the ASTAR Technique : nanoparticles

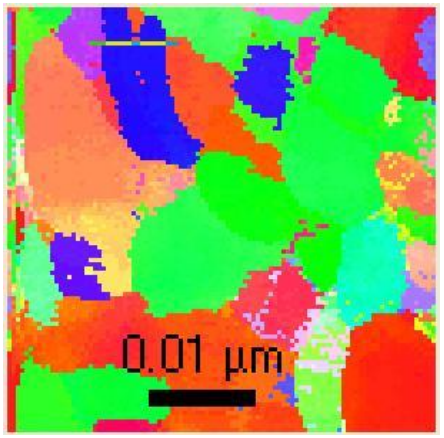


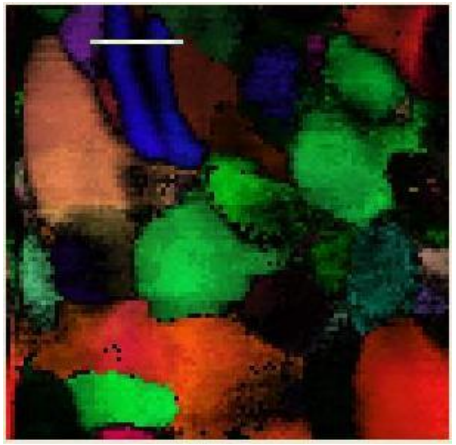


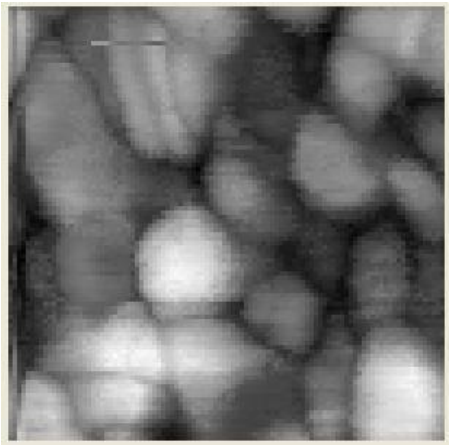
ASTAR : Orientation analysis from Pt ~100 particles ~ 6 nm in size

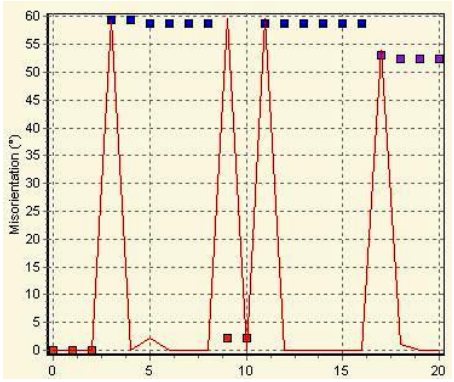
1 nm resolution for orientation map

Data courtesy Prof. P.Ferreira, J.Ganesh Univ Texas at Austin USA **JEOL 2010 FEG**





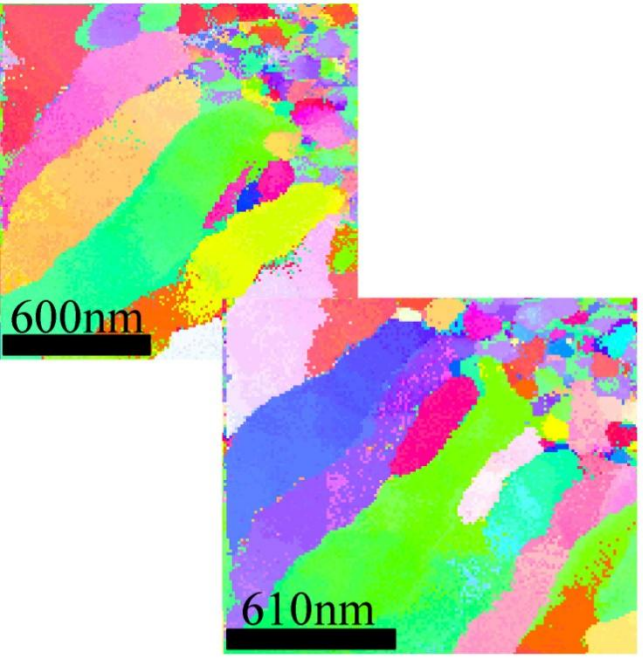


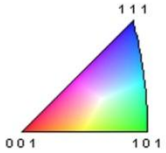


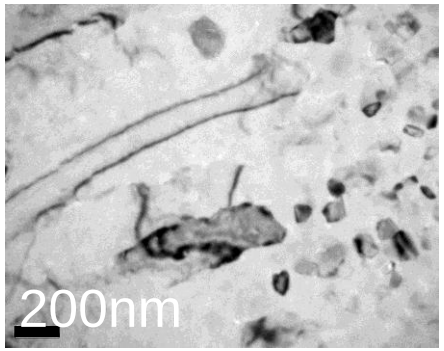
Pd nanoparticles
0.4 nm twin structure details !

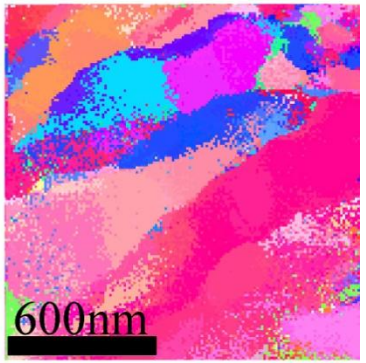
Jeol 2200 FS Humboldt Univ Berlin courtesy Dr. H.Kirmse, I. Heusler

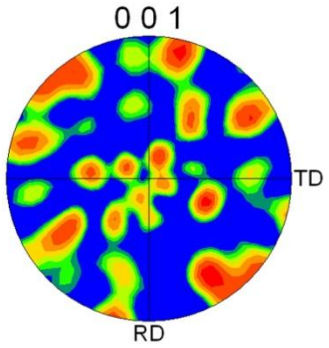
This 8 nm bar is most clearly visible in (b) and divided into 20 sections of 0.4 nm each (that represent the utilized scanning-precession increments of the primary electron beam) in (d). Note that there are jumps in the local mis-orientation profile along the 8 nm bar of almost 60º between sections 3 and 4, 8 and 9, as well as 10 and 11.

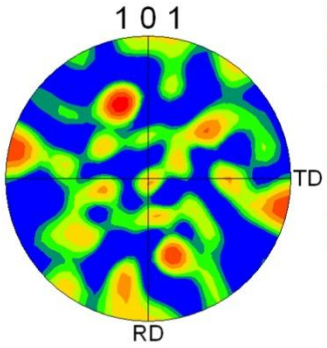


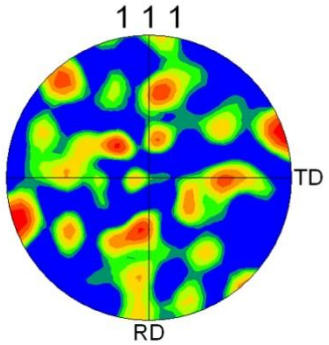




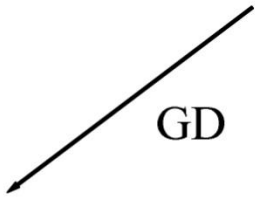








EBSD-TEM like (ASTAR)



COMPARISON –COMBINATION
texture analysis
EBSD-SEM --- EBSD-TEM (ASTAR)

