# Precession Electron Diffraction assisted Orientation Mapping in the Transmission Electron Microscope

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**Abstract.** Precession electron diffraction (PED) is a new promising technique for electron diffraction pattern collection under quasi-kinematical conditions (as in X-ray Diffraction), which enables "ab-initio" solving of crystalline structures of nanocrystals. The PED technique may be used in TEM instruments of voltages 100 to 400 kV and is an effective upgrade of the TEM instrument to a true electron diffractometer. The PED technique, when combined with fast electron diffraction acquisition and pattern matching software techniques, may also be used for the high magnification ultra-fast mapping of variable crystal orientations and phases, similarly to what is achieved with the Electron Backscattered Diffraction (EBSD) technique in Scanning Electron Microscopes (SEM) at lower magnifications and longer acquisition times.

## Introduction

Precession electron diffraction, PED, is a new promising technique for electron diffraction pattern collection under quasi-kinematical conditions (as in X-ray Diffraction), which allows solving "ab-initio" crystal structures of nanocrystals. Diffraction patterns are collected while the TEM electron beam is precessing on a cone surface; in this way, only a few reflections are simultaneously excited and, therefore, dynamical effects are strongly reduced. In comparison with normal selected area electron diffraction, PED has the following advantages:

- Oriented ED patterns may be obtained even if the crystal is not perfectly aligned to a particular zone axis. Thus, reliable ED patterns may be collected very quickly without the need to accurately align the observed crystal along a particular zone axis, which is very useful when dealing with beam sensitive materials (zeolites, pharmaceuticals, proteins, etc.)
- Geometry of PED patterns, when including first order Laue zone excitation, show all symmetry elements necessary to determine space and point group of the nanocrystal under investigation, without the need of applying further special techniques, such as Convergent Beam Electron Diffraction.
- PED intensities are quasi-kinematical, likewise to X-rays , up to a thickness of 100 nm and may be used to solve the structure of nanocrystals in a semi-automatic way (Fig.1 )
- PED technique may be used in TEM instruments of voltages ranging from 100 to 400 kV and constitutes an effective upgrade of the TEM instrument to a true electron diffractometer (Fig.2).

PED has recently gained large recognition in TEM and X-Ray community and several new nanocrystalline structures have been solved with this technique [1]. On the other hand, a new field of precession diffraction has recently been developed, the orientational/phase mapping through rapid precessed electron diffraction data collection, which may be regarded as the equivalent in the TEM to the Scanning Electron Microscopy based EBSD technique (Electron Backscatter Diffraction)[2]. Effectively, EBSD has gained popularity over the last decade as it provides an effective tool for the characterization of bulk crystalline materials, provided lateral resolution demanded on the sample is not smaller than 500 nm [3].
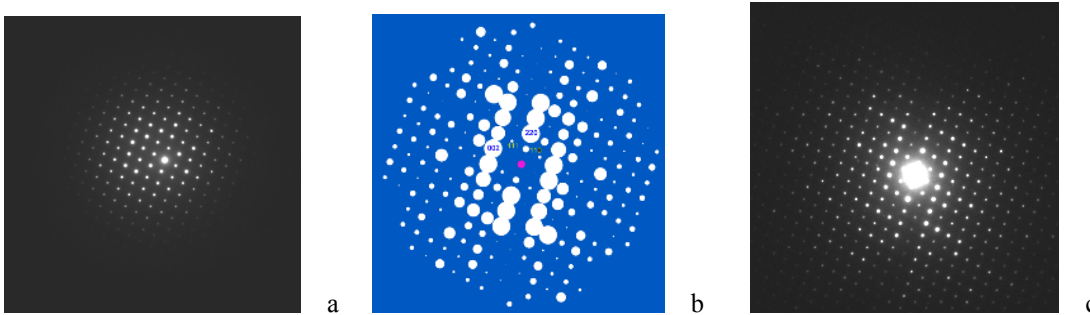


Fig. 1 (a) SAED pattern of spinel MgMoO4 along [1-10], (b) simulated kinematical pattern and (c) quasi-kinematical precession diffraction pattern

If a field emission gun is used in the Scanning Electron Microscope, lateral resolution may be improved down to some 50 nm, and a number of applications have been reported mainly on metals and alloys [4]. The EBSD-SEM technique is based on precise measurements of backscattered Kikuchi line diffraction patterns. However, these lines only appear after incident electron backscattering and double interaction (first inelastic scatter, then elastic diffraction) on surfaces of samples polished to mirror condition, which is a severe limitation on deformed crystalline materials. Moreover, acquisition times, although continously improved, are still on the hour scale.

