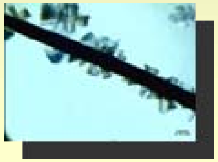
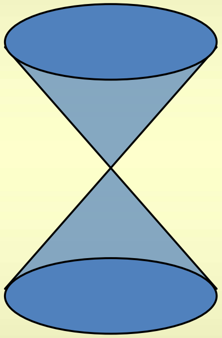
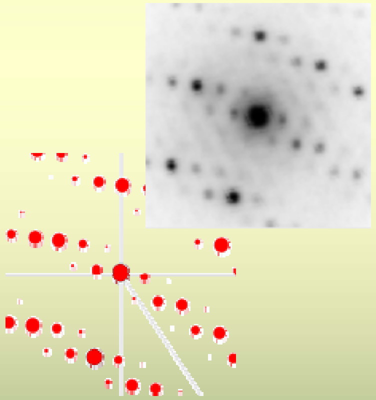
IDENTIFICATION – FINGERPRINTING – SOLVING ab-intio NANOSTRUCTURES

BY PRECESSION ELECTRON DIFFRACTION

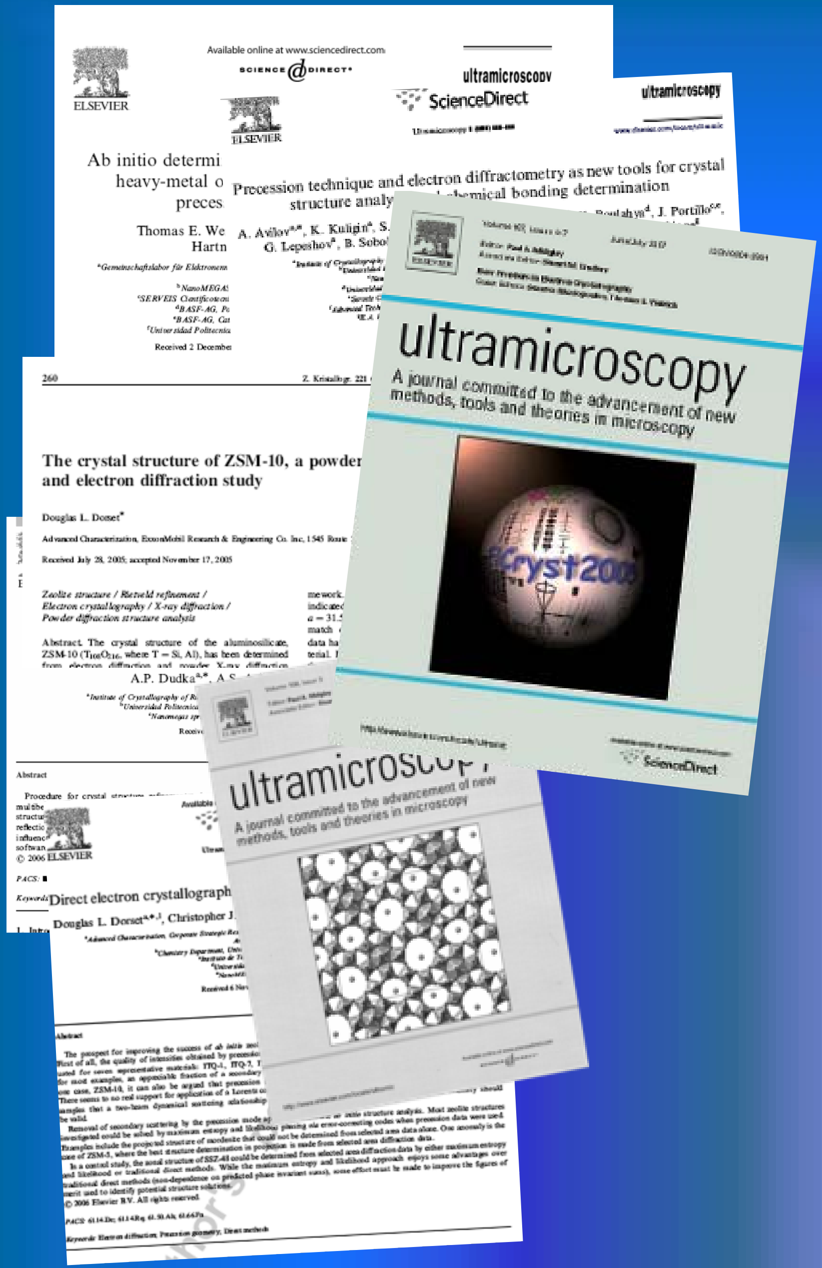






NanoMEGAS
Advanced Tools for electron diffraction

www.nanomegas.com



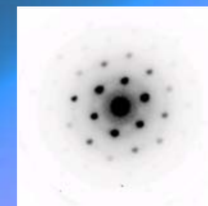
PRECESSION ELECTRON DIFFRACTION

NEW analysis technique

> 25 articles in 2 years !

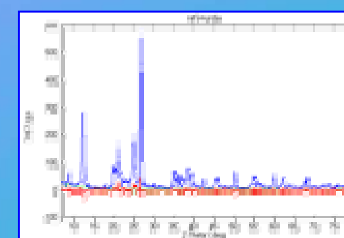
Ultramicroscopy Special Issue vol.107 issue 6-7 June 2007

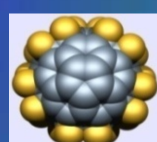
Unknown nanostructures…… HOW analyze them ??



Single crystal > 5 microns
X-ray diffraction

Powder X-ray diffraction





TEM microscopy

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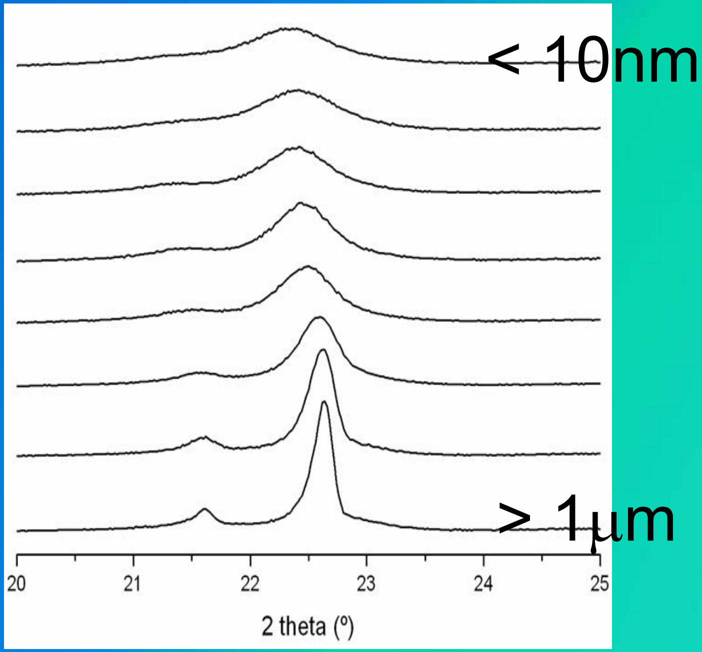
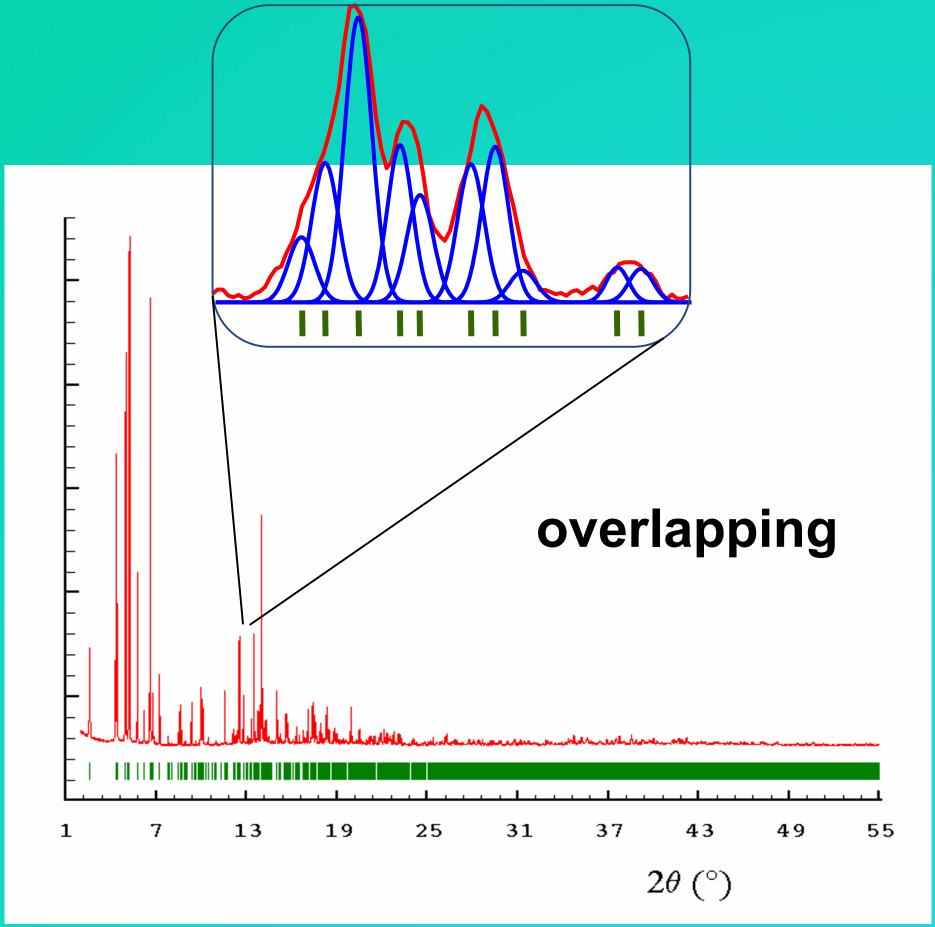
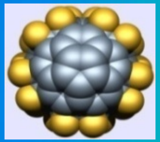
X- Ray powder diffraction: limitations



