

NanoMEGAS

Advanced Tools for electron diffraction



Blvd Edmond Machtens n°79
B-1080 Brussels Belgium

<http://www.nanomegas.com>

Ab initio nanostructure determination by TEM electron beam precession:

Structure Determination of Zeolites

Zeolites are microporous silicates widely used as catalysts in the oil refining and petrochemical industry, being their catalytic properties directly related with their 3D crystal structure. Zeolites rarely grow as single crystals, usually only powder X-ray diffraction techniques can be used for their structure determination; however, use of powder techniques is strongly limited due to their large unit cells, resulting to strong peak overlapping. Electron diffraction in TEM (combined with beam precession) is the only available technique able to resolve ab initio structures of individual zeolite nanocrystals from quasi-kinematical data up to 0.05 nm resolution (much better than conventional X-ray sources).

Method description: By using specially designed precession interface for any TEM (fig 1a), electron beam incident on crystal precesses on cone with semiangle ϕ about zone axis orientation (fig 1b); as result of precession, Ewald's sphere also tilts through rods of ZOLZ as shown in (fig 1c). In a conventional ED pattern (fig 1d) many beams are simultaneously excited, leading to strong dynamical scattering. However, when the same beam is precessed on sequential excitation of reflections dynamical effects are weak (fig. 1e)

PRECESSION TEM interfase SPINNING STAR

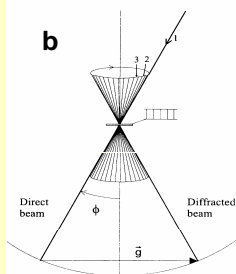
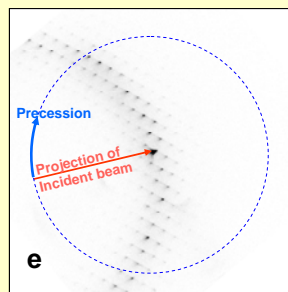
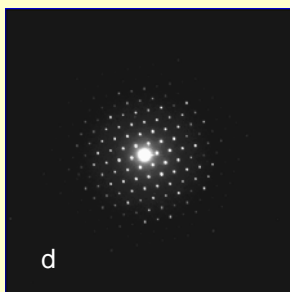
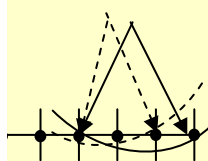


Fig. 1c



- easily retrofit to any TEM 100-300 KV
- precession possible for any beam size 300 - 50 nm
- precession eliminates false spots due to dynamical contributions
- software ELD for automatic Intensity/symmetry measurement
- automatic 3D structure determination with electron diffractometer

Using the precession technique in TEM first developed by Vincent, Midgley (ref.1) a collection of quasi-kinematical 2D or 3D electron diffraction intensities can be obtained up to 0.05 nm resolution. With precession, ED pattern resolution extends dramatically when compared with ED without precession. By measuring precisely ED intensities in different zone axis (electron diffractometry) we can find ab initio complete 2D or 2D structure in analogy with single crystal X ray diffractometry.

Ab initio determination of LTA (A) zeolite framework

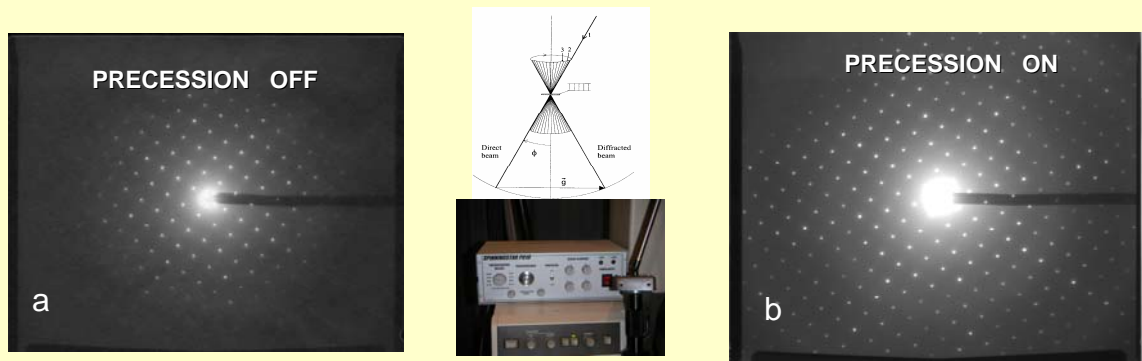


Fig. 2a,b Electron diffraction pattern of Zeolite LTA (001) orientation obtained with 100KV TEM