→ texture analysis of several areas (combined)

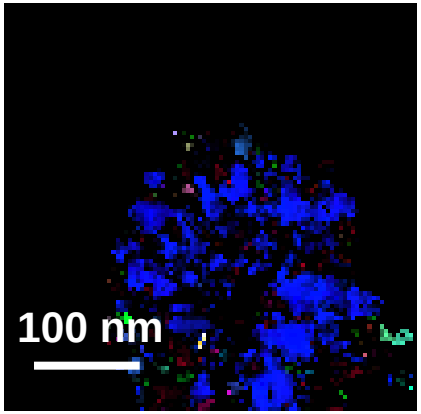
→ 20 nm to 40 nm step size in LaB6-TEM scans sufficient to capture morphology of microstructure with high fidelity (ASTAR)

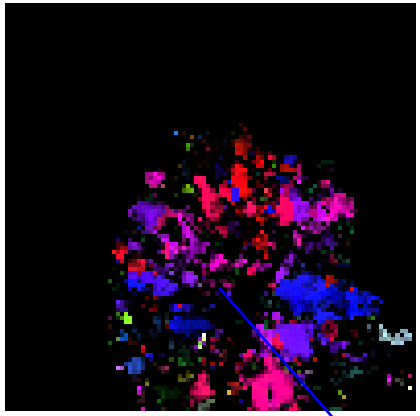
→ASTAR orientation data can be read/analyzed by TSL –HKL software

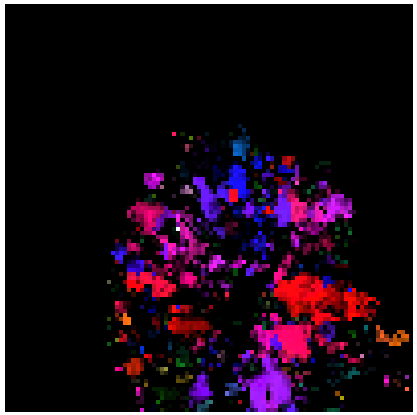
Data courtesy A. Kulovits, G. Facco, H. Kotan, Jörg M.K. Wiezorek

University of Pittsburgh USA

Problem : distinguish nanoparticles rutile - anatase (TiO_2) texture



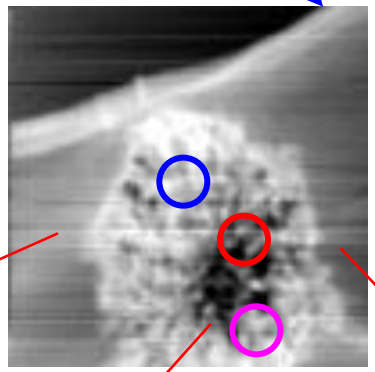


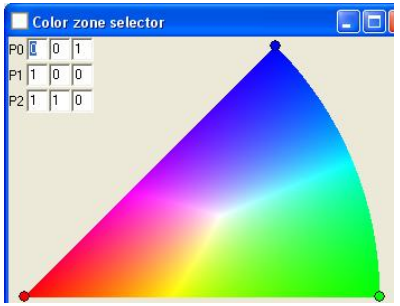


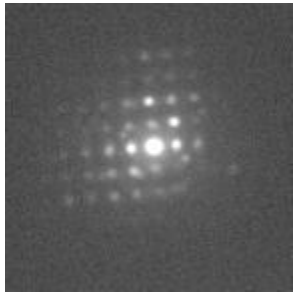
Rutile P4₂ /mnm **a = 4.59 A , c = 2.95 A**

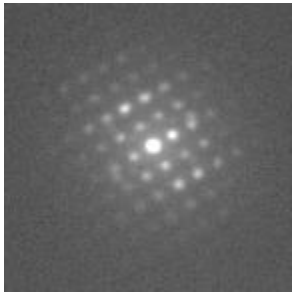
Courtesy Dr. Bakardieva REZ Prague

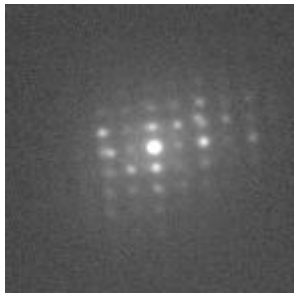
Jeol 3010 – ASTAR











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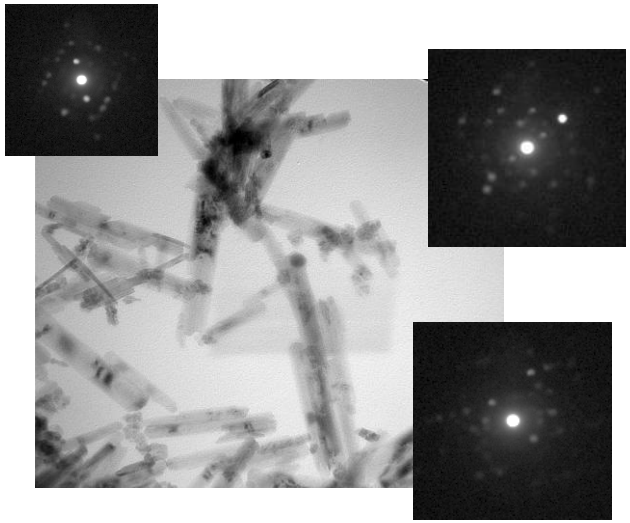
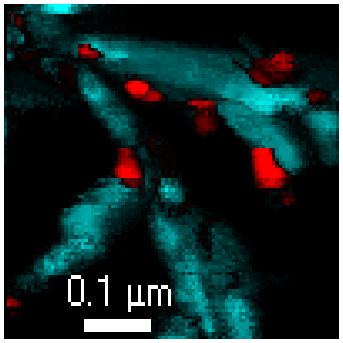
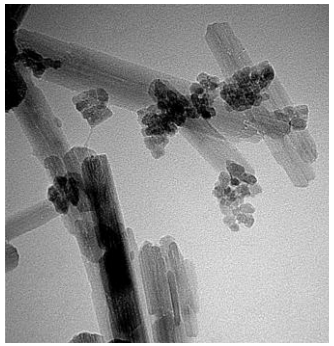
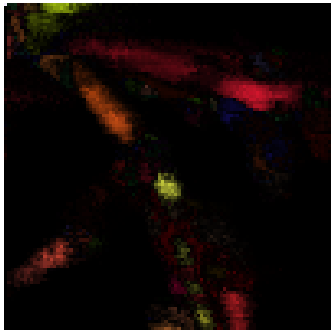
PROBLEM : distinguish between goethite (alpha-FeO(OH)) 300x40x10nm

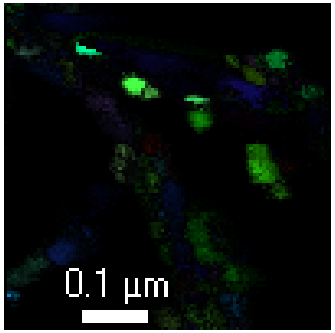
and brookite (TiO2) platelets of 48nm diameter