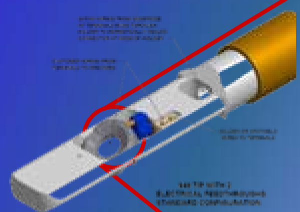




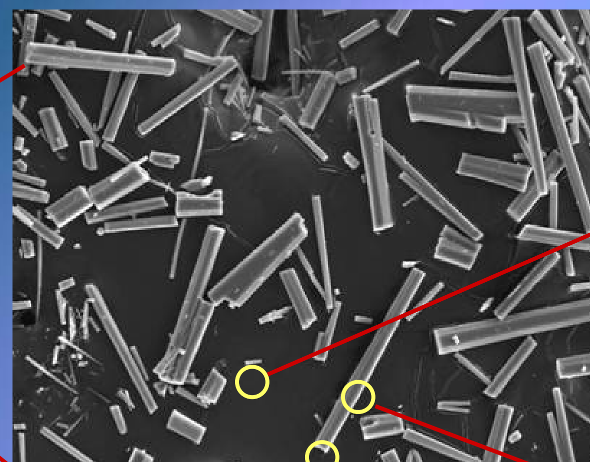
Nanocrystals : peak broadening

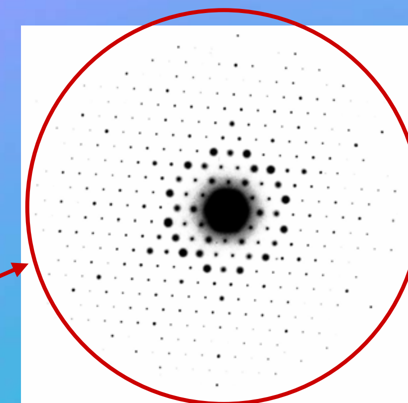
Electron diffraction: advantages

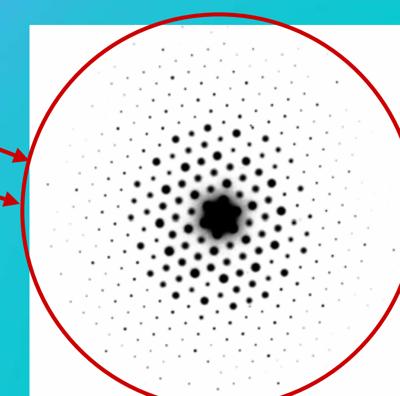
Every TEM (electron microscope) may produce ED patterns from individual single nanocrystals



TEM goniometer





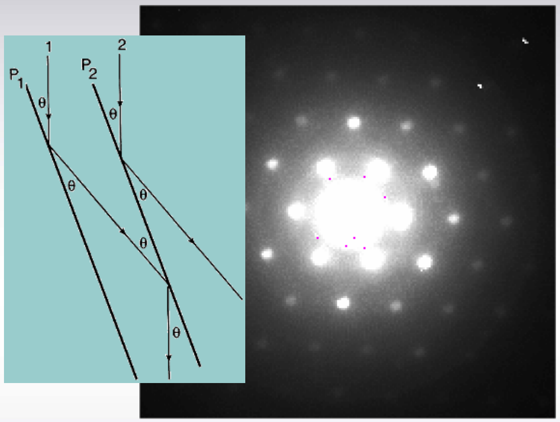


ED information: Cell parameter and symmetry determination

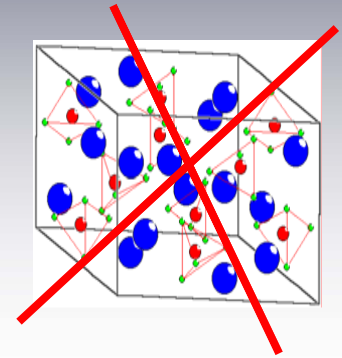
Measuring intensity values leads to structure determination

Electron diffraction : challenges for structure analysis

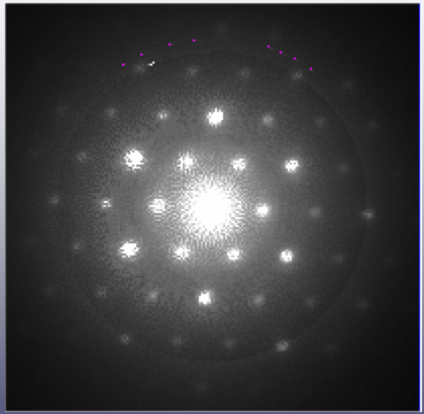
… electron diffraction data can be strongly distorted
by dynamical scattering



Dynamical scattering
(thickness > 10 nm)

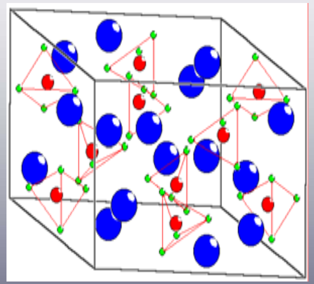


WRONG MODEL
light atoms do not appear
Atomic positions displaced



Kinematical scattering
(very thin crystals)

$$I(k) = |F(k)|^2$$



CORRECT MODEL

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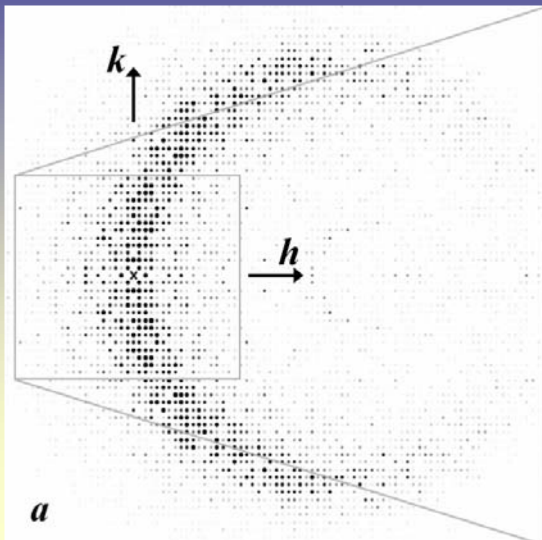
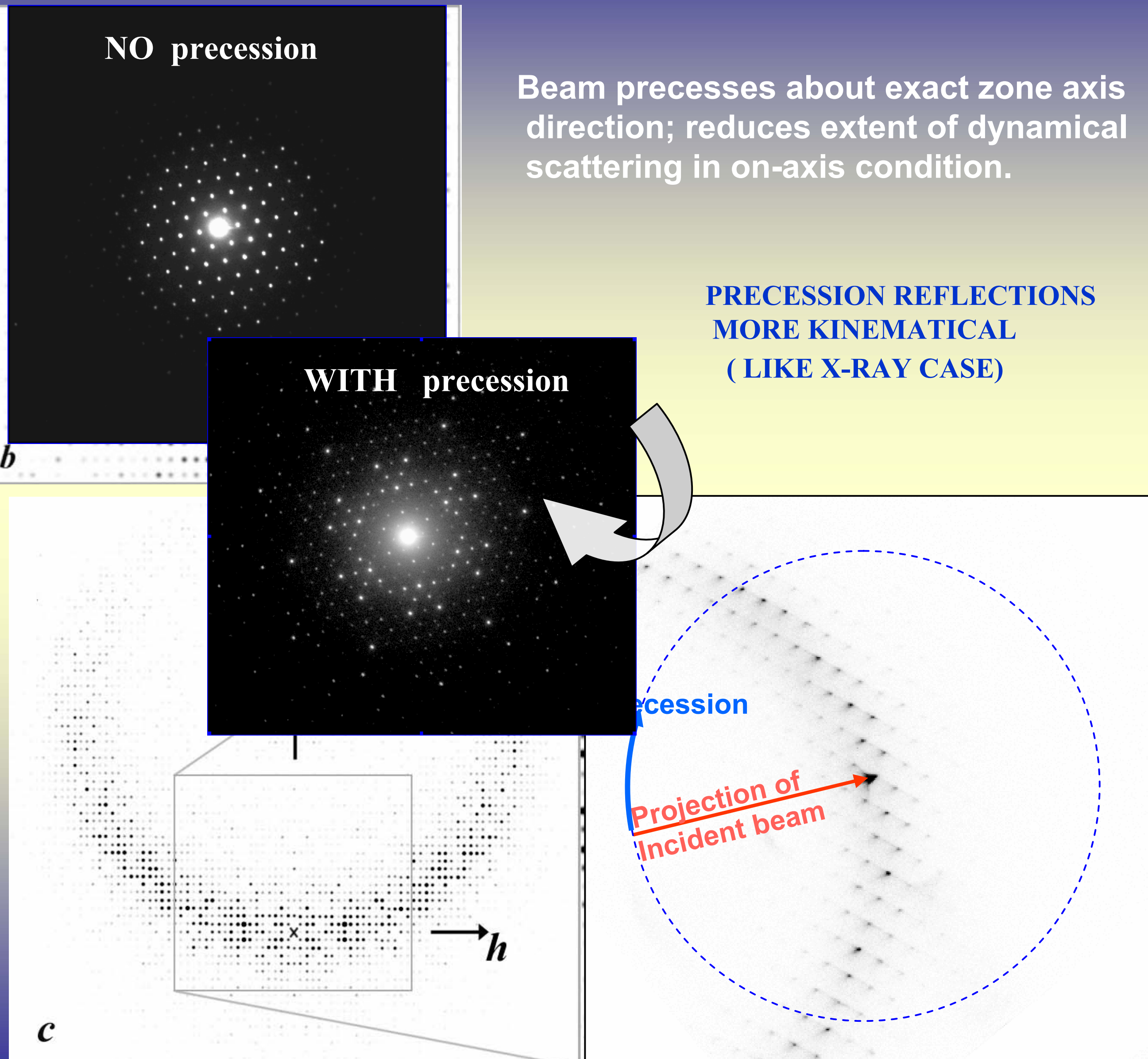
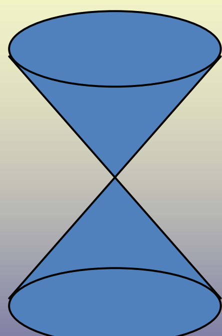
Solution: Precession Electron Diffraction (Vincent-Midgley)