Zeolite A/LTA (cubic, $Pm\bar{3}m$, $a=1.2$ nm, ref.2) is widely used for gas separation and as component for detergents due to its unique atomic pore structure.

The use of electron diffractometry precession data (100 KV) from single zeolite LTA nanocrystal improves largely the ED resolution when comparing with data collected without precession.

Measuring precisely ED precession quasi-kinematical intensities allow us to obtain, using *ab initio direct* methods, a complete framework model (fig. 4b), that after refining give raise to the correct structure (fig. 4a). The resolution achieved using the ED precession technique is around 0.05nm, much better than that obtained with conventional X-ray powder techniques (0.12 nm)

Precession data resolution is comparable with that obtained using synchrotron X ray sources.

Fig.4a

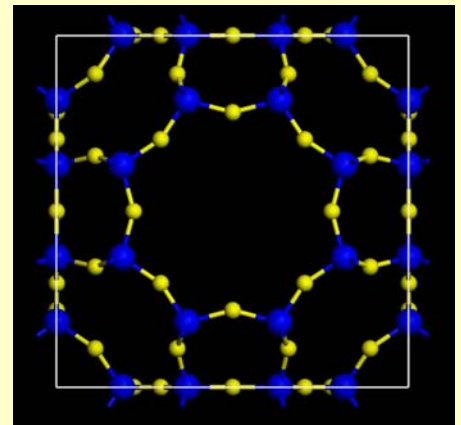


Fig.4b

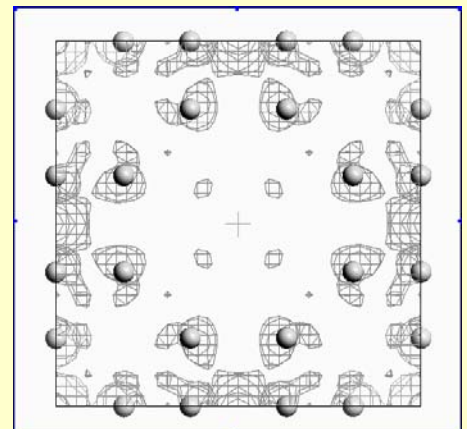
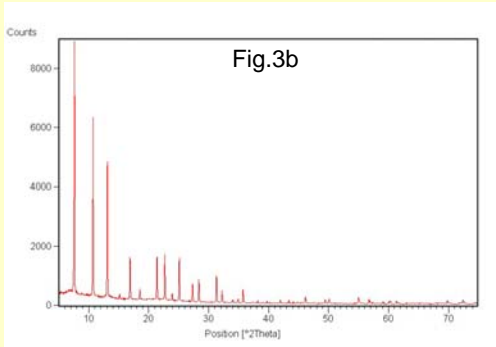
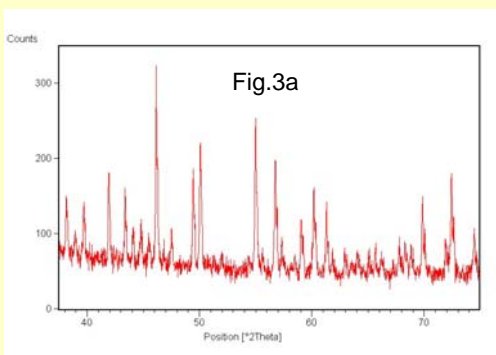


Fig 3a:enlarged part of (b) high resolution X Ray diffraction LTA zeolite

Fig 4(a) Ideal framework of LTA zeolite (001) orientation

Fig 4(b) Using intensities measured from precession ED pattern of fig 2b and ab initio direct methods (SIR, SHELX or MICE software C.Gilmore) experimental LTA refined framework is revealed exacty the same as the ideal one.