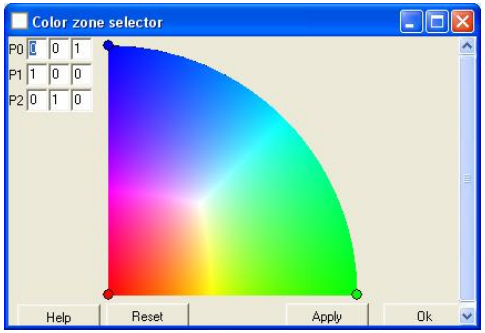












Orientations (alpha-FeO(OH)) *BrookiteTiO2* *Code de couleur*

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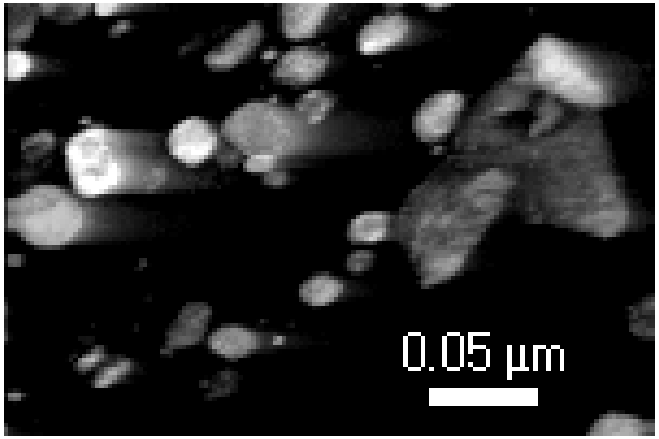
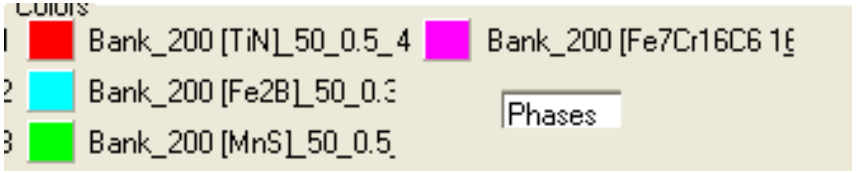
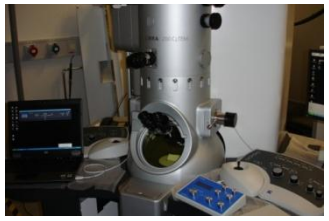
Libra 200-ASTAR : sub-nanometer (< 1 nm) phase map

Replica with TiN, Fe_2B, MnS and Fe_6Cr_6



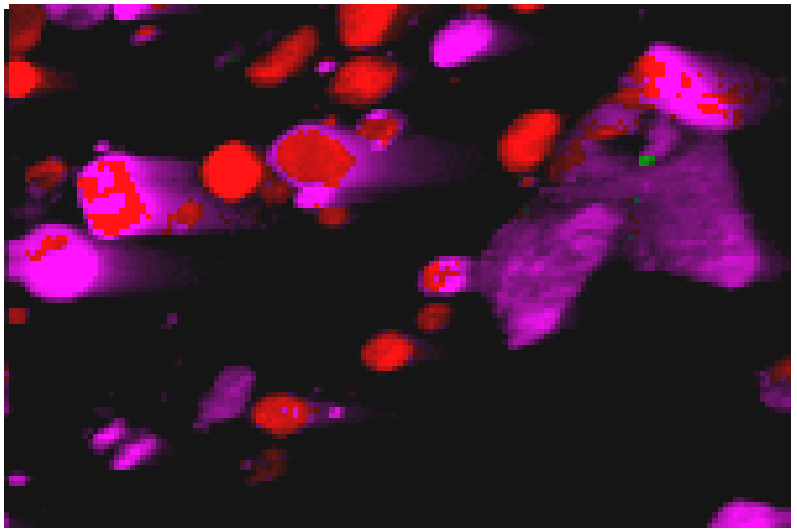
Index correlation map





Phase map can distinguish between 3 phases :