We have shown that it is possible to apply an analogue of the SEM-EBSD analysis in the TEM, by ultra-fast collection of precessed electron diffraction patterns obtained on a user-selectable area of the TEM with a point spread resolution well within the nanometer range (typically, 10 nm) and without the need of additional surface sample preparation [2]. In this paper we present new advances and results on this technique, PED orientational and phase mapping, with new generation precession instrumentation.
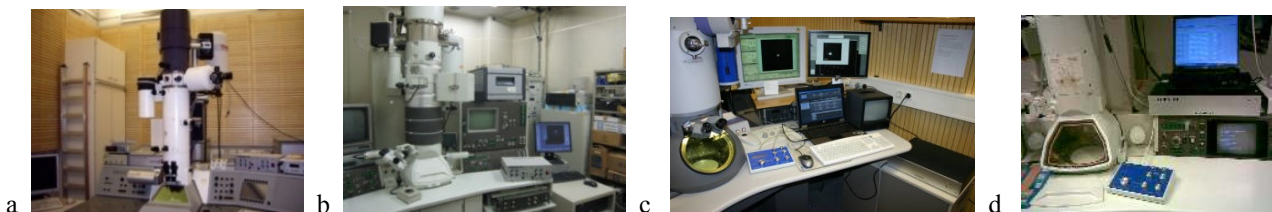


Fig. 2 (a) Precession unit "spinning star" intefaced with Zeiss 912 (120kv ), (b) Jeol 2100 FEG (200 Kv ); (c) Digital precession unit "DigiSTAR" interfaced with Tecnai 30FEG (300 KV) and (d) with Jeol 2000FX (200 Kv)

### New precession instrumentation and methods

A new digital precession instrument has been developed (called DigiSTAR) that can be retrofitted to an old TEM or mounted on a new one, and allows stocking in memory alignment values for driving the beam and image coils simultaneously and at different frequencies and turning (or precession) anglesin the TEM column. It is possible now with this instrument to increase precession angle continously from minimum to maximum with no need to re-align pivot points or readjust descan values, as it is mandatory for the analogue versions of precession instrumentation. Effectively, the most severe limitation imposed on the precession technique is the focused beam deformation and broadening due to several TEM aberrations, namely, spherical and three-fold astigmatism [5]. Thus, the beam spot size diameter is broadened by a factor of at least 3 times when the precession angle increases to 60% of the maximum available on each particular instrument, and at angles of > 2º the spot shape is no longer circular, but highly deformed. The software driving the digital version of the precession instrument enables accurate correction of beam shape and dimension (Fig. 3) even at high precession angles and, therefore, precessed electron diffraction patterns formed on nanocrystals may now be effectively studied under high precession angle illumination for the first time.

Structural information from crystalline materials is present in their electron diffraction patterns, which consist in Kikuchi lines and/or individual diffraction spots. In our Precession Electron Diffraction assisted Orientational and Phase Mapping technique, collected patterns consist exclusively in spots, since Kikuchi lines are smeared out by the high frequency of the precession illumination.
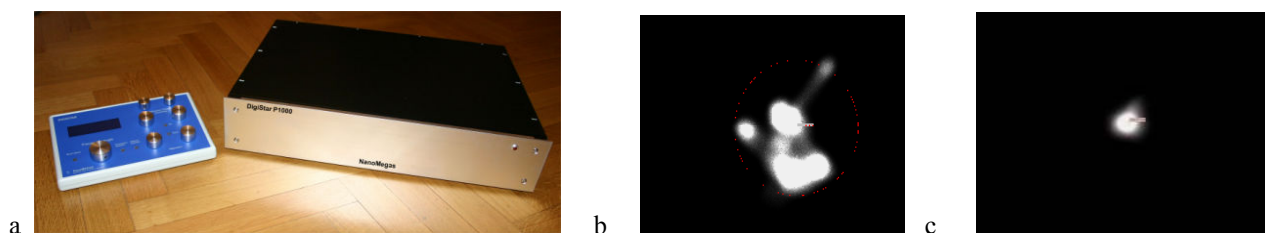