Ab initio determination of mordenite zeolite framework

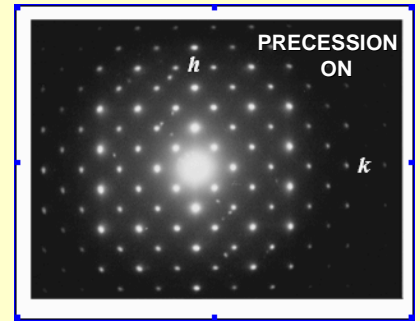
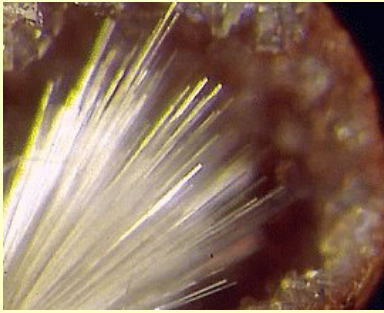


Fig.5

Mordenite (orthorhombic, $Cmcm$, $a = 1.81$ nm, $b = 2.05$ nm, $c = 0.75$ nm) is a zeolite of natural occurrence, but it can be also obtained by synthesis. This zeolite is the third one for industrial catalytic application (just after Faujasite and ZSM-5) and has been used for a large number of petrochemical processes, such as paraffin isomerization, as additive for cracking catalysts, alkylation of olefines, etc.

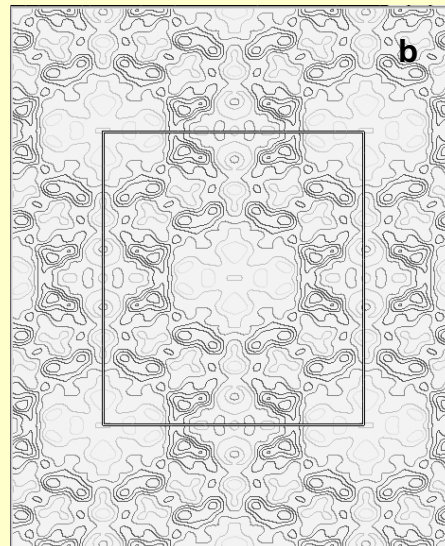
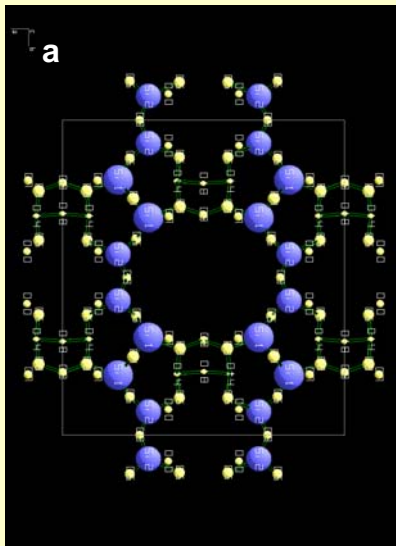


Fig.6

Measuring precisely ED precession intensities from (001) ZA at 100KV (fig.5) is possible after using ab initio direct methods (SIR, EDM software L.Marks) to find the correct framework ; fig 6b shows result of refinement considering experimental (precession) intensities and known phases of reflections.