Beam precesses about exact zone axis direction; reduces extent of dynamical scattering in on-axis condition.

PRECESSION REFLECTIONS MORE KINEMATICAL (LIKE X-RAY CASE)



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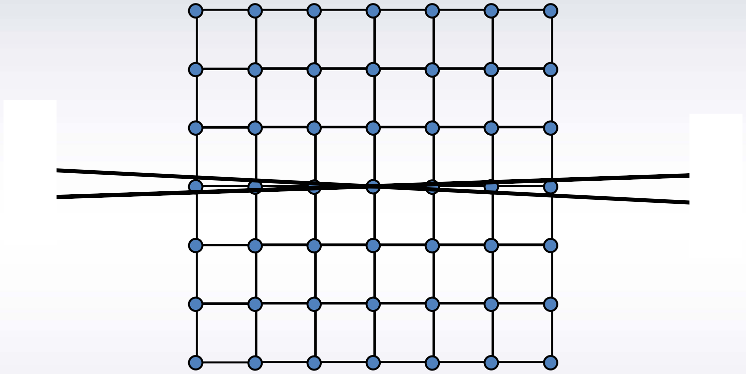
Vincent & Midgley *Ultramicroscopy* **53** (1994) 271, J. Gjønnes et al. *Acta Cryst A* **54** (1998) 306

Advantages of precession in single exposure data collection

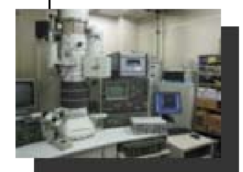


with beam precession, Ewald sphere also precess though the reciprocal space

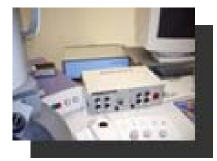
- More fully recorded reflections
- More spots per image
- Reduced dynamic effect

SPINNING STAR

UNIVERSAL INTERFASE FOR PRECESSION ELECTRON DIFFRACTION FOR ANY TEM



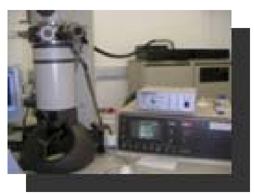
- **JEOL 200 kv,JEOL 120 KV,2010,2100, 2000, 2010 FEG**
- ***FEI Tecnai 30 FEG*, Tecnai 12 (120 kv),Tecnai 20 (200 kv) , Tecnai 10**

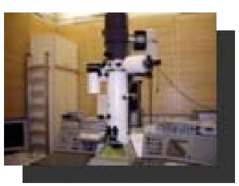


- Philips EMXXX, CM10, CM20, CM30 , STWIN, UTWIN

Topcon 200 KV **(Japan demo facility)**

- **Zeiss 912**
- Hitachi 200 KV





- Can be easily installed to any TEM 100- 400 KV (LaB6-FEG)
- Precession is possible for a parallel or convergent beam
- Precession spot size (5 - 50 nm)
- Precession angle can vary continuously from 0° to 4°, to observe true crystallographic symmetry variation

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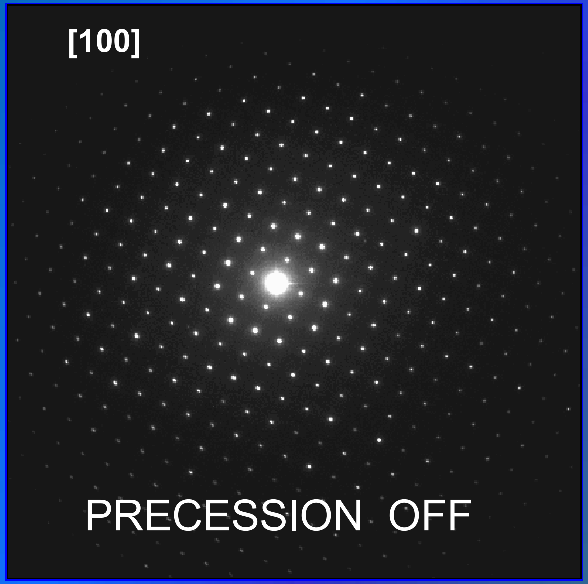
Ab-initio structure solution with precession

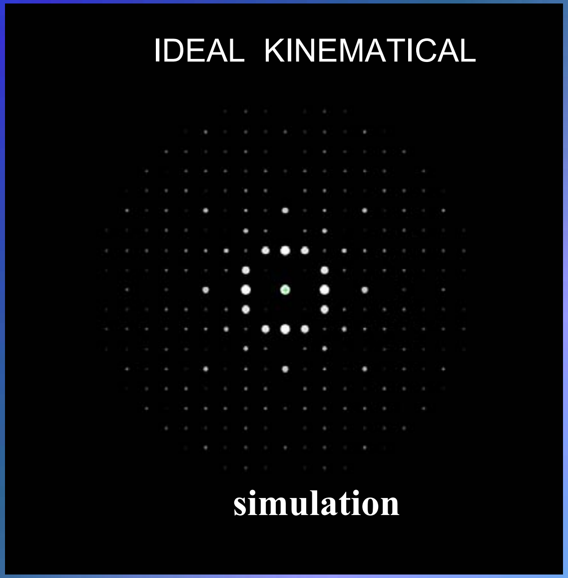
of ……

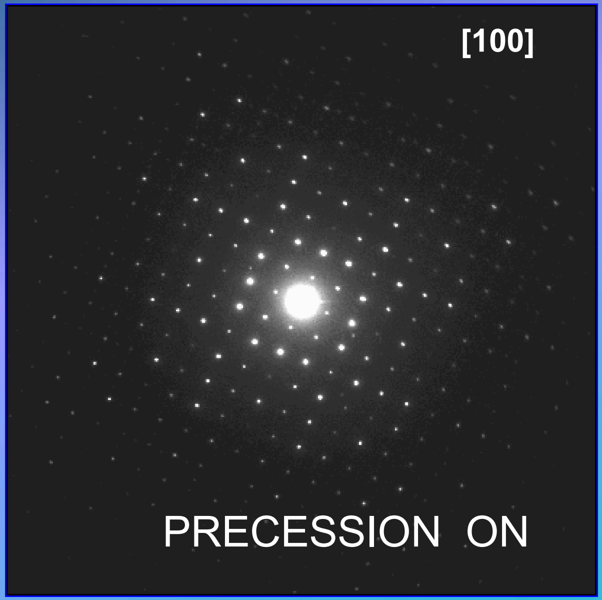
Catalysts (zeolites)
Oxides (perovskites)
Complex oxides (Cs-Nb-O)
Minerals
Polymers
Pharmaceuticals
……

Proteins

APPLICATION : FIND TRUE CRYSTAL SYMMETRY – SOLVING CRYSTAL STRUCTURES







Garnet cubic Ia3d a=1.2 nm

UVAROVITE $Ca_3Cr_2(SiO_4)_3$

Dynamical interactions due to thickness effects may deform intensities in a way that crystal symmetry cannot be recognized; by applying precession true crystal symmetry can be revealed and dynamical scattering is greatly reduced

PRECESSION ED INTENSITIES (PED) ARE CLOSE TO (IDEAL) KINEMATICAL INTENSITIES : WE CAN USE PED TO SOLVE DIRECTLY CRYSTAL STRUCTURES OF NANOCRYSTALS LIKE IN X-RAY DIFFRACTION

Courtesy M.Gemmi Univ of Milano

Is possible from simple ZOLZ/FOLZ symmetry comparison to deduce

point and space group nanocrystal symmetry

J.P.Mornirolli, JW Steeds Ultramicroscopy 1992, 45 , 219

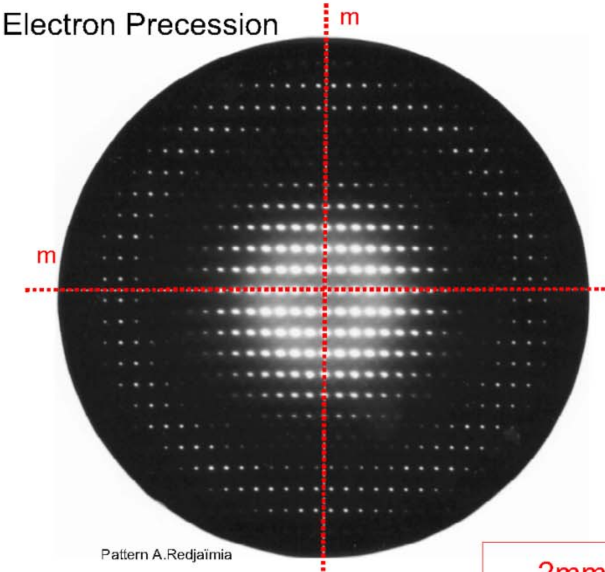
HOW ?

