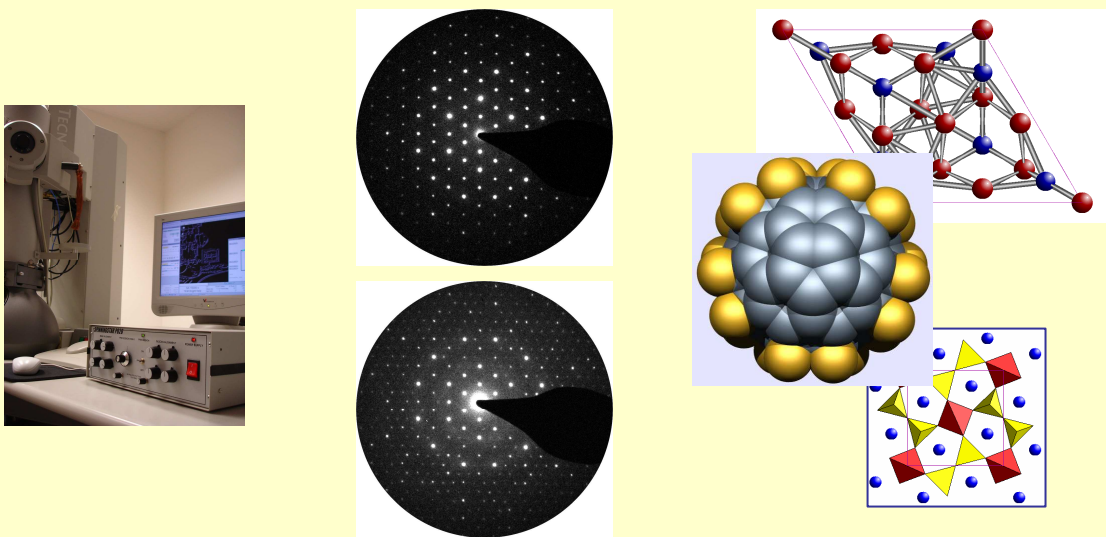




## SPINNING STAR

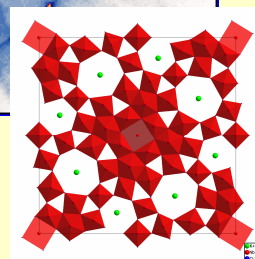
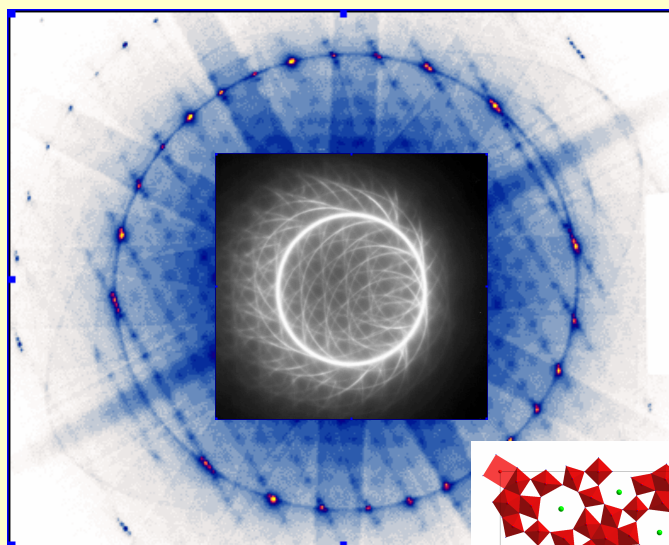
**New tool for structure determination of nanocrystals  
by precession electron diffraction in any TEM**



- **Device easily retrofittable to any TEM 100- 400 KV ( old or brand new)**
- **possible ab-initio structure determination of nanocrystals ( metals minerals, ceramics, semiconductors, polymers, pharmaceuticals...)**
- **Precession is possible for any electron beam size 300- 10 nm ( or less )**
- **Precession is possible for a parallel or convergent electron beam**
- **Precession eliminates false spots to ED pattern that belong to dynamical contributions**
- **Precession angle can vary continuously (0- 50 mrad) to observe true crystal symmetry ( determination of point and space group)**



## Structure determination of nanocrystals by precession electron diffraction in any TEM



### Method description:

Transmission Electron Microscopy (TEM) is very well adapted to the imaging and the analysis of nanocrystals, as it is always possible to select a tiny diffracted area whose size is smaller than the nanocrystal size in order to obtain an electron diffraction pattern.