Ab initio determination of ITQ-7 zeolite framework

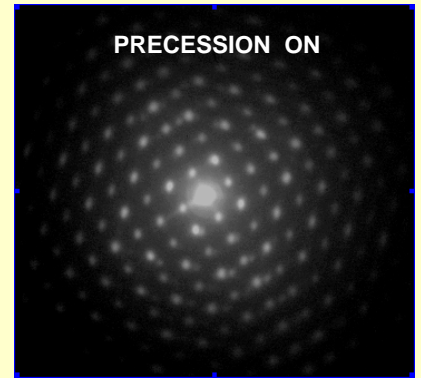
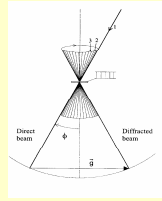
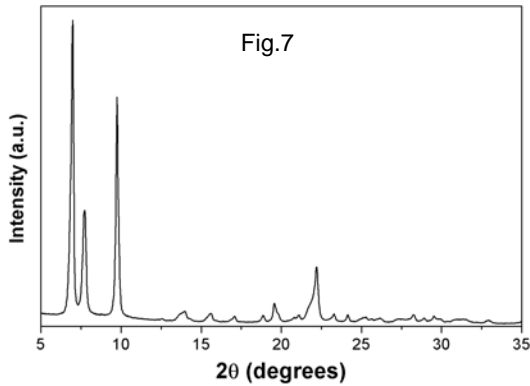


Fig.8 ED of ITQ7 (001) at 200KV

Zeolite ITQ-7 (tetragonal $P42/mmc$ $a = 1.29$ nm, $c = 2.52$ nm, ref. 3) is an example of industrially useful large pore zeolite that usually appears as an intergrowth material. Due to that, it is impossible to solve its crystal structure from X-ray diffraction due to poor data quality (fig.7). Precession quasi-kinematical ED reflections at (001) orientation extend diffraction data information up to 0.08 nm (fig 8), allowing to obtain good model structures even from badly crystallized zeolite samples.

Measuring precisely precession data (at 200KV) from single ITQ-7 nanocrystal we can use ab initio direct methods in order to obtain a correct initial model projection framework (fig 9b).

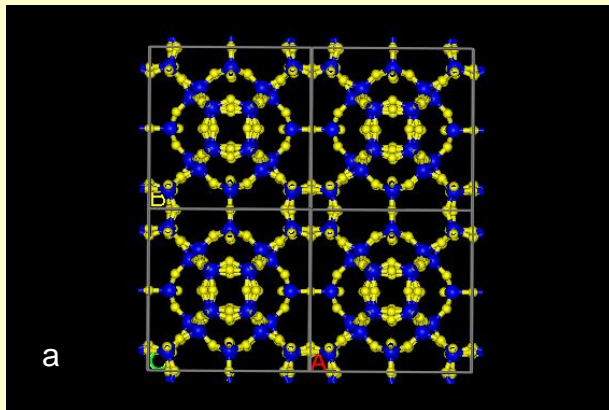
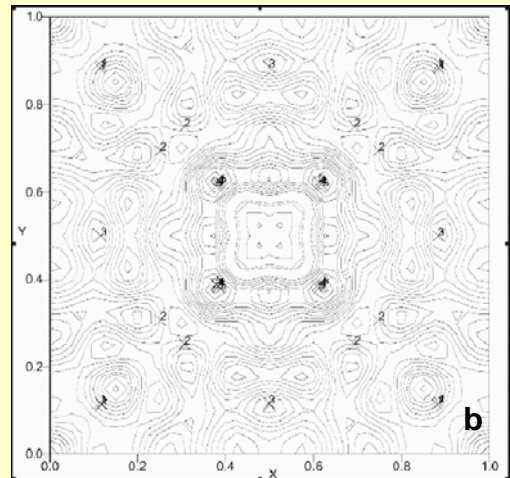


Fig 9(a) Ideal framework of ITQ-7 zeolite (001) orientation (b) resulting framework after ab initio from direct methods from precession ED data/ software MICE, author Chris Gilmore.
(Image courtesy D.Dorset, USA)