a                                                            b                                    c

Fig.3: (a) Digital precession unit "DigiSTAR", shown with manual inteface and control electronics, (b) Deformed beam spot size at precession angle of 2º on a TEM Jeol 2000FX at 8K times magnification, diameter size 1212 nm before software correction, (c) same image after on-line software correction (x8000 magnification, beam diameter 226nm); note beam diameter reduction by factor 6

ED spot patterns are collected sequentially with an ultra-fast optical CCD camera while an area on the sample is simultaneously being scanned by the TEM focused electron beam, which is also being precessed around the direction of incidence at each point. Beam scanning and precessing is controlled by a dedicated external device, which also allows control of beam pivot points and descan pivot points, called "Digistar" and manufactured by the NanoMEGAS company [6]. This device is connected to the beam and image deflector coil control boards present in the TEM. Thus, a TEM retrofitted with this precession device need not necessarily include a scanning option itself. An external ultrafast optical CCD camera, with only 8 bit dynamical range and 250 x 250 pixel image size, mounted in front of the TEM screen is used for the diffraction pattern image collection. This camera records the rapidly changing patterns appearing on the fluorescent screen of the TEM and is the key to a high collection speed since it may work as fast as 180 frames/sec, although fluorescent screen remanence slightly slows down this performance. During the scanning and precessing of the primary electron beam, thousands of ED spot patterns are recorded and stored in

memory of a dedicated computer[2]. In order to proceed with nanocrystal orientation and/or phase identification, each one of the experimental ED spot patterns is compared to one or several sets of thousands of computer generated ED spot patterns, the so-called templates. The software technique for the comparision is based on optimal template matching using cross-correlation (Fig.4 ).
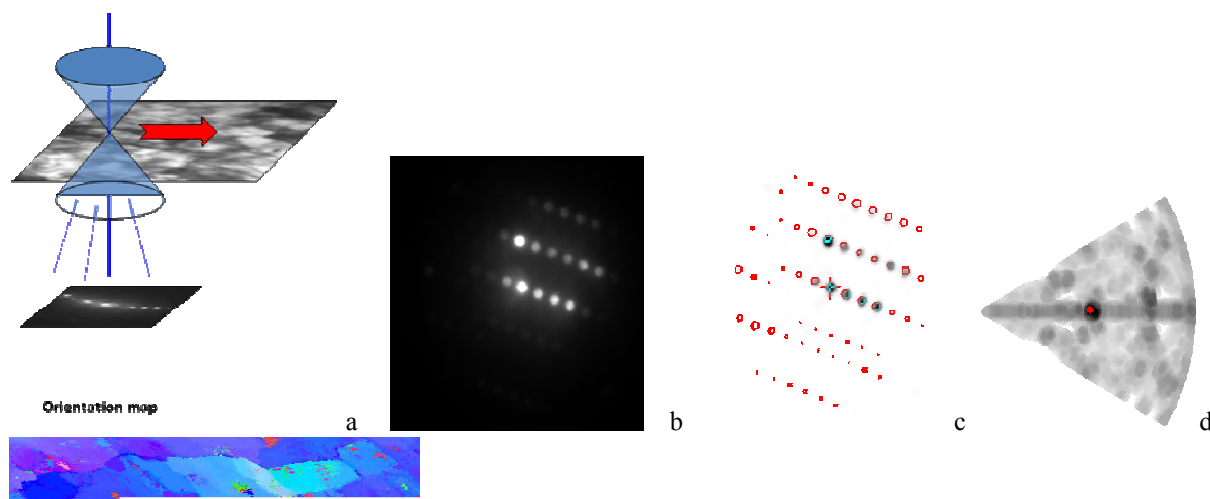