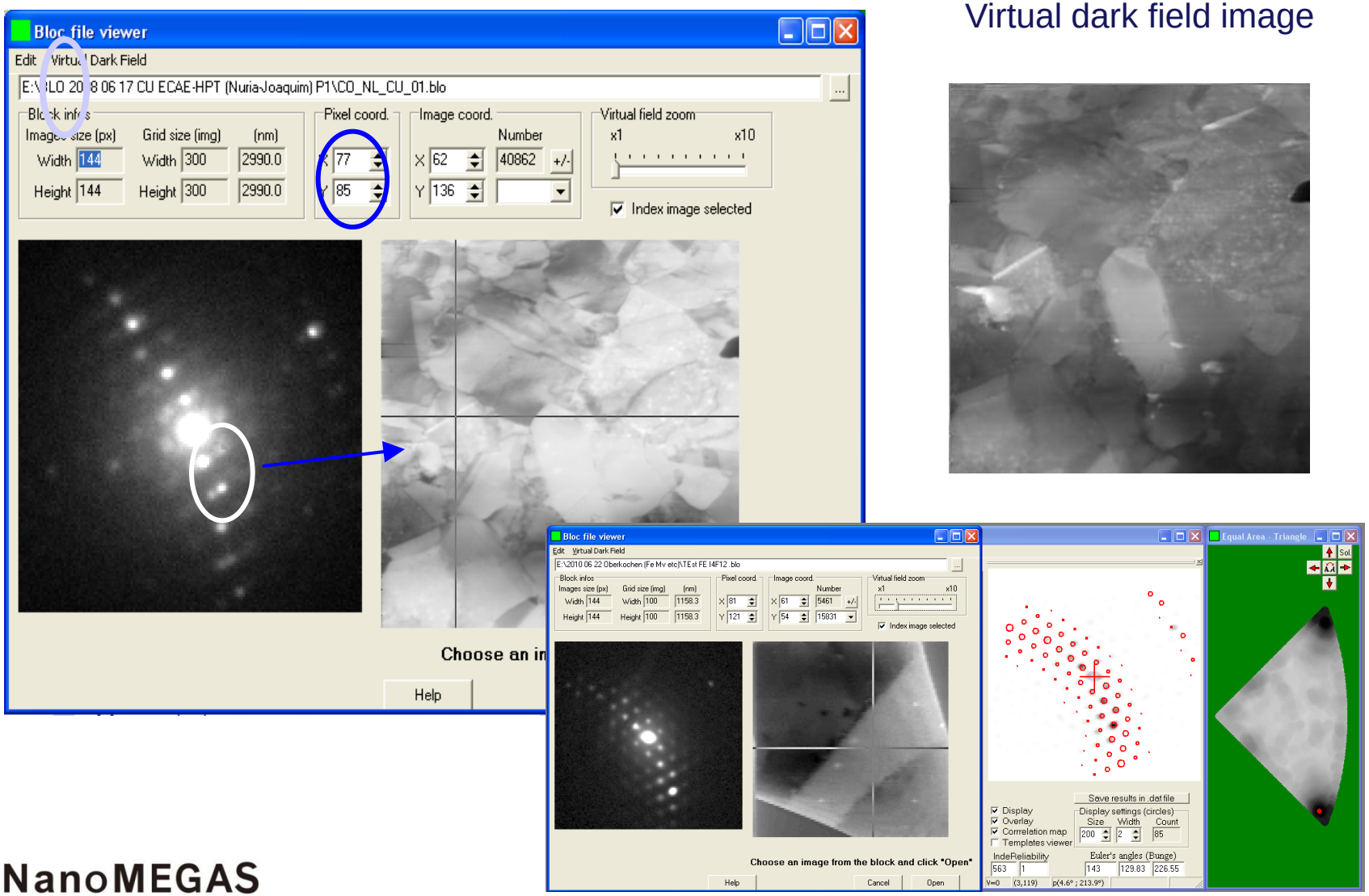
TiN, Fe_2B, MnS and Fe_6Cr_6



< 1 nm resolution phase map

INDEX and create virtual dark and bright field maps

Diffraction Pattern viewer with virtual aperure



Virtual dark field image

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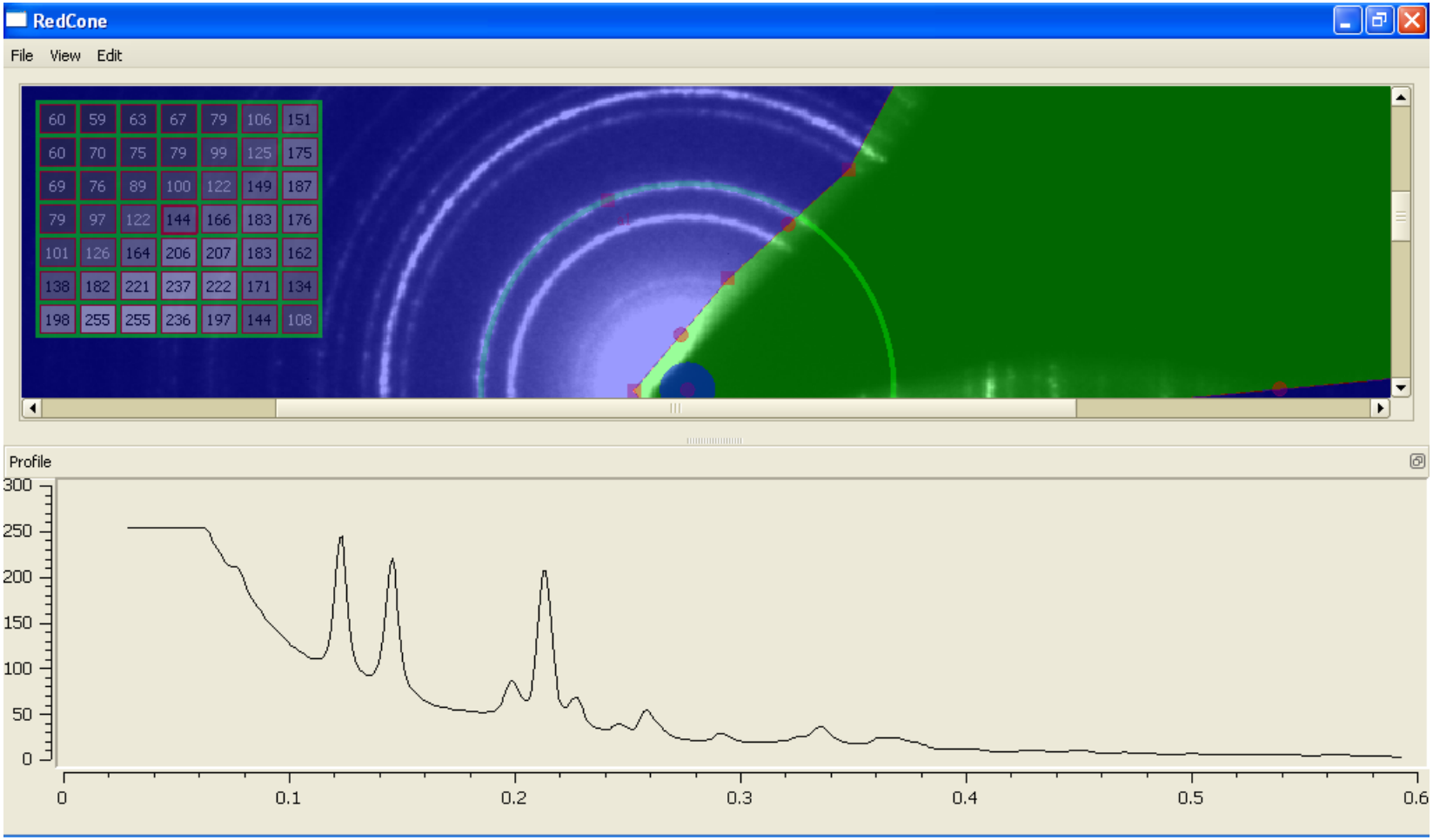
Polycrystalline Electron diffraction

“ X-Ray amorphous” OR nanocrystalline ?



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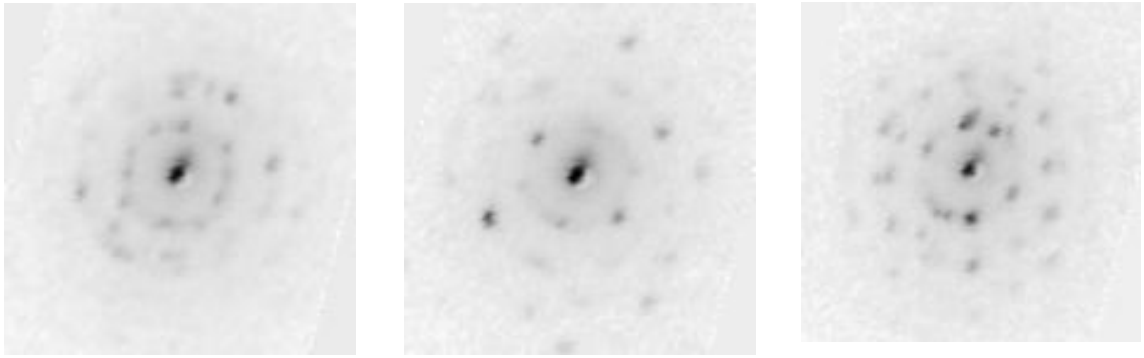
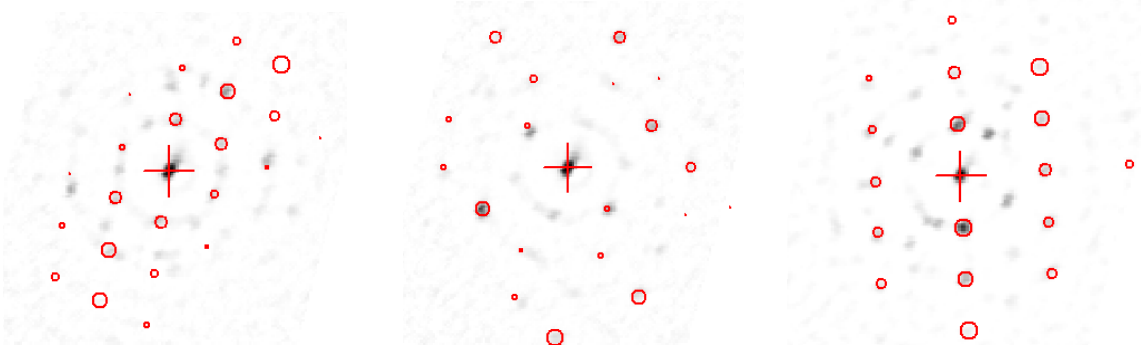
Orientation mapping on Nanocrystallized polycrystalline Ni-Fe sample

Pollycrystalline thin film of Ni-Fe nanocrystals (average size 5-20 nm)

Data taken with JEOL JEM 2200F operating at 200 kV spot size 1-8 nm



ASTAR can index even overlapping diffraction patterns from polycrystalline sample