Fig.9



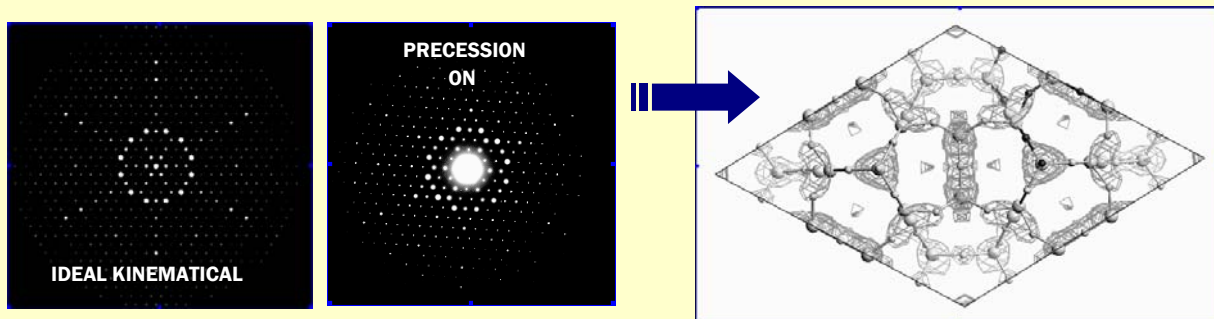
Atomic T positions appear clear in the initial potential projection map, although slightly displaced in relation with ideal framework positions. After further refinement, all T atoms can be localized correctly in the zeolite framework..

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

ITQ-1 is the all-silica analogous of zeolite MCM-22, which has been applied in industry as a selective catalyst for alkylation of aromatic compounds.

This zeolite possesses a relatively large unit cell (hexagonal, $P6/mmm$, $a = 1.42$ nm, $c = 2.49$ nm, ref; 4); high quality ED data are obtained by using the Spinning Star on a 200KV microscope. These data allowed to solve the structure using direct methods

FROM DIFFRACTION PATTERN TO 2D STRUCTURAL PROJECTION AT ONE STEP



Using precession intensities of (001) ZA of ITQ1 (200KV) nanocrystal and ab initio direct methods crystallographic software (MICE, Chris Gilmore) we can easily resolve (001) atomic framework map at atomic resolution. T positions coincide perfectly with max density envelopes (image courtesy Douglas Dorset, USA)

AB-INITIO 3D CRYSTAL STRUCTURE DETERMINATION

Electron diffractometry consists of collecting and combining automatically quasi-kinematical precession electron diffraction intensities from different zone axis to one 3D electron diffraction data set

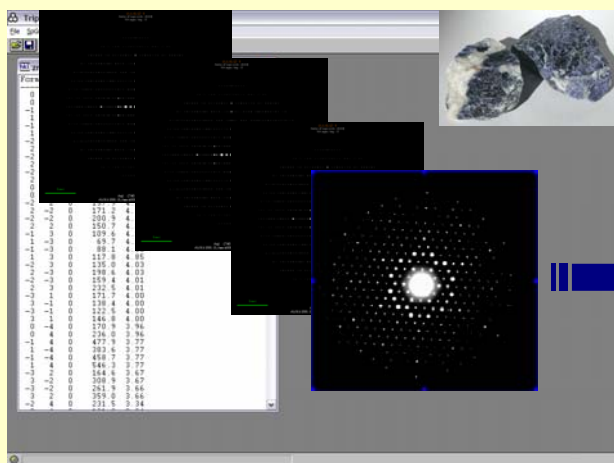
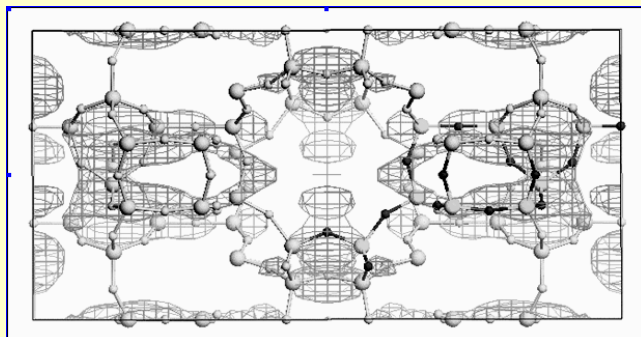