Fig. 4 Schematics of PED assisted Orientational and Phase Mapping: (a) beam scanning with DigiSTAR over a user-defined sample area combined with precession (b) experimental spot PED pattern serial recording in computer memory (c) superposition of individual ED template (red dot pattern) which best matches experimental PED pattern (grey dot pattern), and (d) orientation directional map with grey intensity plot of matching index for the experimental spot PED pattern.

For a typical map of 500 x 300 pixels, the beam scanning (and precessing) over the sample area and associated PED pattern recording may last only 15 minutes. Comparison with simulated templates can be done off-line and takes about 5 minutes for highly symmetric cubic materials and 2 to 24 times longer for unit cells with lower symmetry, because more templates must be generated and compared with experimental ED spot patterns for the same angular resolution (typically 1°). The scanning step chosen for the rastering is about half the size of the primary electron beam size, that is 12 nm for a 25 nm spot size on a TEM with $LaB_6$ electron gun, and the resulting lateral resolution of the obtained map will be of the order of the latter value. Template generation is done on the basis of unit cell dimensions and geometry as well as inherent atomic positions, for each of the known phases present in the examined sample. Using this data a complete spatial set of ED spot patterns is generated under purely kinematical conditions. The comparison of these templates with experimental ED spot patterns is run searching a maximum match for spot positions and their relative intensities, and the parameter quantifying the match is called the correlation index.

The software developed specifically for the technique allows obtention of crystal orientation maps, virtual bright field maps, correlation index maps and reliability index maps. The latter are related to the statistical significance of the orientational assignation chosen for each point of the map.

Essentially, the virtual brigth field map is obtained by plotting the intensity fluctuations of the central spot in the PED spattern. Such maps are often more helpful for comparision with the final orientation map of the scanned area than real bright-field TEM images of the same area, since these are usually suffering from diffraction contrast and curvature contrast (which fades significantly under precessed illumination). Correlation index maps are mainly used to emphasize

structural details such as crystals having different orientations. The reliability index, which is analogous to the SEM-EBSD confidence index, is defined in such a way that it has a minimum when more than one solution is proposed. Such reliability maps clearly reveal grain boundaries and textures (Fig. 5 ).
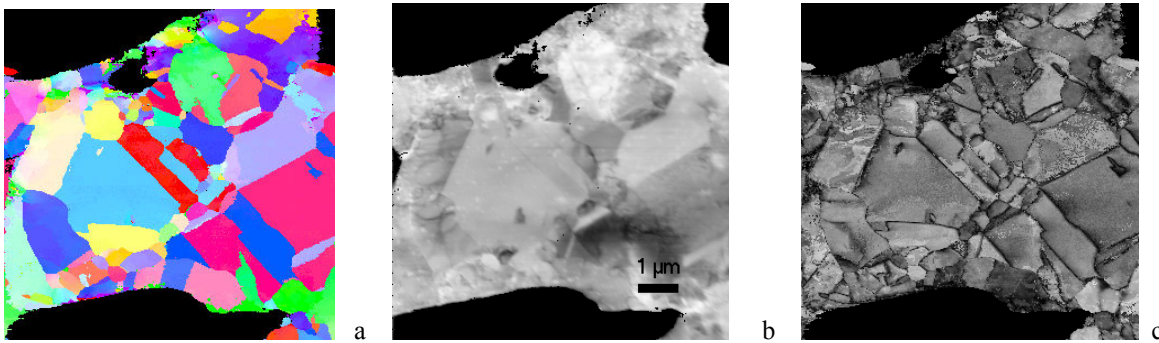


Fig. 5 (a) orientation map revealing nanotwins in Cu thin foil sample (Jeol 3010 LaB6 TEM, 300KV , spot size 12 nm, step 5nm (b) pseudo-bright field area of the same sample (c) Reability map showing clearly grain boundaries.