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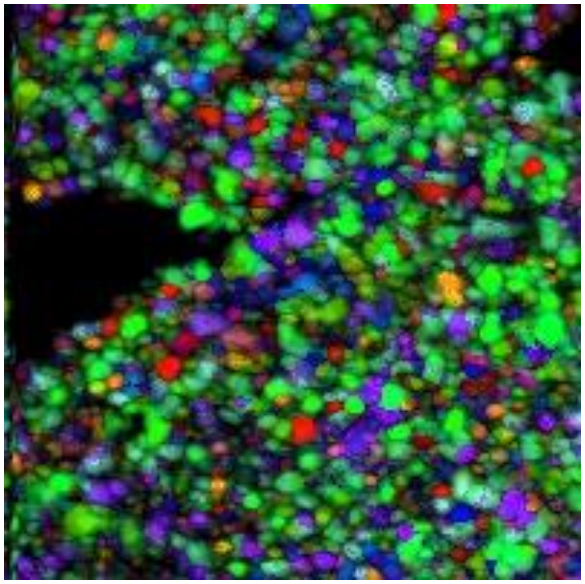
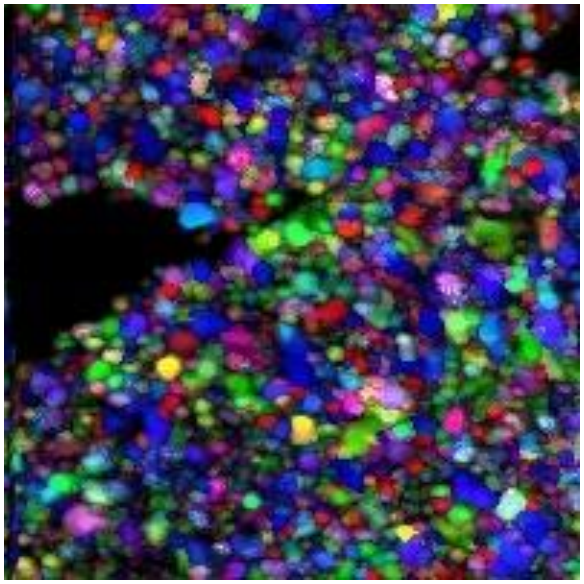
Results courtesy Prof. Dr. E.Rauch CNRS Grenoble

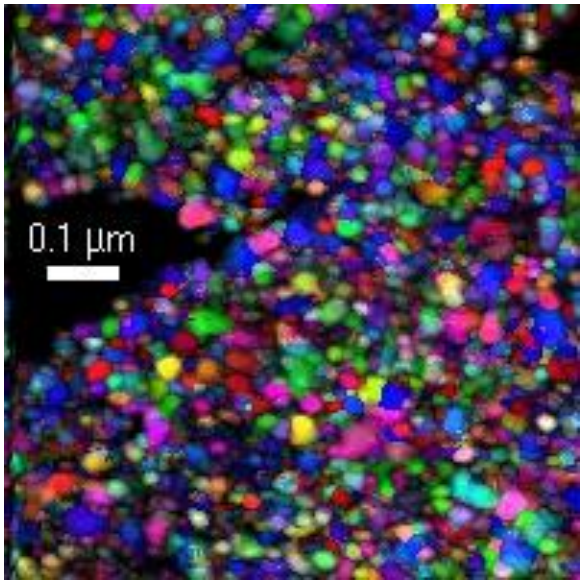
Crystallographic orientation map



Orientation map (z)
+ index



Orientation map (x)
+ index



Orientation map (y)
+ index

As for EBSD equipments, the orientation of one particular axis (usually the z axis) is given through a colour code. This enables the individual crystals to be recognized and/or their size to be estimated (step size 4 nm)

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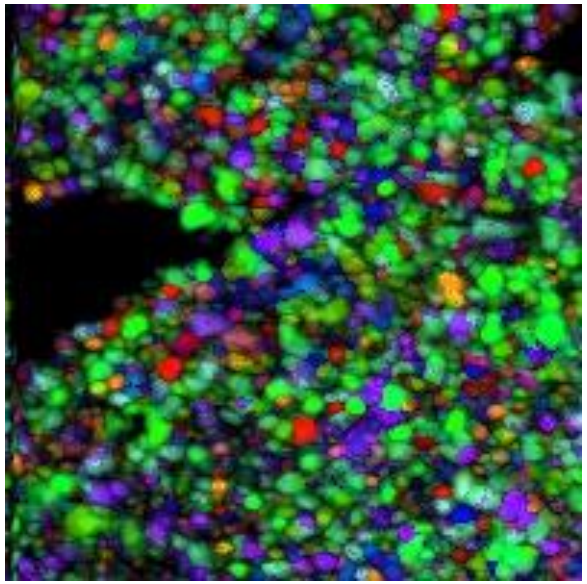
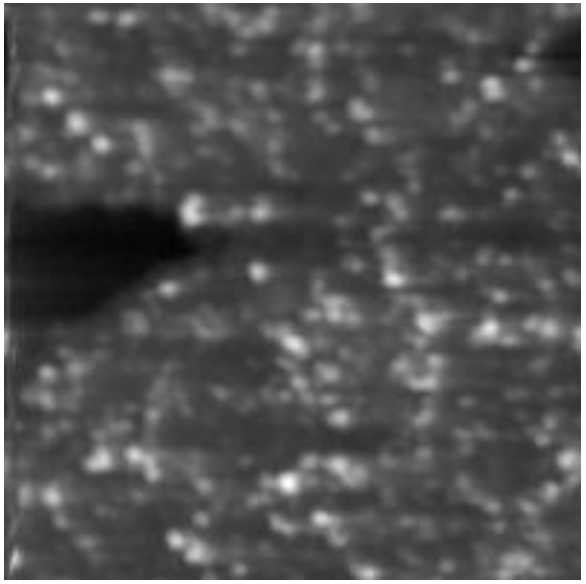
JEOL 2200 FS 200 KV, Humboldt Univ Berlin

Step size 4 nm



Orientation map (z)

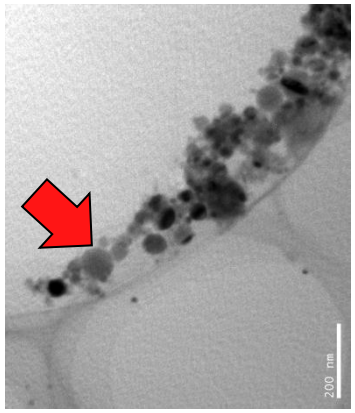


Virtual dark field map

A STEM type image is reconstructed from the collection of diffraction patterns. Virtual Dark Field images (VDF) may be reconstructed as well by selecting a particular reflection placing a virtual aperture on that selected spot on a diffraction pattern

JEOL 2200 FS 200 KV, Humboldt Univ Berlin

Nanoparticle (50 nm) phase identification



cubic 8.32 A

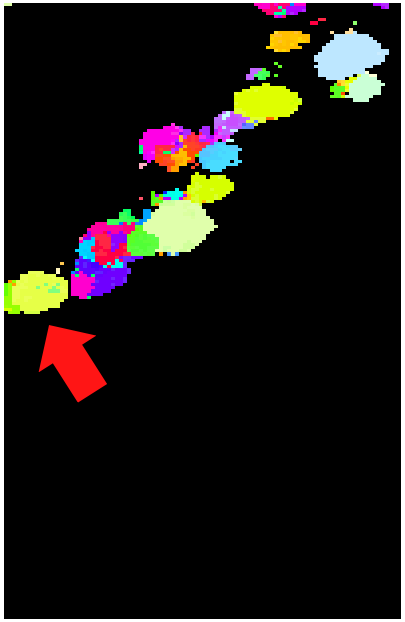
$Fd\bar{3}m$

Magnetite or maghemite ??