by simply increasing precession angle , FOLZ /ZOLZ reflections and their relative symmetry becomes visible in ED patterns

Microdiffraction and Electron Precession

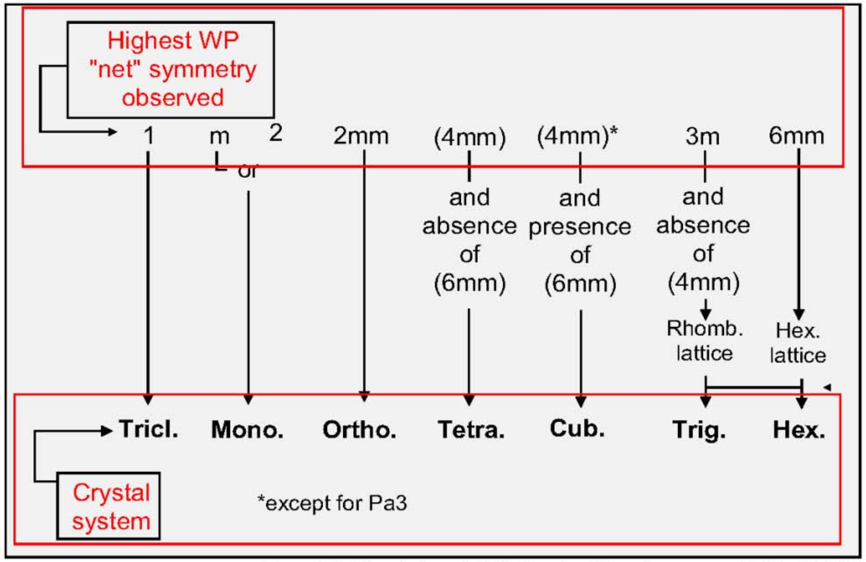
"net" symmetry (position)

Connected with the crystal system



2mm symmetry

The WP "net" symmetries are connected with the CRYSTAL SYSTEM



From J.P. Morniroli and J.W. Steeds, Ultramicroscopy, 1992, 45, 219

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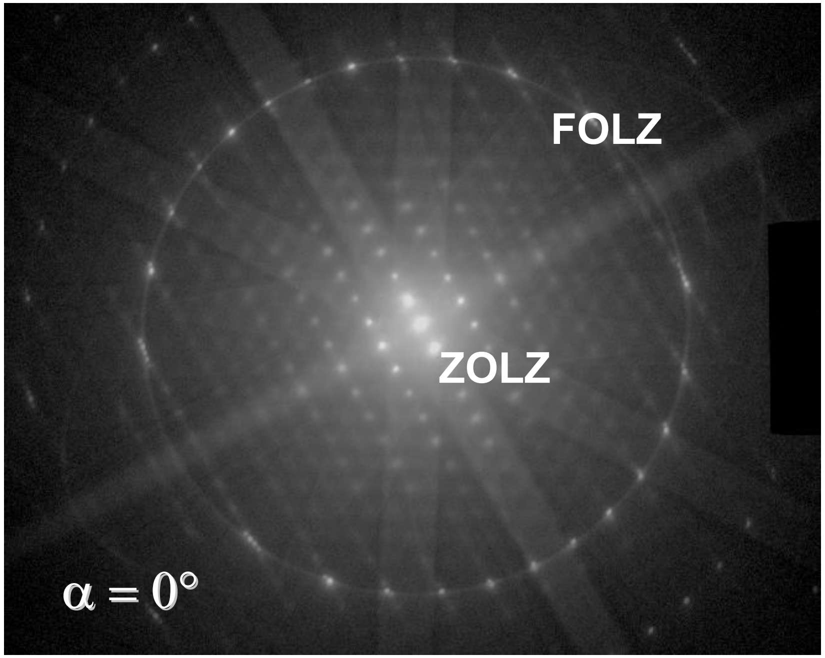
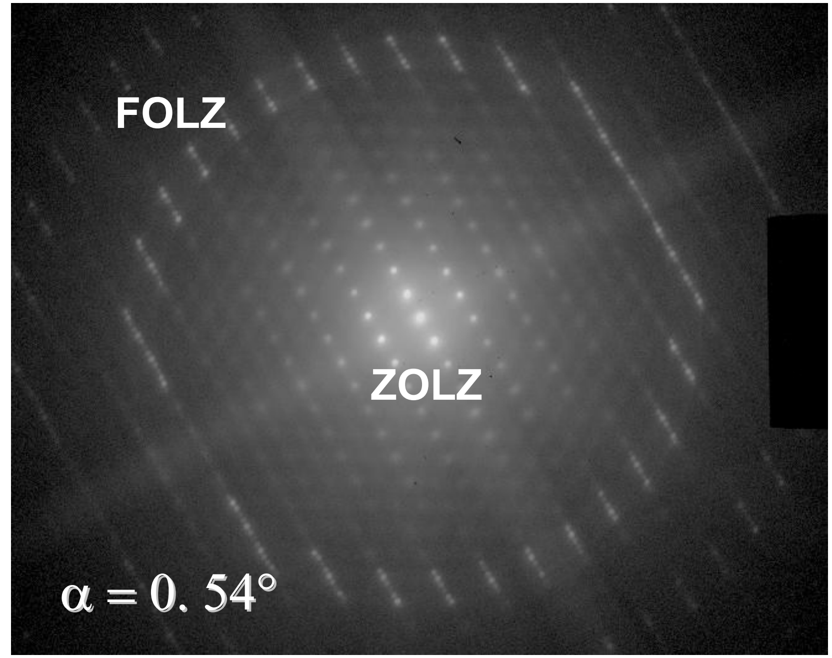
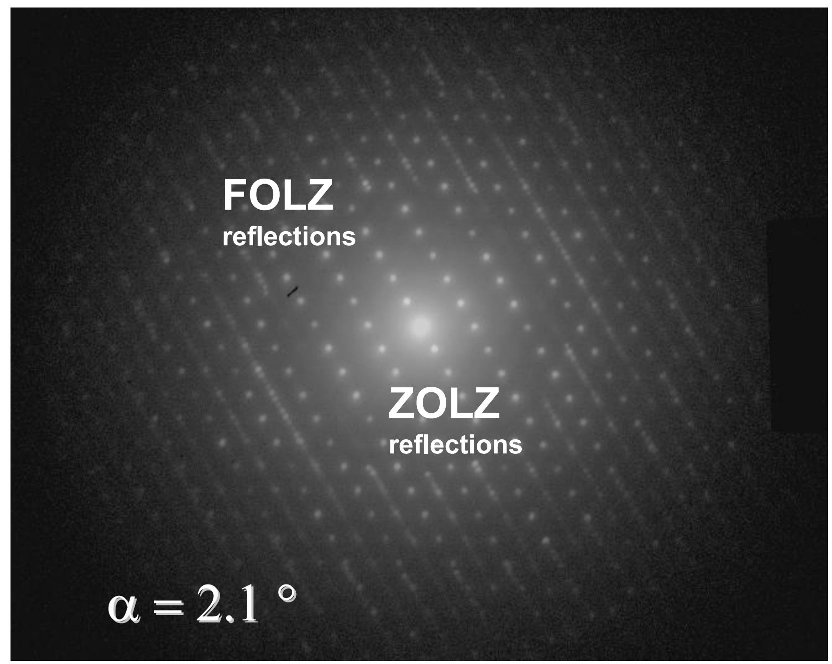