Despite these interesting features, electron diffraction was rarely used in the past as a standard tool for crystal identification mainly because the electron interactions with the matter are about 10,000 times stronger than the ones observed with X-Rays. As a result, the scattering is not kinematic but dynamical so that the diffracted intensities are so much altered that they cannot be trusted and used for crystal structure determination, unless the crystal thickness is very thin or very heavy dynamical calculations are undertaken.

The electron beam precession technique recently proposed by Vincent & Midgley [1] offers a solution to this problem by decreasing the dynamical behaviour of electron diffraction.

This technique is equivalent to the Buerger precession technique used in X-Ray diffraction where the specimen is precessed with respect to the x-ray incident beam. In the electron precession technique, this is the electron beam which is tilted and precessed along a cone surface having a common axis with the TEM optical axis and with a zone axis.

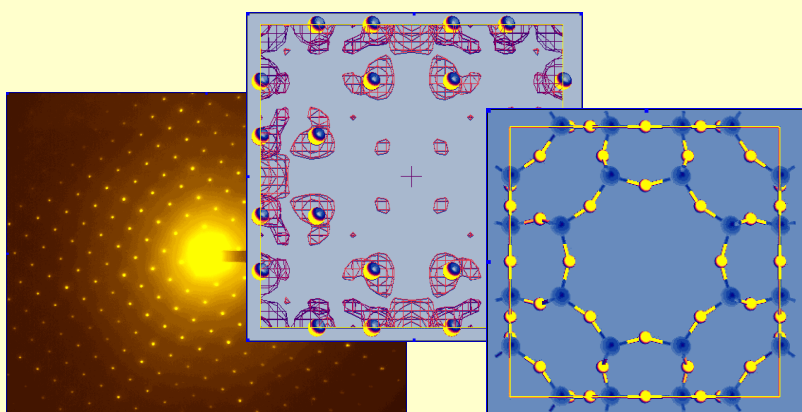
As a result of this precession diffraction only a very few reflections are simultaneously excited and much more reflections are visible in the ED pattern; the diffracted intensity of the beams is the integrated intensity and the resulting diffraction pattern intensities can be used directly for ab-initio structure determinations of unknown nanomaterials. By using quasi-kinematical precession intensities, several mineral, catalyst, and complex oxide structures [2-3] have already been ab-initio solved.

Every TEM (old and new) can be updated easily to perform precession electron diffraction by means of special precession device “spinning star” developed and manufactured by NanoMEGAS.

## Structure determination of catalysts by precession electron diffraction

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 the use of powder techniques is strongly limited due to their large unit cells, resulting to strong peak overlappings.

In this case, electron diffraction combined with beam precession is well suited to solve the structures of individual zeolite nanocrystals. The following example has been solved with 100KV TEM interfaced with “spinning star”.



**Fig. 1** Precession electron diffraction pattern of LTA zeolite (left), refined structural model from ED data (middle) and ideal LTA model framework (right).

Zeolite A/LTA (cubic,  $Pm\bar{3}m$ ,  $a=1.2$  nm, [4]) is widely used for gas separation and as component for detergents due to its unique atomic pore structure.