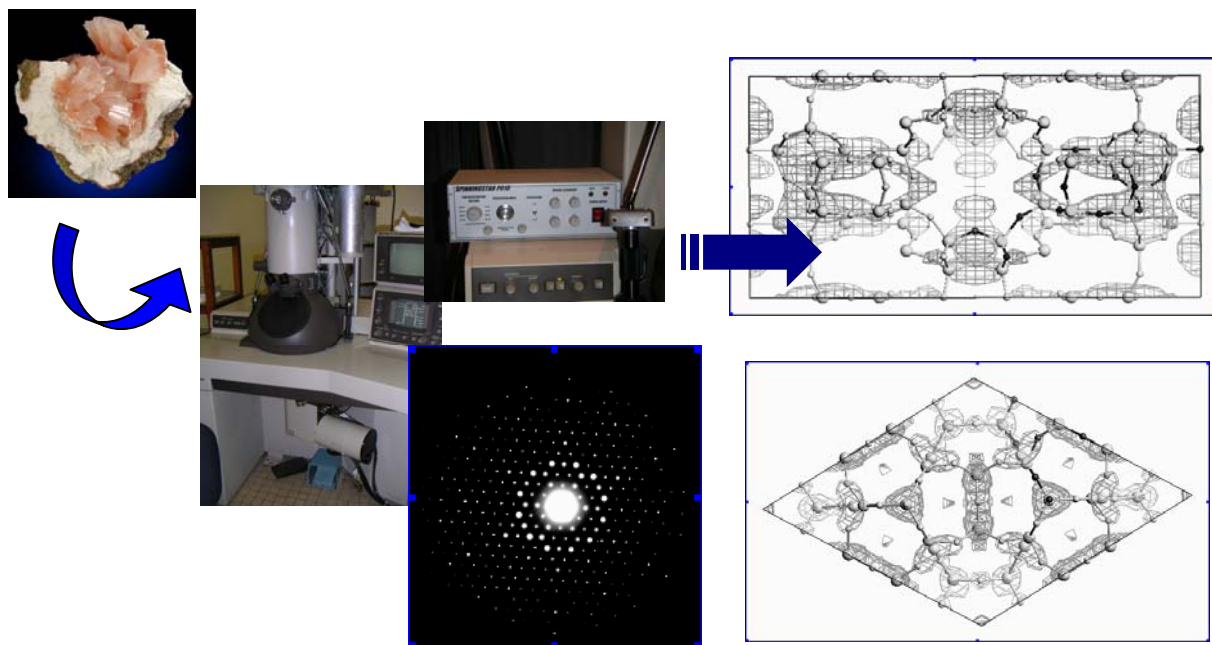
Fig.10



In case of ITQ1 nanocrystal quasi-kinematical precession intensity data have been combined from 4 different zone axis; intensities were further symmetrized according to $P6/mmm$ space group. Using that set of reflections and by means of ab initio direct methods crystallographic software (MICE) atomic density envelopes coincide with correct T positions in (110) projection. Elongated atomic density envelopes are result of missing additional ZA reflections from 3D data collection. Resulting 3D structure (fig.10) is same as ideal one obtained after refinement from synchrotron X-Ray data (image courtesy Douglas Dorset, USA).

CONCLUSION

Using advanced precession unit interface to any TEM (120-300 Kv) electron diffraction intensities from small zeolite nanocrystallites are close to kinematical ; as a result zeolite structure model (2d projection or 3d structure) can be directly found and refined using ab initio direct methods. Resulting structures are in close agreement with single crystal X-Ray diffraction data



With electron diffractometry we can measure, collect and combine automatically quasi-kinematical precession electron diffraction intensities from different zone axis to one 3D data set , resolving ab-initio 3D structure from any nanocrystallite

Acknowledgements

We would like to thank for valuable contributions to this application note Dr Jose Luis Jorda, Dr Fernando Rey and Prof Avelino Corma from Polytechnic University of Valencia (Spain)

References

1. Vincent & Midgley *Ultramicroscopy* **53** (1994) 271
2. A Corma et al *Nature*, vol 431 2004 P 287-290
3. L A Villaescusa et al *Angew Chem Int Ed* 1999, 38 N° 13-14 1997_2000
4. Leonowicz et al *Science* 264, 1910-1913 (1994)