Although orientation and phase mapping coupled with template matching works satisfactorily for a number of materials without using precession of the primary electron beam [6,7], some limitations are present in the form of ambigous orientation/phase maps due to the poor quality of experimentally acquired ED spot patterns. This is the case for thick crystals where ED patterns show a combination of a strong diffuse inelastic scattering background with Kikuchi lines and a reduced number of faint diffraction spots. For such thick crystals and in general, precessed ED patterns exhibit a higher number of ED spots with especific intensity distribution and do not show Kikuchi lines. Consequently, the template matching software routine will produce higher values of the correlation index when using PED patterns, and orientation maps will exhibit less ambiguity.

A specific experiment was designed in order to outline the influence of beam precession on template matching/indexing for local orientation determination. A series of ED patterns were acquired on a single nanocrystal of mayenite, with formula $Ca_{12}Al_{14}O_{33}$ and cubic unit cell of 11.94 Å, starting from an initial electron beam incidence parallel to the (100) direction in the crystal and then tilting the TEM sample holder along its axis off this (100) direction in steps of 0.05º until a final off-initial incidence direction of 18º was attained. The series of experimental ED patterns were recorded twice, first without and then with a precession angle of 0.35º,  while keeping the beam stationary, unrastered on the same point of the crystal. Over 400 diffraction patterns were collected for each tilt series and then analysed with the template matching software. The results are shown as misorientations calculated for every experimental pattern with respect to the initial orientation. The origin of both graphs starts in 0º misorientation for the first data point and should extend towards 18º for the last measured data point (number 400). The blue unprecessed data show significant ambigous orientation assignation, while the red precessed data nicely scale along a constant slope. The stepwise shape of the red curve is due to the fact that the database is generated in orientation steps of half a degree. When comparing the experimental spot ED patterns shown in figure 6, it is worth remarking the absence of Kikuchi lines and the increased number of spots present in the precessed pattern compared to the unprecessed pattern, which explains the cause of the orientation assignation ambiguity in the blue curve.
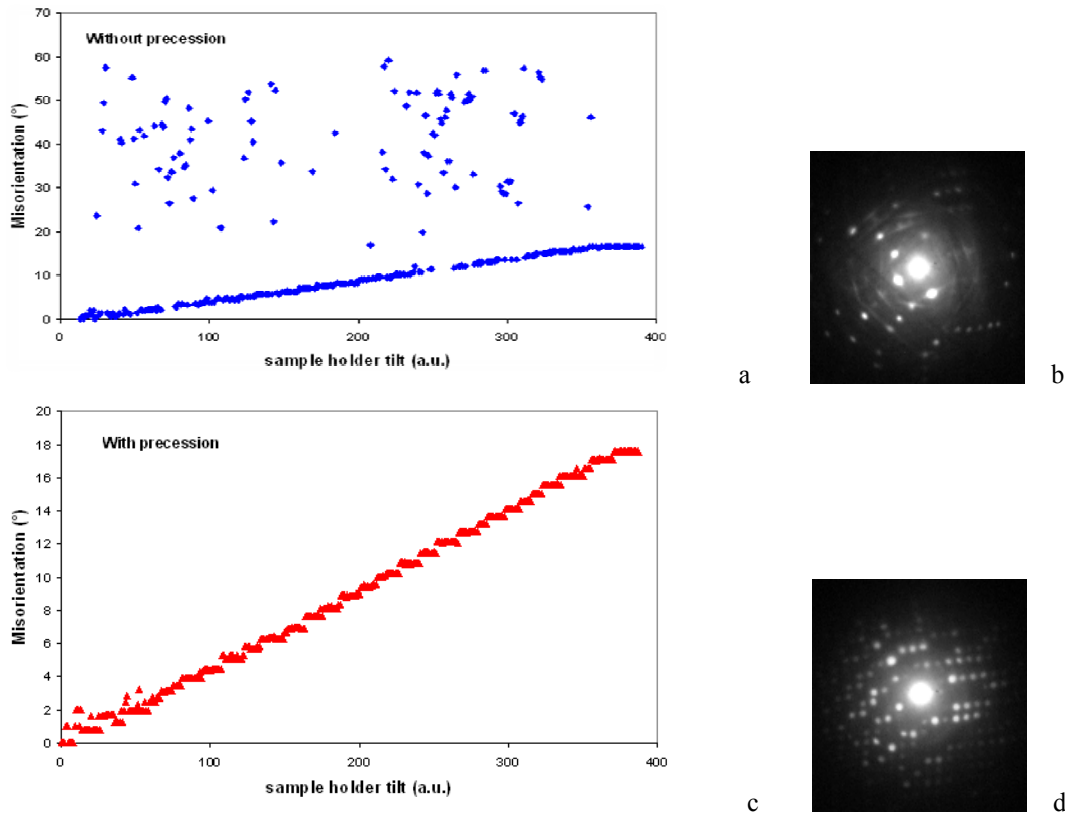
Fig. 6 (a) Orientation values of mayenite $Ca_{12}Al_{14}O_{33}$ (100) nanocrystal obtained after tilting it off this axis from 0 to18º with step of 0.05º along TEM sample holder direction; orientation values obtained by pattern matching-technique applied over set of simulated templates containing whole angular range (b) experimental spot ED pattern originating one point in blue curve, (c) the same experiment with 0.25º precession angle, (d) experimental spot ED pattern originating one point in red curve (note absence of Kikuchi lines and increased number of spots)