SiC

Space group determrmination by

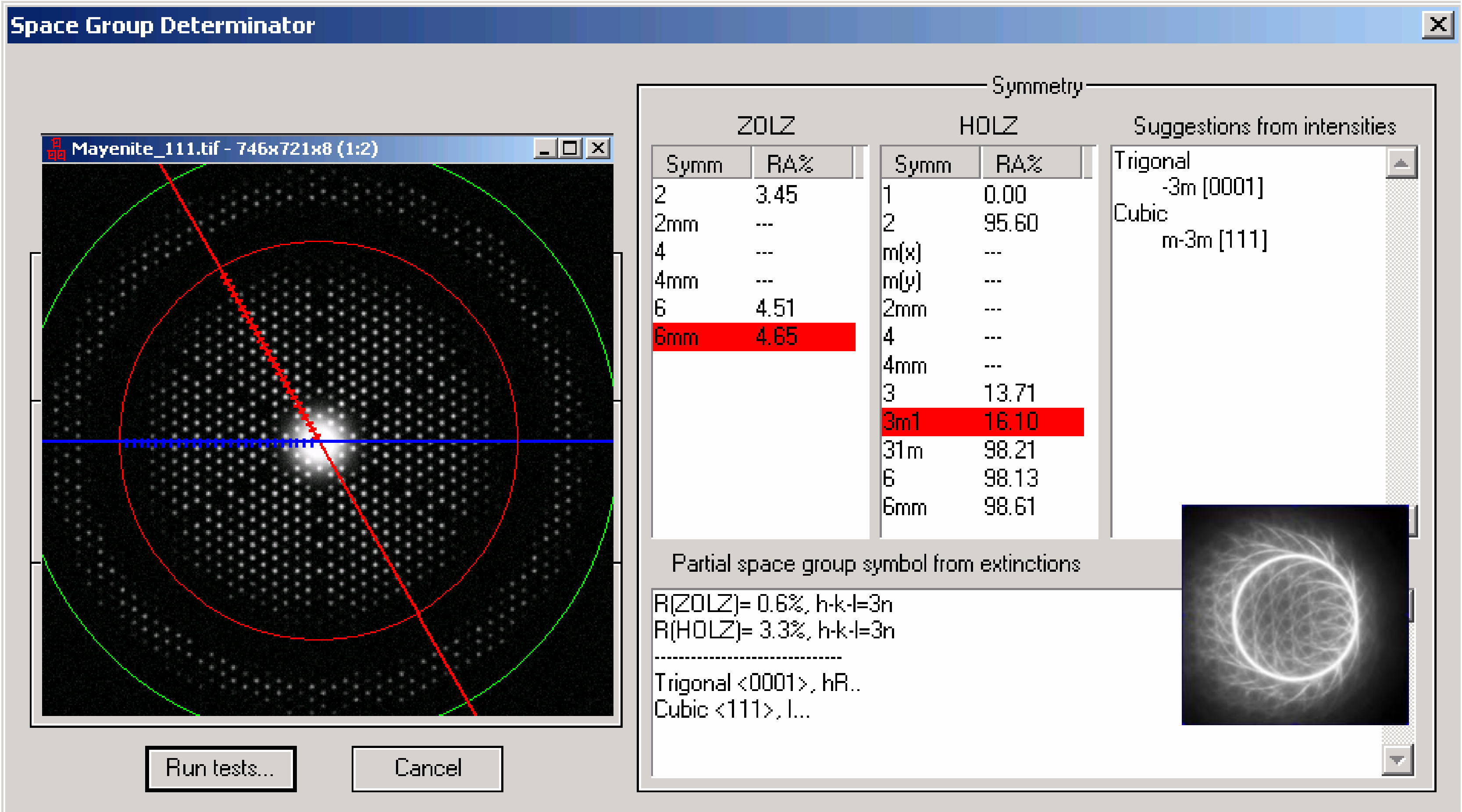
PRECESSION ELECTRON DIFFRACTION



SiC 4H hexagonal P6_3mc

Courtesy JP Mornirolli Univ of Lille France

AUTOMATIC crystal symmetry determination by analysis of ZOLZ @ FOLZ precession patterns



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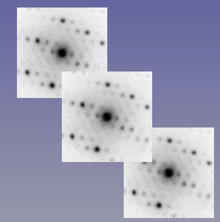
Precession electron diffraction :

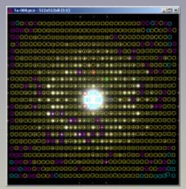
ab initio determination of nanostructures

TEM crystal experiment



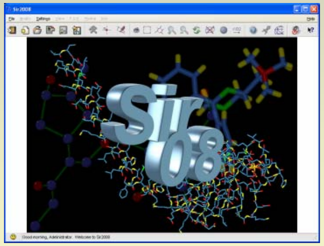
↓

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



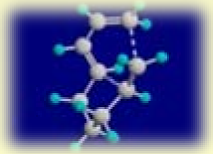
↓

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



↓

Refinement crystal structure



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Electron diffraction intensities are measured automatically (ELD software)

FROM

Image plates

Photo film

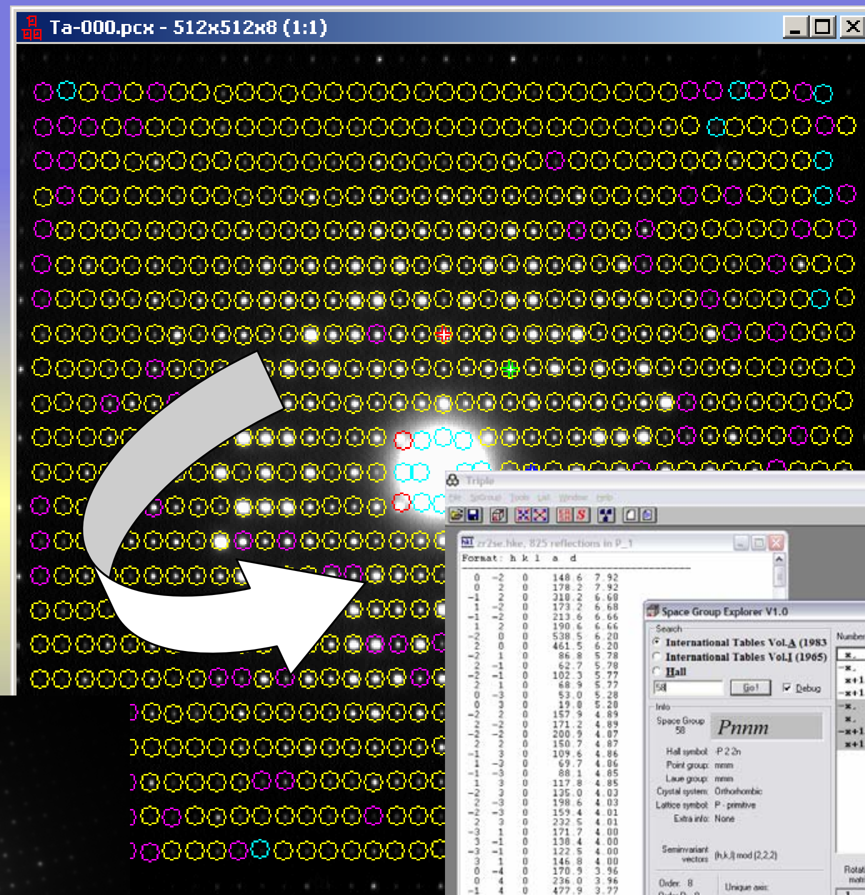
OR

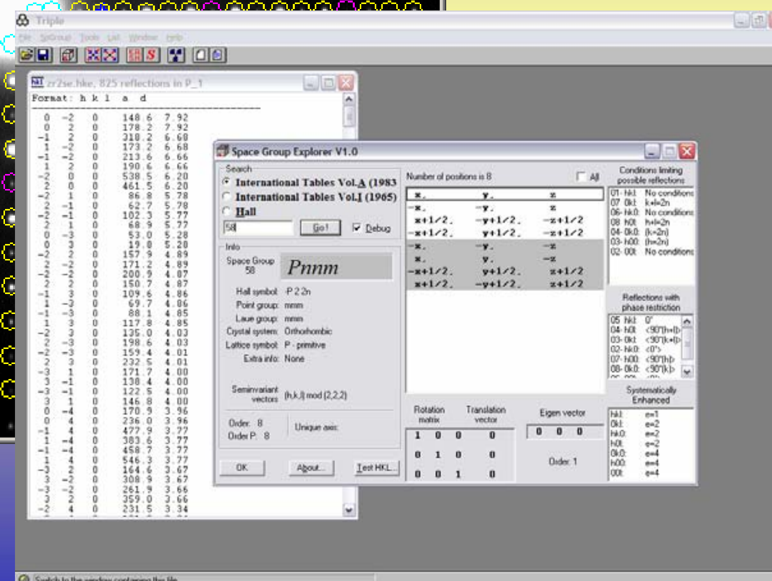
CCD camera

1k x 1k

2k x 2k

4k x 4k





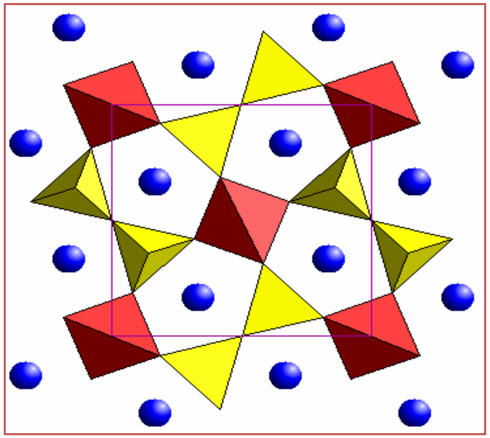
or from electron diffractometer

3D structure solution examples

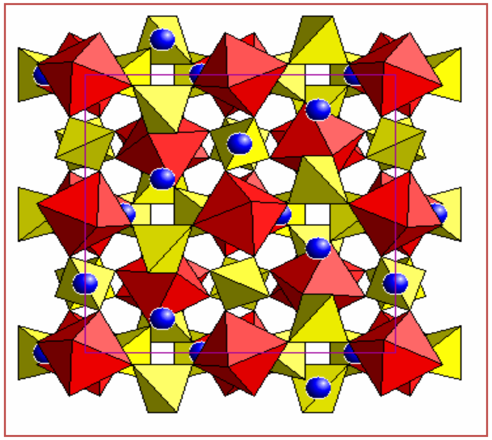
Mauro Gemmi and Stavros Nicolopoulos

Structure solution with three-dimensional sets of precessed electron diffraction intensities

Ultramicroscopy, Volume 107, Issues 6-7, June-July 2007, Pages 483-494



Åkermanite



Uvarovite

Structure	Composition	Space Group	Cations	Oxygens
Åkermanite	($Ca_2MgSi_2O_7$)	P-42_1m	3	3
Uvarovite	$Ca_3(Al_{0.4}Cr_{0.6})_2Si_3O_{12}$	I a –3 d	3	1