$P4_132$ **γ-Fe_2O_3**

Fe_3O_4

cubic 8.32 A



ALL Nanoparticles

REVEALED AS

magnetite (RED)

Orientation map precession 0.3º

PHASE map precession 0.3º

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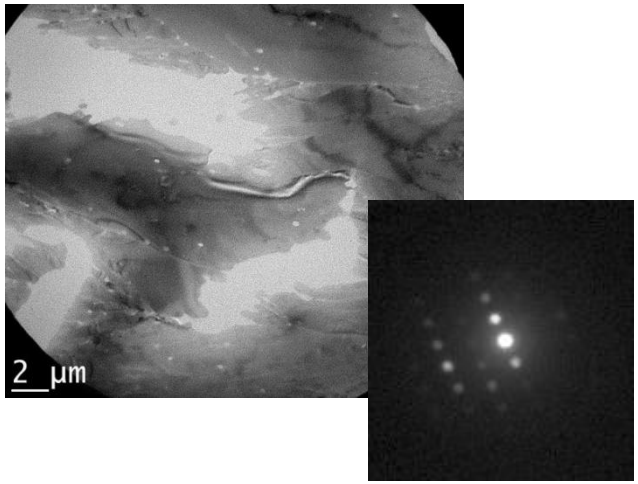
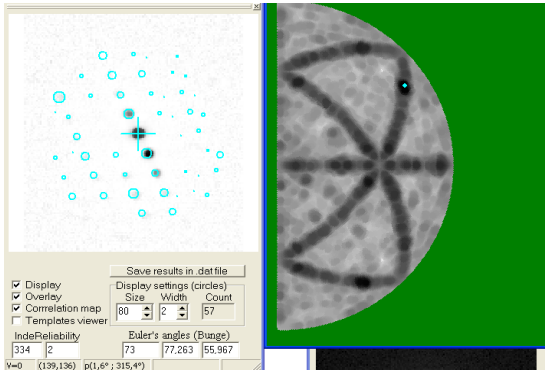
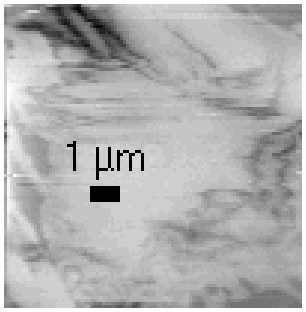
New application : ASTAR on organic structures

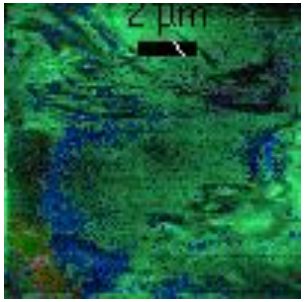


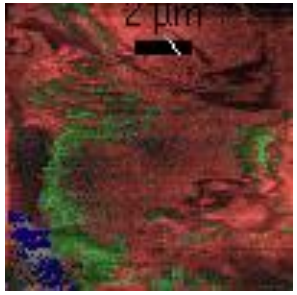
TRIS structure $C_{16}H_{48}N_4O_{12}$

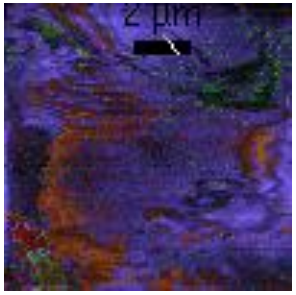
$Pna2_1$ cell 0.7768 X 0.8725 X 0.8855 nm

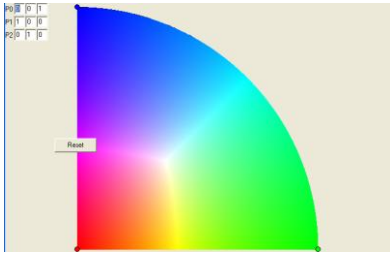












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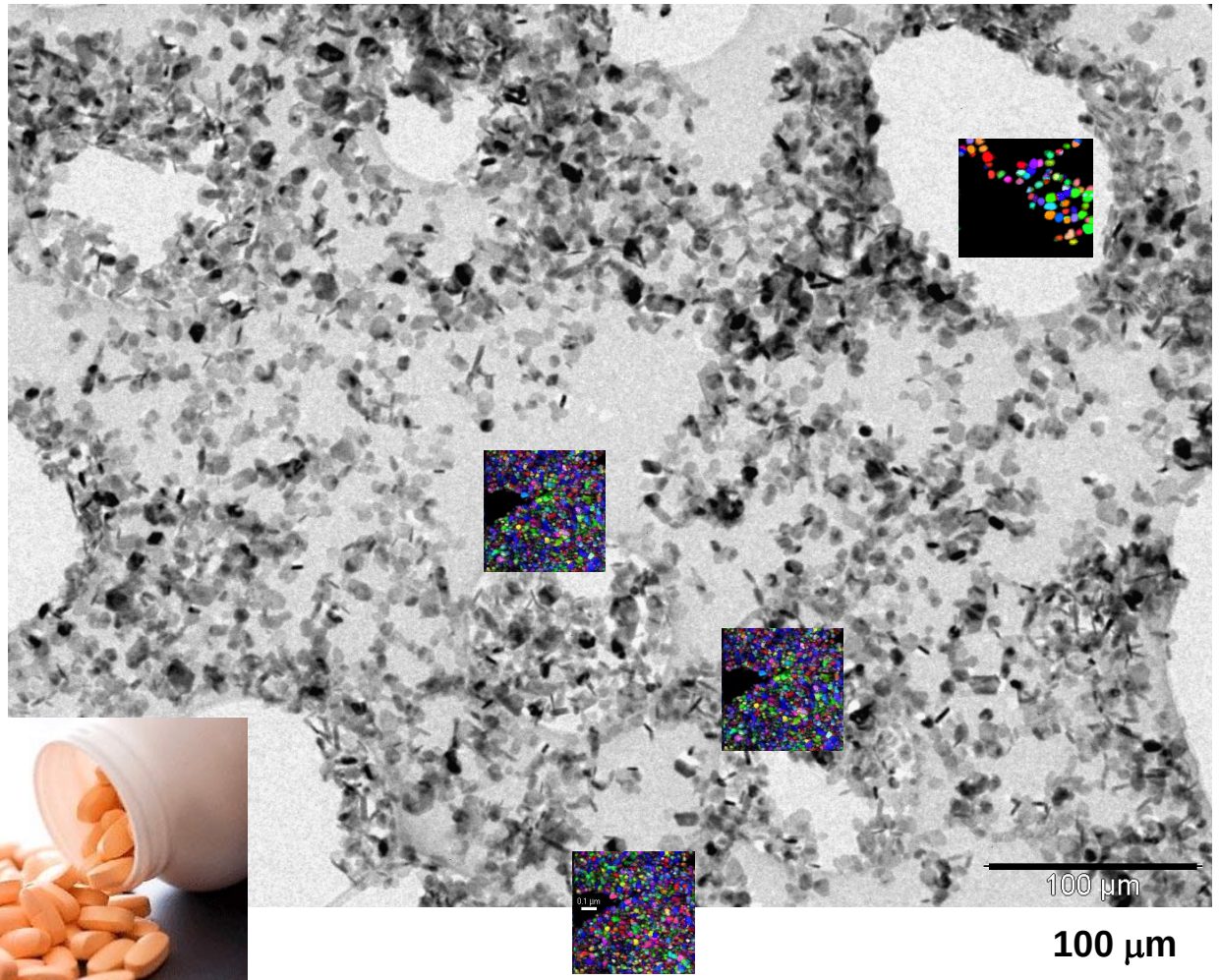
ASTAR texture – (multi) phase analysis from different sample areas