This demonstrates that even at small precession small angles, a substantial quality improvement is obtained in orientation maps obtained in the TEM when activating precession illumination.
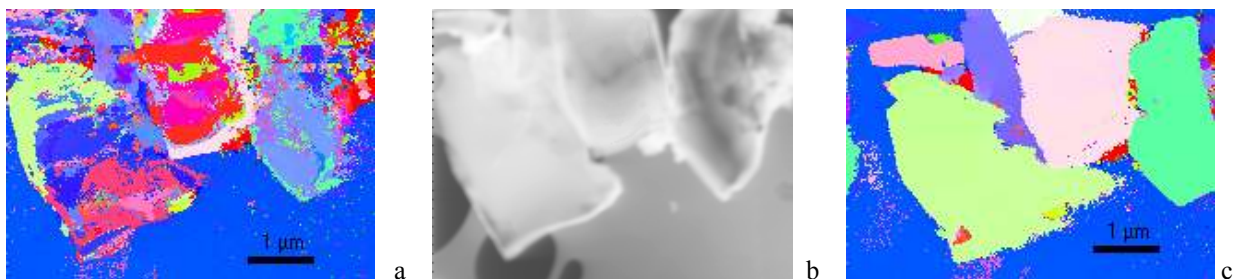


FIG.7 (a) Orientation mapping of mayenite crystals without precession (b) virtual bright field and (c) orientation map obtained with precession angle of 0.35º

This clear improvement of orientation determination can also be shown in the maps of Fig. 7 where an area that contains randomly oriented mayenite crystals was scanned twice (with and without precession). The orientation map in Fig. 7a shows color fluctuations indicating frequent misassigned patterns because of their low quality when compared with simulated templates. The

map in Fig. 7c was obtained under the same conditions as in Fig.7a but using precession at 0.35º angle during beam scanning. As it can be observed, orientation map quality increases with precession, since each colour domain corresponds to a single crystal grain with a definite orientation and should not show colour fluctuations, as it is the case.

## Conclusions

Precession Electron Diffraction assisted Orientation Mapping is a novel automated crystal phase and orientation mapping technique that benefits from the high spatial resolution (nm size) of TEM. This novel technique has been implemented onto a single instrument called ASTAR which enables beam precession along incident direction and simultaneous scanning over a micrometer or nanometer sized sample area. It can successfully be mounted onto new or old TEMs and uses beam size and shape correction via a digital precession device, termed DigiSTAR.

## Acknowledgements

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