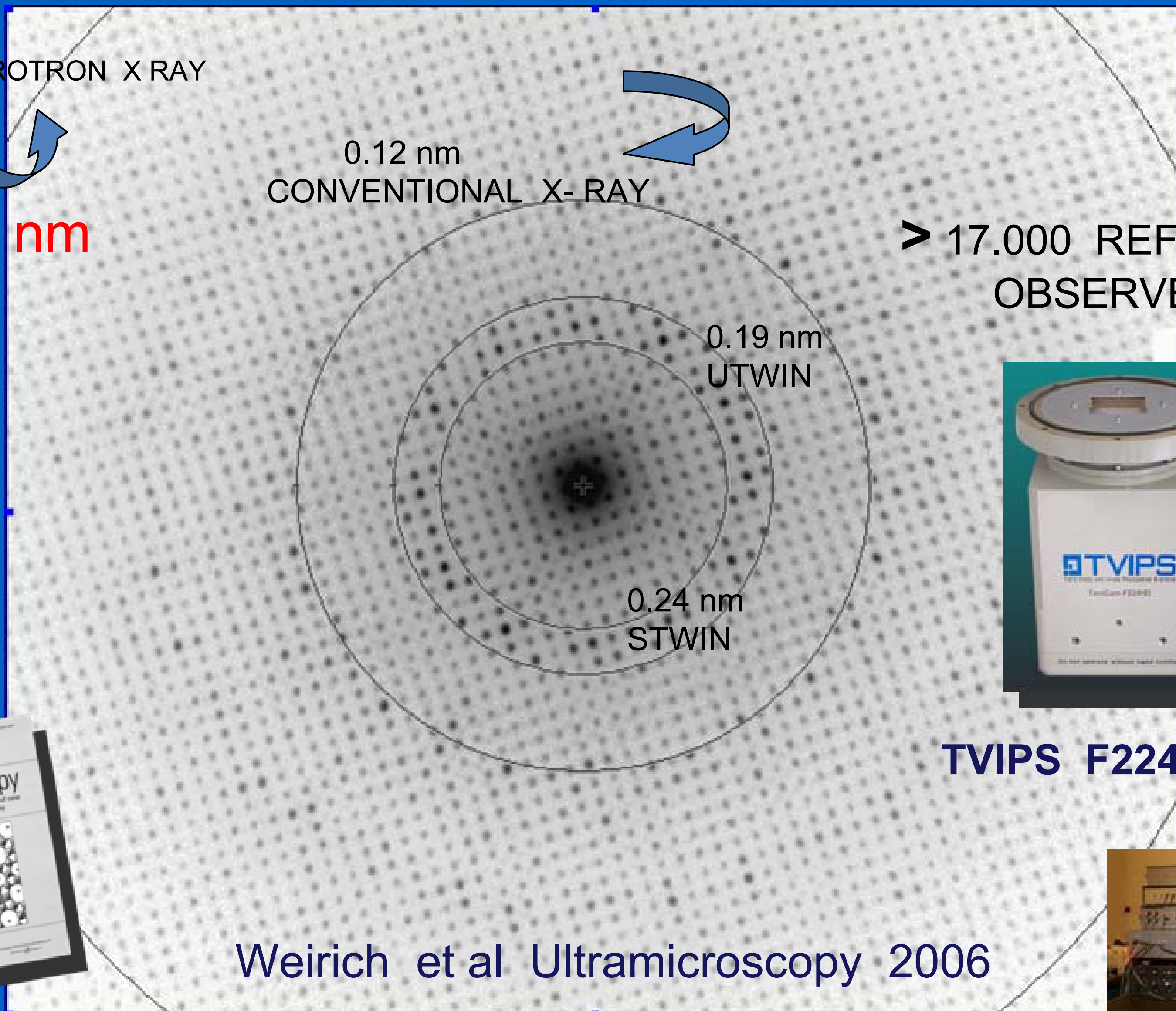
Structure solution with precession diffraction: Åkermanite

Three-dimensional set of ***precession electron diffraction*** intensities obtained merging [1 0 0] [0 0 1] [1 0 1] [1 0 2] zone axes.

All atoms found, correctly labelled, <Distance> = 0.1262 from published coordinates.

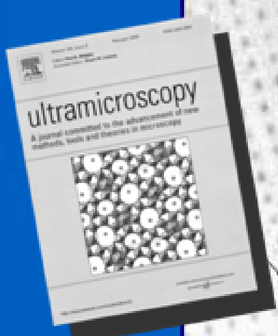
Atom	X(Sir)	Y(Sir)	Z(Sir)	X(Pub)	Y(Pub)	Z(Pub)	Distance
Ca	0.843	0.343	0.486	0.832	0.332	0.494	0.12498
Si	0.648	0.148	0.060	0.640	0.140	0.065	0.09056
Mg	0.500	0.500	0.000	0.000	0.000	0.000	0.00000
O	0.654	0.154	0.801	0.860	0.640	0.256	0.32573
O	0.567	0.330	0.211	0.581	0.314	0.217	0.16526
O	0.500	0.000	0.193	0.000	0.500	0.817	0.05064

PRECESSION RESOLUTION - X RAY RESOLUTION

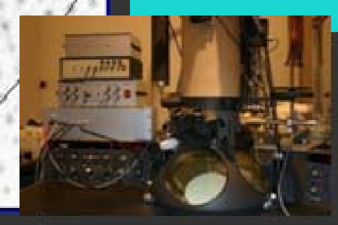


> 17.000 REFLECTIONS OBSERVED

TVIPS F224 HD

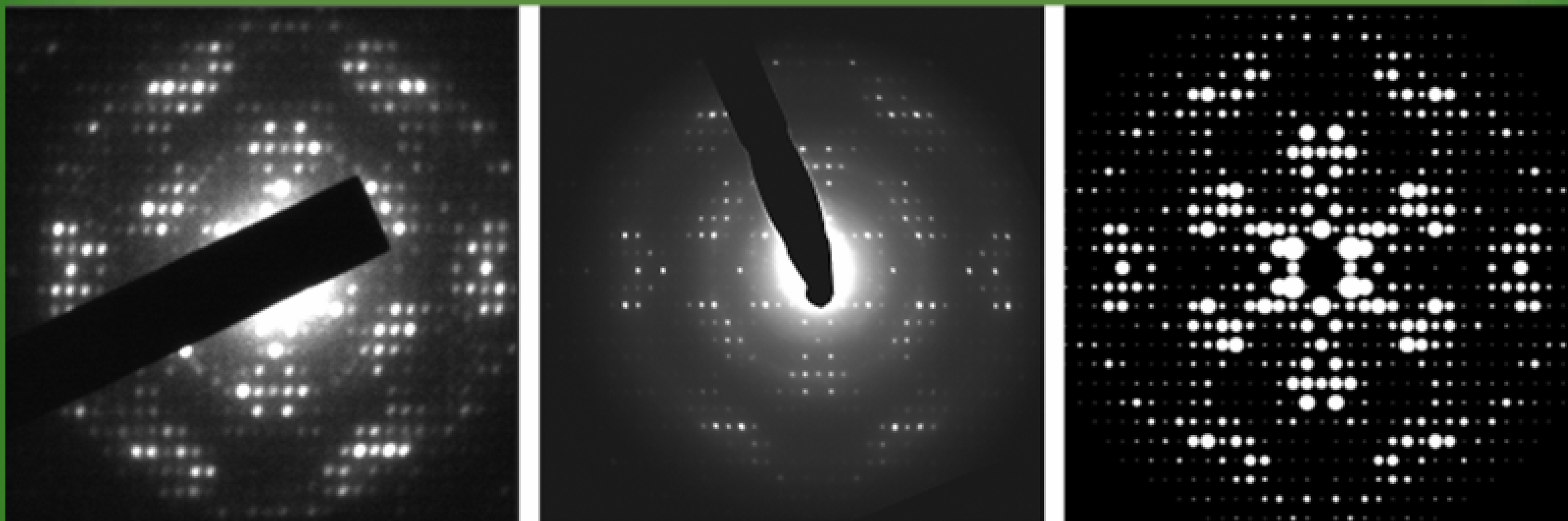


Weirich et al Ultramicroscopy 2006



Cs-Nb-W-0 oxide , ALL heavy atoms revealed by precession diffraction

PRECESSION OFF | PRECESSION ON | simulation



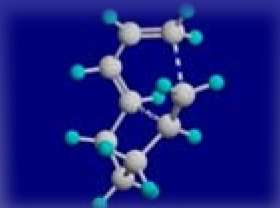
PRECESSION on POLYMERS

Melon

$([C_6N_7(NH_2)(NH)]_n$, plane group *p2gg*

a = 16.7 Å, b = 12.4 Å, g = 90°, Z = 4

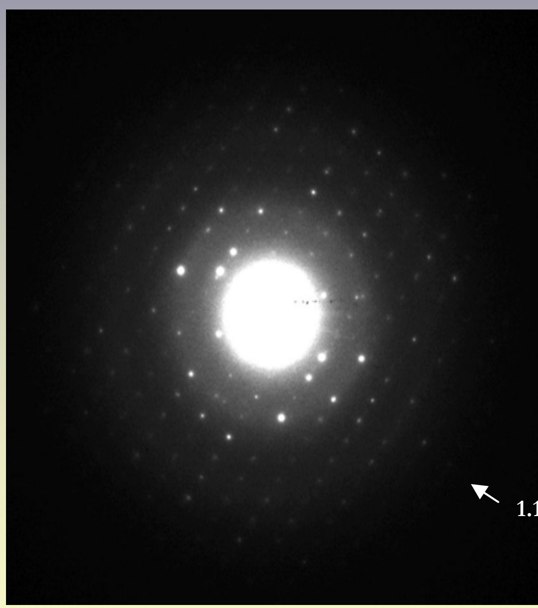
Courtesy M. Doblinger Univ of Munich Germany