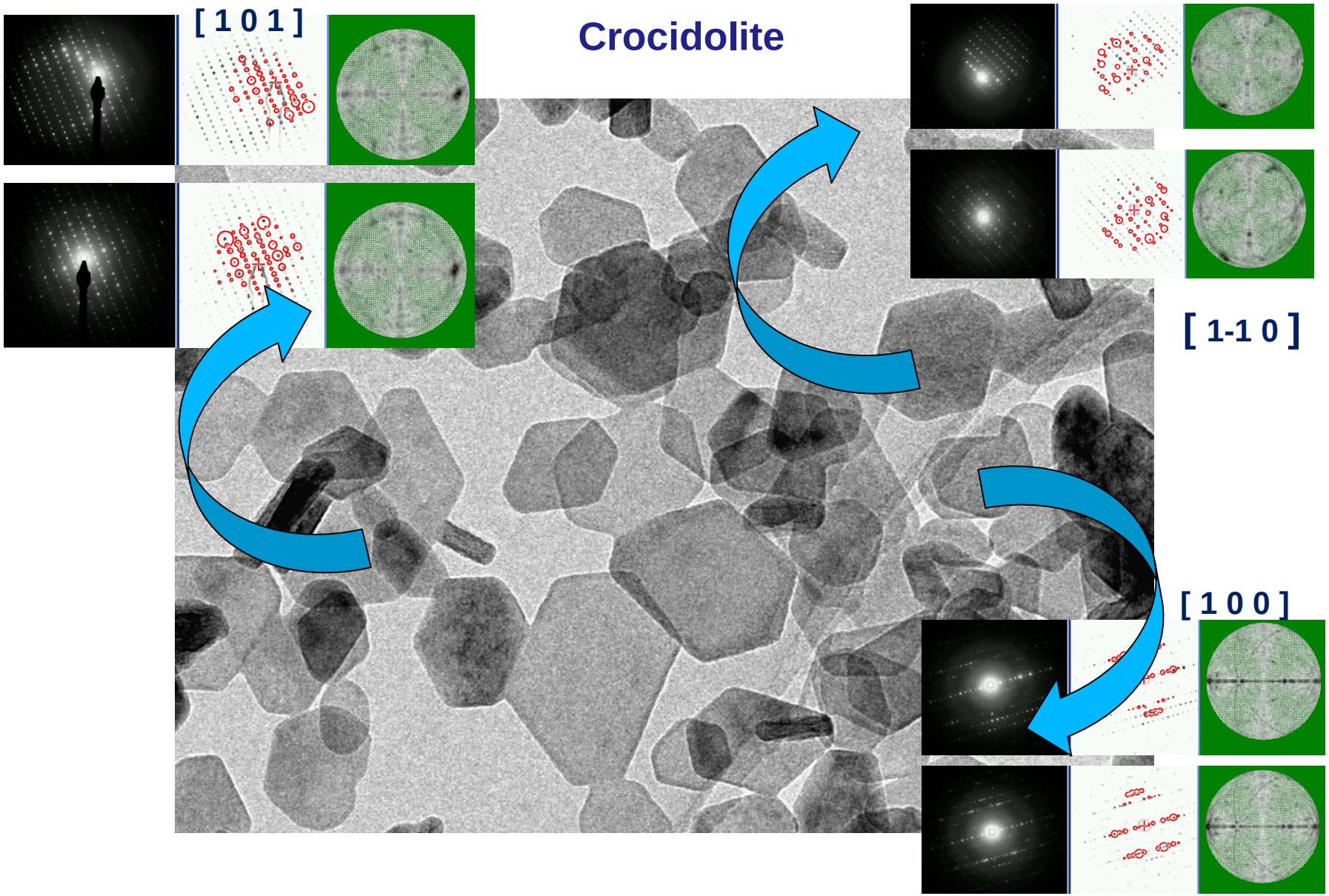


100 µm

% amophous phase ?

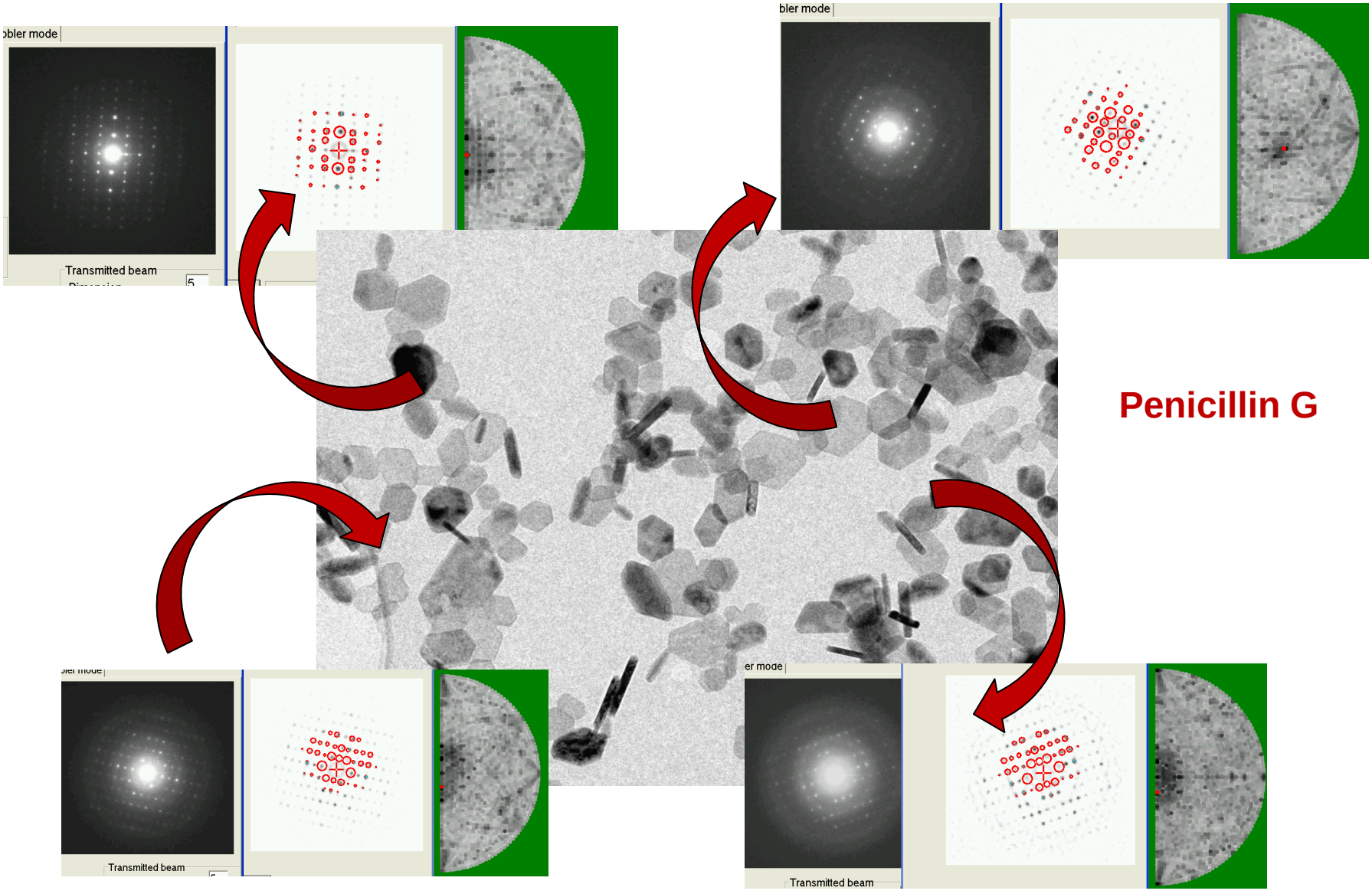
What is the % of each phase ?

detection limit ?