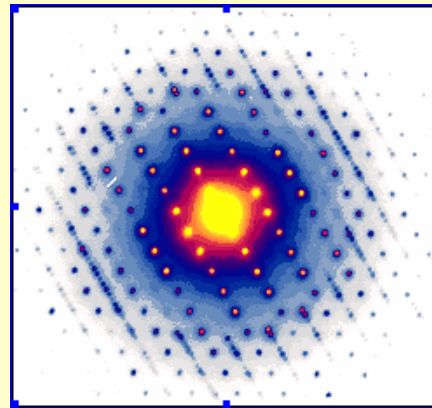
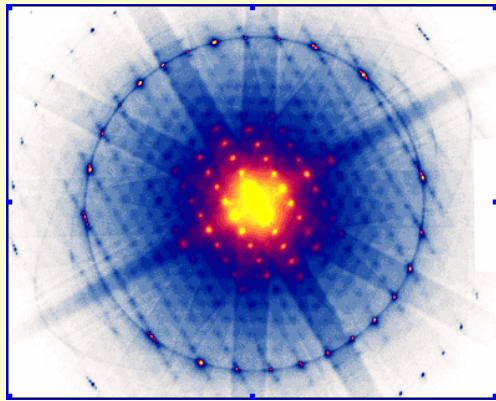
Accurate measurements of the electron diffraction intensities allow us to obtain, through *ab initio direct* methods, a full framework model (fig.1), which, after atomic positions refinements, gives the correct structure [4]. The resolution achieved using the ED precession technique is around 0.05nm, which is much better than that obtained with conventional X-ray powder techniques (0.12 nm).

The resolution is comparable with that obtained from synchrotron X ray sources.

## Symmetry determination of nanocrystals by precession electron diffraction

By using electron diffraction in precession mode, the number of reflections present in the Laue zones is strongly increased and it becomes very easy to identify, on specific zone axis patterns, the shifts and the difference of periodicity between the reflections located in these Laue zones.

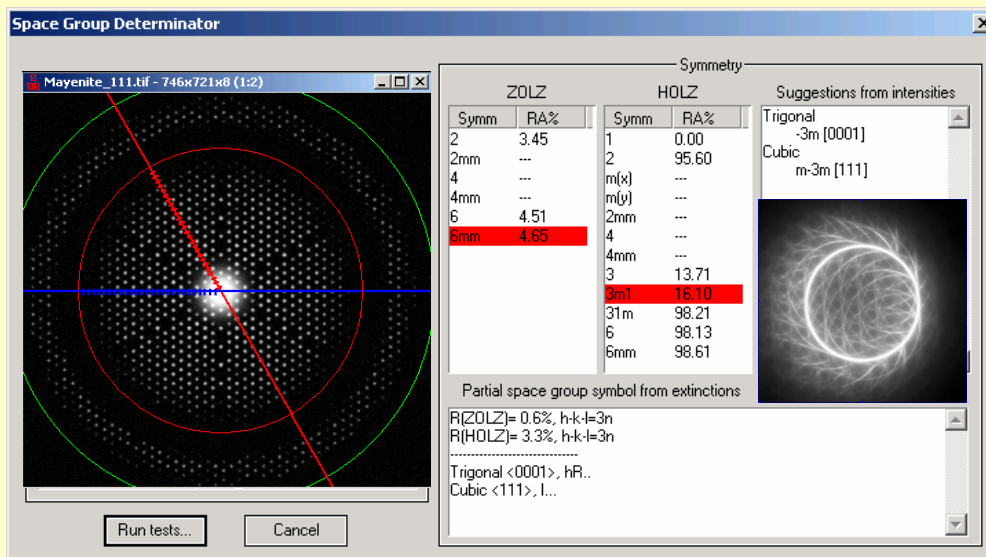
Shifts are connected with the Bravais lattice and the periodicity differences with the presence of glide planes; they can be used to identify a few possible space groups.



**Fig. 2**  $[1 -1 0 0]$  zone axis pattern of SiC 4h crystal obtained without precession (left) and with  $0.7^\circ$  precession angle(right). The Zero Order Laue Zone (ZOLZ) and the First Order Laue Zone (FOLZ) are clearly superimposed.