Precession from pharmaceutical nanocrystals

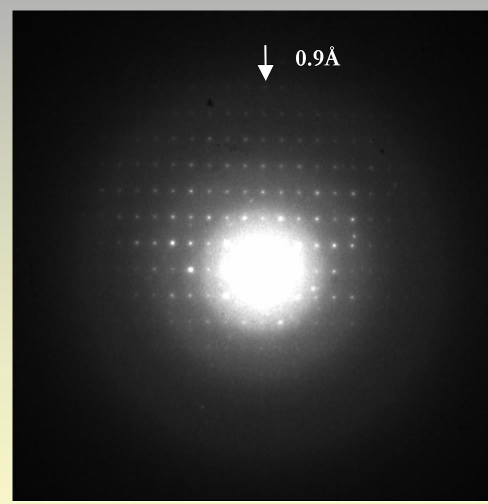
PED patterns in pharmaceutical crystals allow to work with close or with ZA oriented patterns , revealing true crystal symmetry and kinematical intensities good for structure determinations

amoxycillin

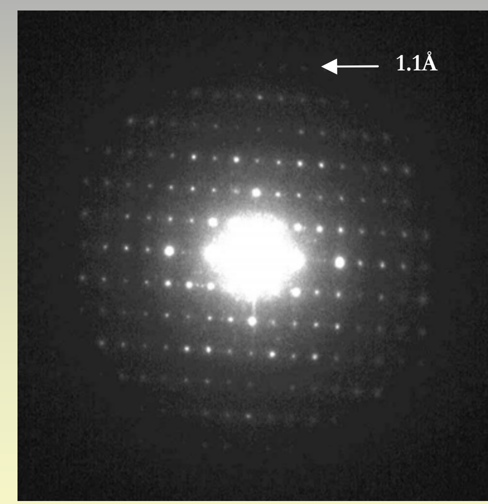


without precession

penicillin G-potassium



without precession



with precession

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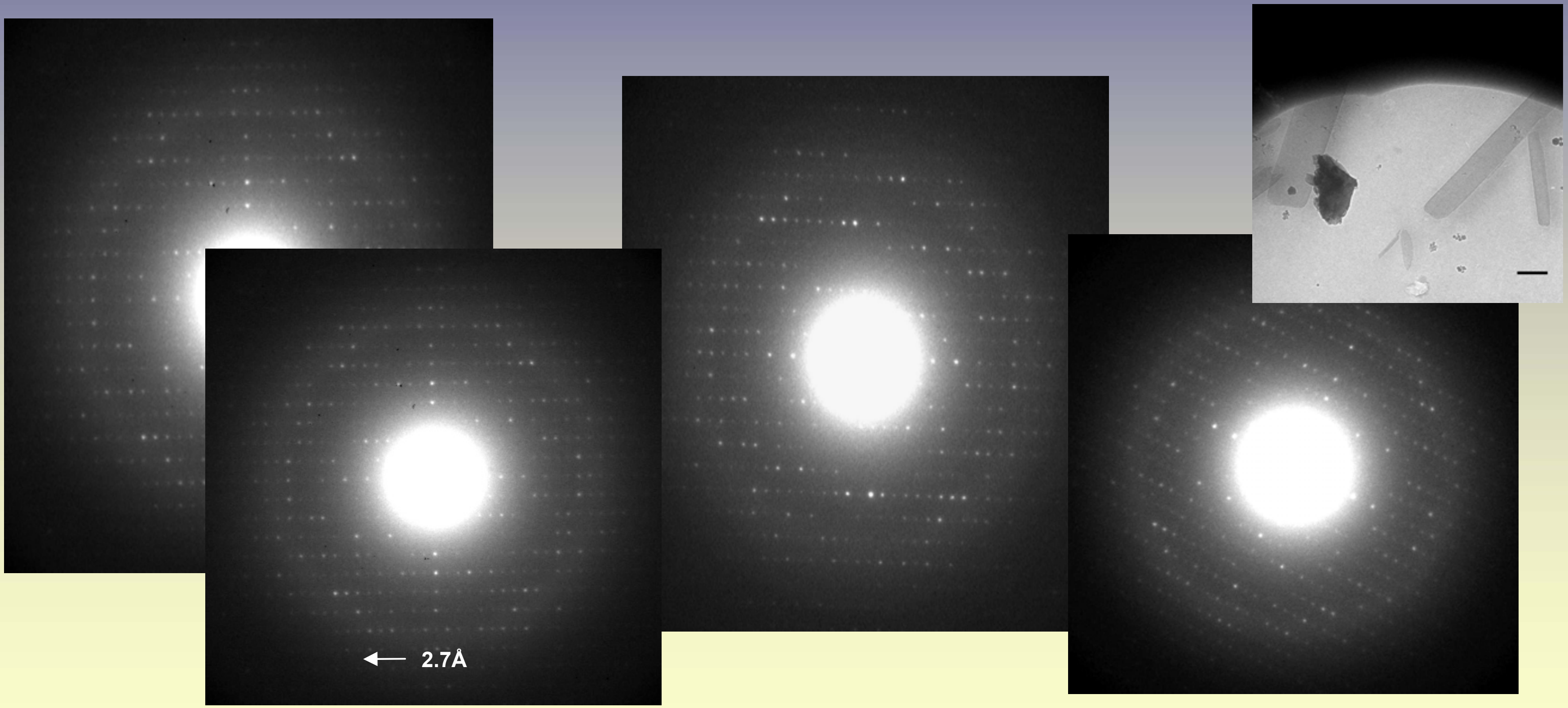
Samples C.Giacovazzo CNR Bari

Courtesy JP Abrahams, D.Georguieva Univ Leiden

Precession ED from 3d **protein** lysozyme nanocrystals

protein crystals show much better quality PED patterns (suitable for symmetry and structure determination) than conventional SAED patterns



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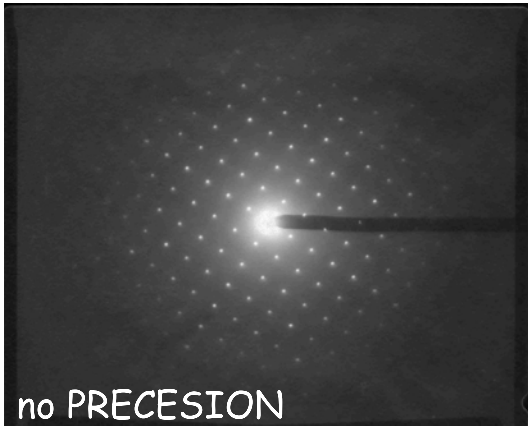
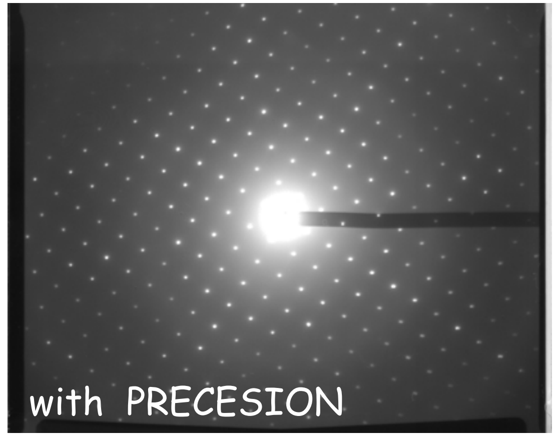
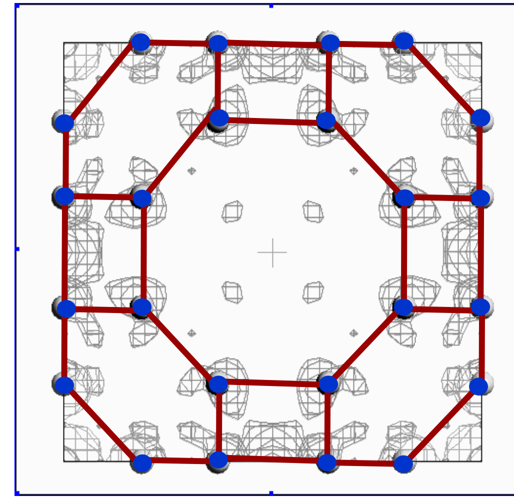
Courtesy JP Abrahams, D.Georguieva Univ Leiden