“Random 3D tomography” - ASTAR

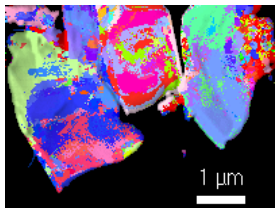
Cell determination & basic structure model building - INORGANIC CRYSTALS

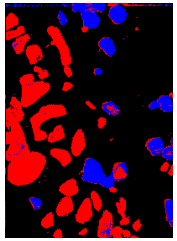


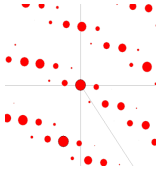
“Random 3D tomography” - ASTAR

Cell determination & basic structure model building – ORGANIC CRYSTALS

TEM advanced ELECTRON DIFFRACTION SOLUTIONS
for pharma-organic crystals

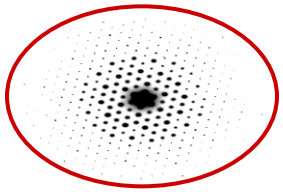


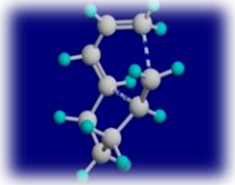


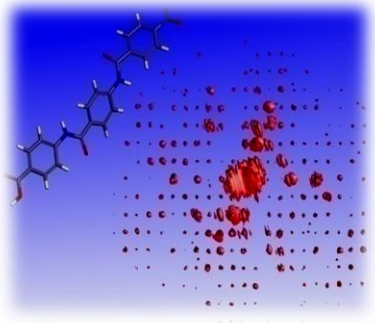


AUTOMATIC ORIENTATION / PHASE MAPPING

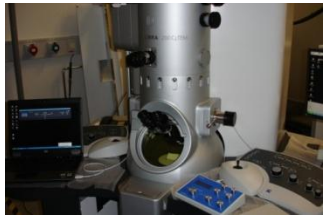
ASTAR



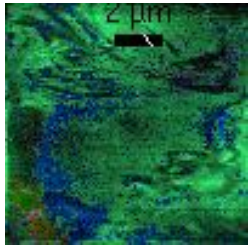


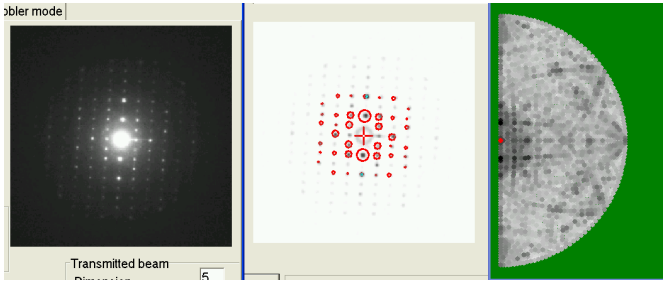


ADT -3D diffraction tomography



PRECESSION
« SpinningStar- DigiSTAR »





NanoMEGAS
Advanced Tools for electron diffraction

ASTAR combinations (examples)

Laurence Livermore Lab (Berkley –California) USA
CM300 FEG – Jeol 2000

Portland State Univ –Oregon USA
Tecnai 20F - Jeol 2000

Alabama Univ USA Tecnai 30F

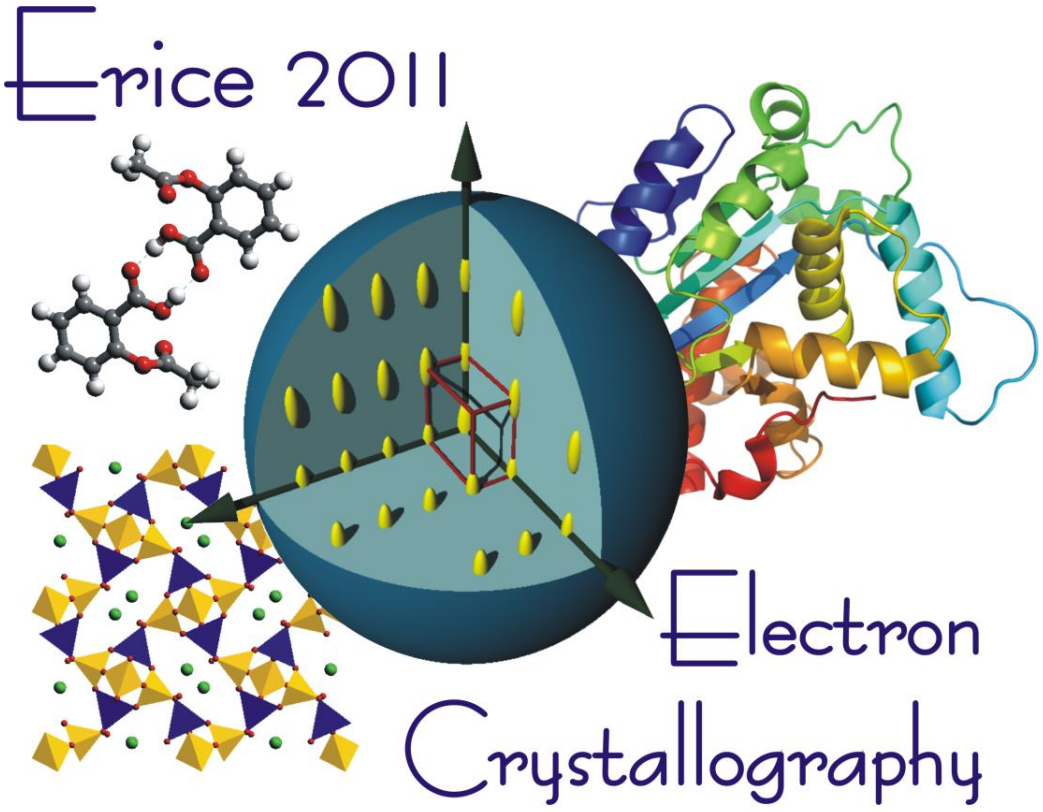
Univ of Texas –Austin USA Jeol 2010 F

Humboldt Univ Berlin Jeol 2200 FS

KBSI Korea Jeol 2100F

Osaka Gas , Japan Jeol 2100F

Zeiss Application Lab (Germany) Libra 200 FE Cs – Libra 120



NATO summer school in Erice, Sicily

2.-12. June 2011 (parallel to Powder Diffraction)

www.crystalerice.org

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Thanks for your attention !!