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From powder diffraction to structure resolution of nanocrystals by precession electron diffraction

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Abstract. Despite today's possibilities, X-ray powder diffraction has some limitations for the ab-initio structure resolution of nanocrystals. In the present work, we show how electron diffraction combined with an electron beam precession device can be used as standard tool for the ab-initio resolution of unknown structures of nanocrystals. We give several examples of structure resolution of catalysts, minerals, and pharmaceutical compounds made by electron diffraction.

Introduction

X-ray crystallography is very well adapted to the structure analysis of perfect and large single crystals. The X-ray crystal interactions are largely kinematical and the structure factors can be directly derived from the diffracted intensity data. For nanocrystals, powder X-ray diffraction must be used but this technique presents severe limitations when the grain size is very small, when the powder is not well crystallized or when it contains several unknown phases.

Then, it becomes very difficult to solve ab-initio unknown structures from X-ray diffraction of nanocrystals**.** Due to its high lateral resolution, Transmission Electron Microscopy (TEM) is very well adapted to the imaging and the analysis of nanocrystals.
By means of the electron micrograph of the studied specimen, it is possible to select (eventually in a defect free area) and probe a tiny diffracted area whose size is smaller than the nanocrystal size in order to obtain an electron diffraction pattern.
Despite of 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 mat-

ter 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 movement: only very few reflections are simultaneously excited, many more reflections are visible, the diffracted intensity of the beams is the integrated intensity and the resulting diffraction pattern can be considered less dynamical.

This means that kinematically forbidden reflections and multiple scattering are greatly reduced making easier the space group identification. By using quasi-kinematical precession intensities, several mineral, catalyst, and complex oxide structures [2-5] 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 (figure 1).

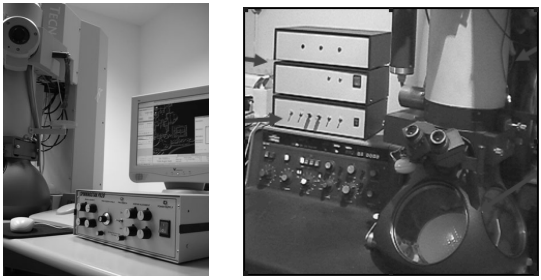

Figure 1. Modern (left) and older TEM equipped with electron diffraction precession device "spinning star"

Structure determination of catalysts nanocrystals by precession electron diffraction

Zeolites are microporous silicates widely used as catalysts in the oil refining and petrochemical industry, their catalytic properties are 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 in strong peak overlap. In this case, electron diffraction combined with beam precession is well suited to solve the structures of individual

zeolite nanocrystals. Zeolite A/LTA (cubic, Pm3m , a=1.2 nm, [6]) 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 (figure 2), which, after atomic position refininements, 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.

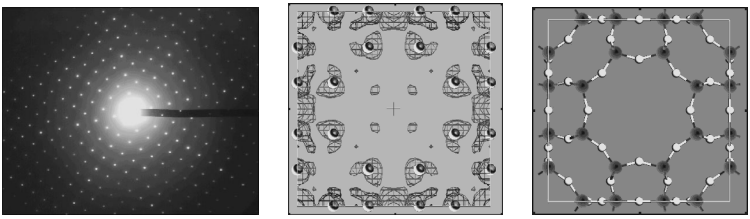

Figure 2. Precession electron diffraction pattern of LTA zeolite (left),refined structural model from ED data (middle) and ideal LTA model framework (right).

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. Thus, on the example given in figure 3, two electron diffraction patterns with zone axes[1 1-2 0] and [1-1 0 0] were enough to restrict the 4H- SiC space group among the three following possible space groups : P63mc , P-62c and P63/mmc [5].

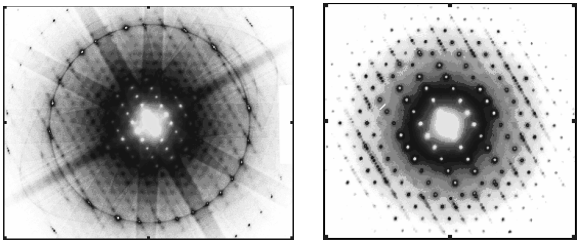

Figure 3. [*1 -1 0 0*] *zone axis pattern of 4H- SiC crystal obtained without precession (left) and with 0.7° precession angle(right). The Zero Order Laue Zone (ZOLZ) and the First Order Laue Zone (FOLZ) are clearly superimposed*

Characterization of pharmaceutical nanocrystals by precession electron diffraction

Usually pharmaceutical compounds are in powder form and this powder may contain more than one polymorph. For quality control and for Patent filling of new polymorphs, it is very important to reliably characterize these powder samples. X-ray powder diffraction cannot always give the correct structure especially when more than one poorly crystallized phase is present in the powder. Electron diffraction in precession mode allows the characterization of individual nanocrystals (figure 4) and therefore the accurate structure identification of crystals belonging to specific polymorphs.

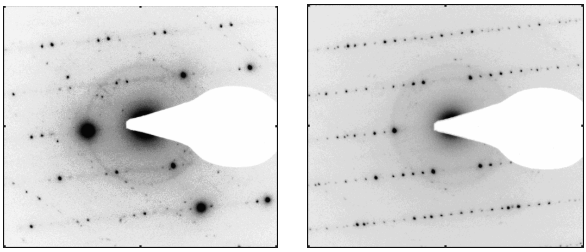

Figure 4. Electron diffraction pattern of an aspirin nanocrystal without precession (left) and with precession (right). Electron diffraction patterns made at liquid nitrogen temperature.

From precession electron diffraction to crystal structure of minerals

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. 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 $Ca_3Cr_2(SiO_4)_3$. 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 figure 5) 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.
The diffracted intensities obtained from four different zone axes were first symmetrized according to the m-3m Laue class.

Then, by means of direct methods using the SIR and SHELX software, all the atom species were located at correct positions (close to the ones deduced from single crystal X-ray diffra-

tion).The resulting 3-dimensional structure (Table I) is very close to the ideal one refined from X-ray data.

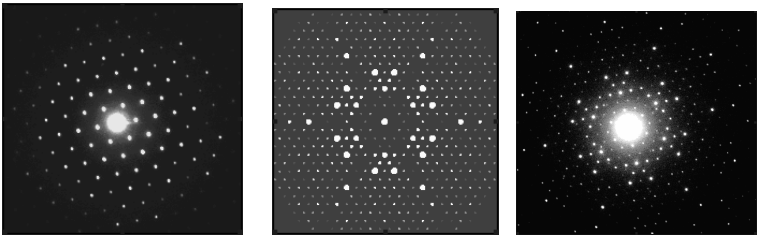

Figure 5. Electron diffraction pattern of an uvarovite crystal. [*111*] zone axis *obtained without precession (left) and with precession (right).Ideal simulated kinematical pattern(middle).*

Conclusion

By using electron diffraction in the precession mode, it is possible to solve the structures of nanocrystals otherwise impossible to solve by conventional powder X-ray diffraction or synchrotron. Every TEM (old or new) can be updated to perform « precession diffraction» to solve structures of nanocrystals.

Table 1. Fractional coordinates deduced from electron precession data (x,y,z) computed with single crystal X-ray diffraction data(x exp, y exp, z exp).

Atom	x	x exp	y	y exp	z	z 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

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