ZEOLITES

ITQ-29 *ab initio* structure determination



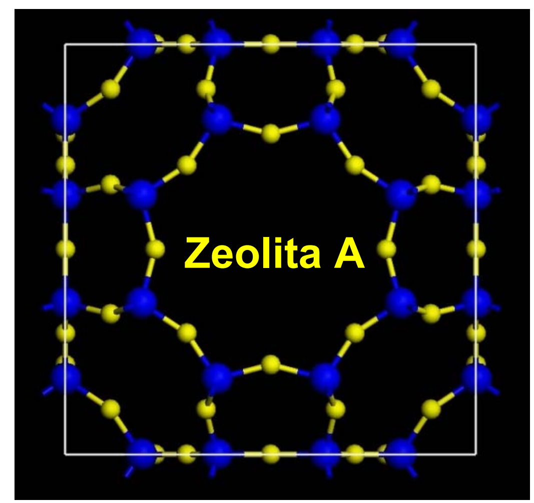




Is possible to determine complete structure from a single ED obtained at 100 kV

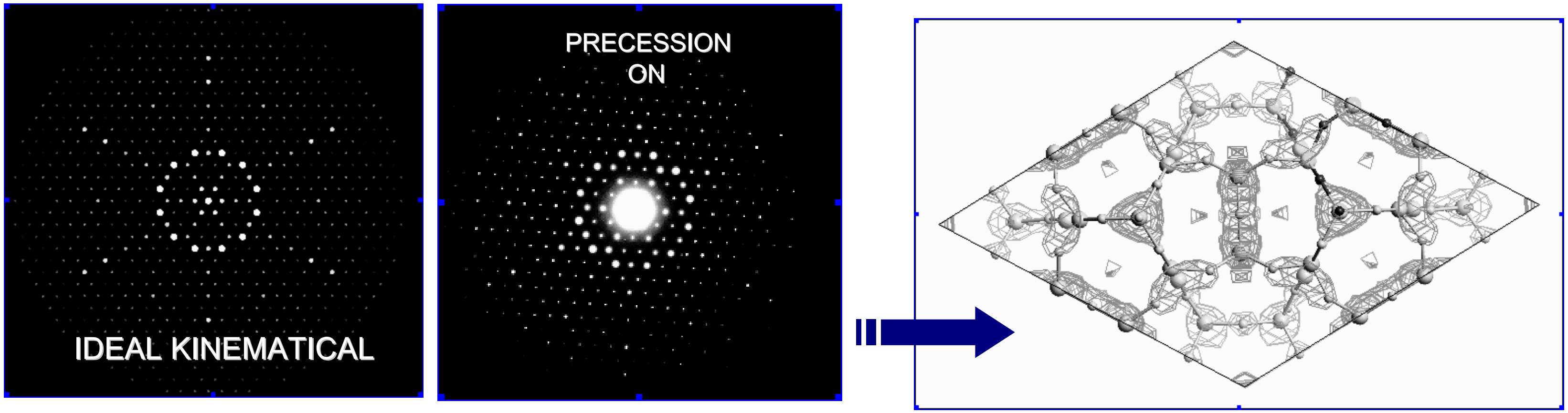
Different methods: direct methods (FOCUS), maximun entropy (MICE), real space (FOX), ...

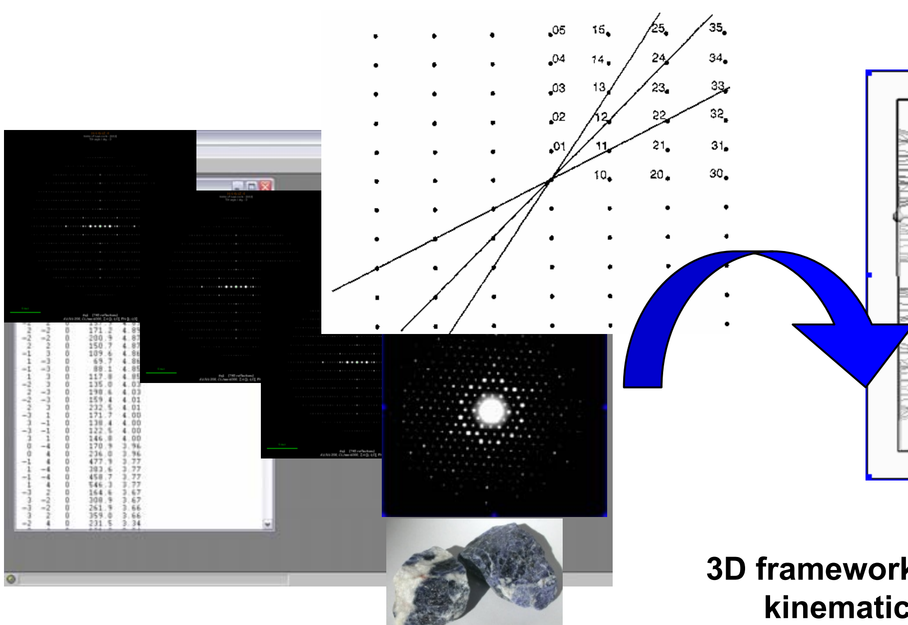
I_{hkl} proportional to $|F_{hkl}|^2$

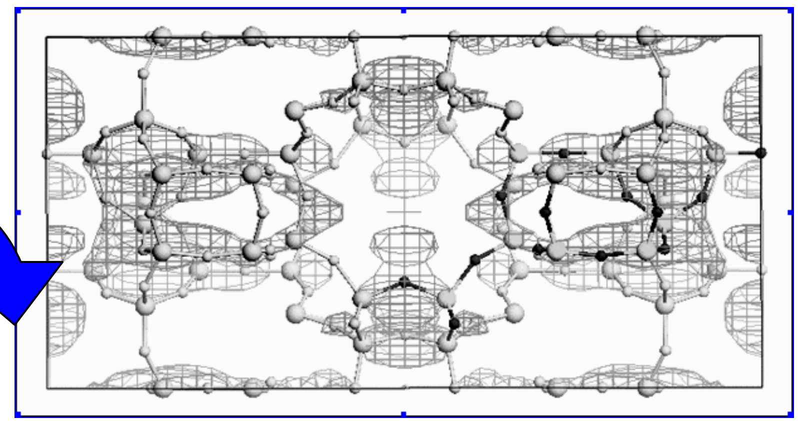


$Pm\bar{3}m$, a=11.87Å

ZEOLITES : 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)

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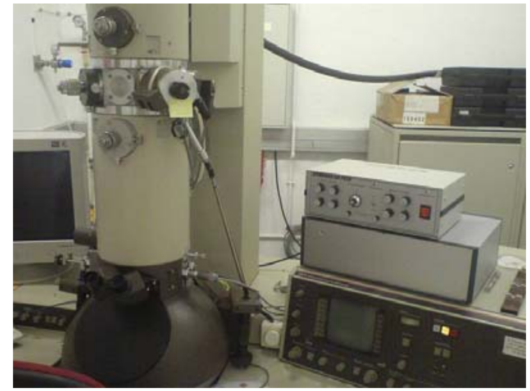
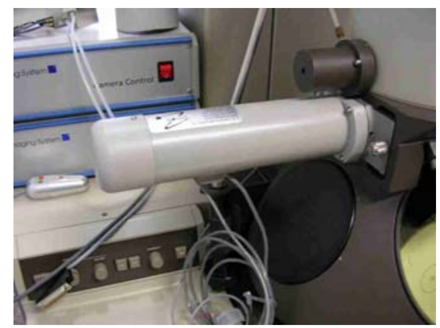
PRECESSION ON **old TEM…… works well !**





SOLUTION: <u>ENHANCE NEW TEM</u>

> 36 installations world-wide

OR <u>UPGRADE OLDER TEM</u>

TO POWERFUL
STRUCTURE DETERMINATION

NanoMEGAS
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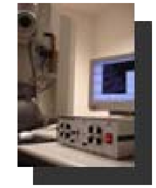
NanoMEGAS   INSTALLATIONS   WORLDWIDE



PHILIPS TEM

CM30 , CM 20 , CM12, CM10 , EM 400

JEOL TEM

JEOL 2000, JEOL 2100, JEOL 2010, JEOL 2010 FEG , JEOL 1400

FEI TEM

TECNAI 10, TECNAI 12, TECNAI 20 , TECNAI 20 FEG STEM, TEM 30 FEG STEM

ZEISS   TEM

912 OMEGA FILTER

DEMO SITES

PARIS   Philips CM12

JAPAN Tokyo Topcon   EM 002B 200 kv

TVIPS Munich JEOL 2010, Tecnai12

TOTAL

> 36 INSTALLATIONS

1st precession electron diffraction user meeting

IC CI
CNR Istituto di Cristallografia

Martina Franca 8-9 May, 2008

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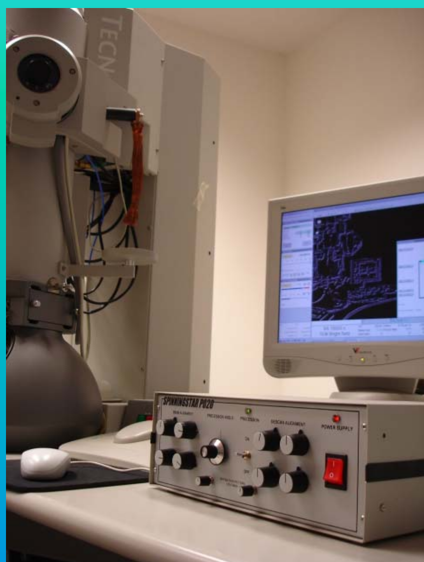
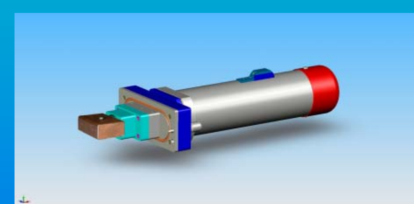
TEM



PRECESSION UNIT



ELECTRON DIFFRACTOMETER

EDS

EELS

STEM

CCD

HAADF

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