Thus, on the example given in fig. 2 , two electron diffraction patterns with zone axes  $[11-2 0]$  and  $[1-1 0 0]$  were enough to restrict the SiC , 4h space group among the three following possible space groups : P63mc , P-62c and P63/mmc [3].

## Automatic symmetry (point group) determination by precession diffraction



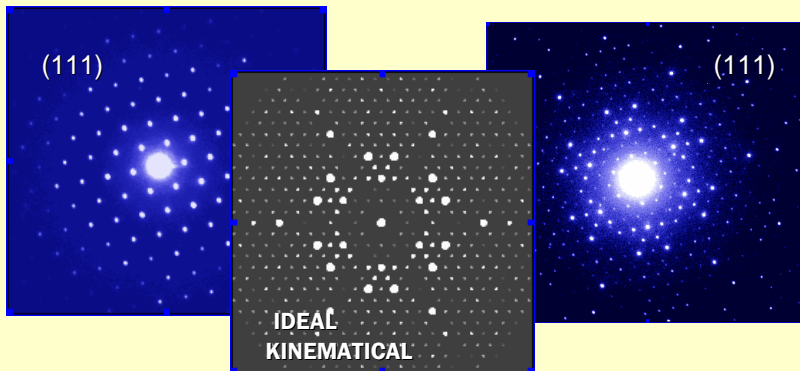
**Fig. 3** Software User interface where automatic point group determination can be done by input symmetries of the observed ZOLZ and FOLZ precession reflections.

As in precession diffraction patterns they generally appear ZOLZ and FOLZ reflections comparison of periodicities can be made automatically by dedicated software.

In the photo shown before automatic comparison of ZOLZ and FOLZ of mineral mayenite (cubic) shows the different indexing possibilities of the ED pattern without any prior knowledge of the sample.

## Ab-initio nanostructure determination by electron beam precession

Minerals are everyday used as beautiful gems, but also because of their chemical, physical and industrial properties. Those properties are directly related with their complex 3d structure.



**Fig.4** Electron diffraction pattern of an uvarovite crystal obtained without precession (left) and with precession (right). Ideal simulated kinematical pattern (middle).

Minerals often grow as single nanocrystals or often contain polymorphs and twins at nanoscopic level. Electron diffraction in TEM (combined with beam precession) is the only available technique to solve ab-initio crystal structures of single nanocrystallites with a resolution up to 0.05 nm which is comparable to the resolution obtained from single crystal X-Ray crystallography.

Uvarovite is a green garnet with chemical formula  $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ . Its structure is cubic with lattice parameter  $a=1.2$  nm and space Group  $Ia-3d$ . By applying electron beam precession, the crystal symmetry of this compound is easily revealed (see fig.4) because the precession diffraction pattern is closer to a kinematical pattern; in addition, the integrated diffraction intensities can be used for ab initio structure analysis.

Diffraction intensities obtained from four different zone axis intensities were first symmetrized according to  $Ia-3d$  space group. Then, by means of direct methods software, all the atom species were located at correct positions. The resulting 3D structure (see table) is same as the ideal one refined from X-Ray data

Atom	x	$x_{\text{exp}}$	y	$y_{\text{exp}}$	z	$z_{\text{exp}}$
Ca	1/8	1/8	0	0	1/4	1/4
Si	3/8	3/8	0	0	1/4	1/4
Cr	0	0	0	0	0	0
O	0.547	0.544	0.153	0.160	0.539	0.530

**Table I** This table shows how the positions deduced from electron precession data are close to those refined with single crystal x ray diffraction data.

### References

1. Vincent & Midgley *Ultramicroscopy* **53** (1994) 271
2. T Weirich, J Portillo, G Cox, H Hibst, S Nicolopoulos *Ultramicroscopy* 106 164-175 (2006)
3. JP Morniroli, A Reijmnia, S.Nicolopoulos *Ultramicroscopy* vol.107 issue 6-7 June (2007) p. 524-522
4. A Corma et al *Nature*, vol 431 2004 P 287-290