

Resolution of nanostructures by precession electron diffraction

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Abstract

Although, X-Ray crystallography is very useful for the structure analysis of large single crystals (< 5 microns) with no imperfections, there are lots of limitations, which appear in the analysis of nanostructured materials. Alternate approach based on electron diffraction is more adequate tool for structure determination in cases where X-ray diffraction is not sufficient, e.g. multi-phase/ nanometre-sized powders. We describe a new experimental approach, precession electron diffraction, that improves dramatically the quality of electron diffraction patterns by reducing dynamical effects.

Electron diffractometry system with the combination of the precession technique can be very perspective experimental instrumentation for precise structural investigations. 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 by using modern high intense X-Ray synchrotron radiation sources. Every TEM (old or new) can be updated to perform "precession diffraction" to solve structures of nanocrystals.

1. Introduction

These are times of intense research activity and importance of new materials with new and specific properties. In modern materials science and engineering is essential to know and understand the atomic structure and physical properties of materials at microscopic level. There are two basic, alternative approaches we use in order to reveal the atomic structure of new advanced industrial materials:

- X-Ray techniques (powder) ; a serious limitation however can be crystal size close to nm scale as may cause serious broadening of X-RAY diffraction peaks ; on the other hand peak overlapping is a serious obstacle for structure identification and determination
- Transmission electron microscopes (TEM) through high resolution imaging (HREM) and electron diffraction, usually working from 100-300 KV and magnifying images up to x1.000.000. Although TEM-HREM is a more useful technique as can reveal a picture of the atoms in the materials, however this picture is difficult to interpret. On the other hand, radiation damage from the electron beam is an issue (in HREM observations), as long periods of TEM observation (>1 min) usually can alter or damage seriously the structure of many materials like organic chemical compounds, zeolites, polymers, etc. Advanced materials structure analysis

by electron diffraction in a TEM presents a lot of advantages over conventional X-Ray diffraction: the size of studied crystallites in TEM can be very small (even tens of Angstroms), therefore individual phases in Industrial powders (nm size) can be examined.

2. X-Ray powder diffraction limitations

X-Ray crystallography is very useful for the structure analysis of large single crystals with no imperfections. The X-Ray crystal interactions are kinematical and the structure factors can be directly derived from the diffracted intensity data. In the case of nanocrystals, powder X-Ray diffraction technique presents severe limitations dealing with very small grain size, not well crystallized powders or powders, which contains several unknown phases. In those cases, it becomes very difficult to solve ab-initio unknown structures from X-Ray diffraction of nanocrystals.

Historically, X-ray diffraction techniques have been at the forefront of structural crystallography [3]. These techniques with development of probabilistic phasing algorithms in the 1950s, collectively called direct methods, which overcame the crystallographic phase problem (Hauptman 1991), enabled recovery of the critical phase portion of the Fourier components that describe the structure, enabling straightforward determination of structure models from diffraction intensity measurements. While highly suitable for many types of materials studies, evidenced by the vast number of atomic structures elucidated using X-ray radiation over the past 50 years, high-resolution X-ray techniques have some disadvantages from the perspective of nanomaterials characterization:

- Laboratory X-ray sources are not bright enough for studying very thin crystals, surfaces, and interfaces. To obtain scattered intensities with large dynamic range, a bright source such as a synchrotron is necessary.
- The beam diameter from high brightness sources are on the order of 1 μm , and on the order of 0.5 μm in specialized fine-probe laboratory instruments (an exception is the use of Fresnel zone plates that can obtain 100 nm probes in synchrotrons (Suzuki et al. 2005), however they are extremely rare due to cost).

In particular:

- Single crystal dimensions generally must be on the order of the probe size. Heterogeneous materials cannot be studied unless crystallites are larger in size or can be isolated.
- Nanocrystal studies require powder specimens or homogeneous polycrystals, which generate ring patterns from simultaneous sampling of all orientations of the crystal. Symmetry information is lost in ring patterns and must be acquired using other techniques such as transmission electron diffraction (TED). Additionally, because reflection number scales roughly with the cube of spatial frequency, large cell structures will have overwhelming peak overlap.
- Peak resolution (line width) is limited by the width of the probe. Decreasing the probe size can cause ring overlap in dense diffraction patterns from large cell materials or superstructures.
- X-ray imaging optics with adequate resolution is not available; the only information from experiments is diffraction intensities. Morphological and defect information is thus not simultaneously available.
- Being a shared resource, synchrotron-based research projects have strict time constraints and shared maintenance costs.

Therefore, using an X-Ray diffraction technique, only an average structure can be obtained, usually over a few thousands of particles. Also, many phases may be present. New synthesized materials are often in powder form and usually present poor crystallinity for precise X-Ray structure determination. Even modern high intense X-Ray synchrotron radiation sources can account only for crystals bigger from several cubic micrometers.

3. Transmission electron microscopy (TEM)

Electron diffraction: Advantages and challenges

On the other hand, electron diffraction is widely used in structure investigations, for identification of Bravais lattices, for symmetry determination of superstructures and defects - and increasingly for ab-initio determination of structures and subsequent structural refinement.

The study of crystals at atomic level by electrons – electron crystallography – is an important complement to X-ray crystallography. There are two main advantages of structure determinations by electron crystallography compared to X-ray diffraction:

- crystals millions of times smaller than those needed for X-ray diffraction can be studied
- the phases of the crystallographic structure factors, which are lost in X-ray diffraction, are present in transmission electron-microscopy (TEM) images.

Transmission Electron Microscopy (TEM), due to its high lateral resolution, is very adequate for the imaging and the analysis of nanocrystals. By forming a parallel beam in the transmission electron microscope (TEM) and selecting a crystal with an aperture, or by forming a fine convergent beam of only a few nanometres diameter, a diffraction pattern can be recorded from crystals too small to be studied by x-ray diffraction.

Electron crystallography has proven to be a unique technique for atomic structure determination of nano-sized crystals, from inorganic through organic to protein crystals. There is no overlapping problem of diffraction peaks from nanosized single crystals as in X-ray powder diffraction.

TEM has traditionally played a complementary role to X-ray methods in crystallography, partly because image resolution was insufficient except in specialized high-energy instruments and also because data quality from TED was limited by multiple scattering. Nevertheless, the ability to form a fine probe and to simultaneously collect diffraction patterns are distinct advantages. In recent years, the field has seen a huge leap in the imaging capabilities of high-resolution imaging (HREM) and scanning modes (STEM) due to the introduction of aberration-corrective optics allowing point resolutions of less than 1 Ångström (Haider et al. 1998; Batson et al. 2002; Haider et al. 1999; Nellist et al. 2004). Unfortunately, atomic resolution images are beyond the reach of most researchers because aberration correctors are still extremely expensive; the vast majority of TEMs are still limited by the resolution of the image-forming optics.

Electron diffraction is a complementary technique that is capable of extracting structural information — albeit incomplete because phase is lost — to much higher resolution (sub-picometer regime) than imaging techniques because it is virtually immune to the resolution-limiting aberrations of the objective lens. It can often be combined with imaging to enhance the resolution of HREM images through the phase extension technique.

A probe size of less than 25 nm is readily achieved on modern instruments, enabling precise study of very small particles, individual crystallites within a

heterogeneous matrix, and fine structures such as interfaces and surfaces in the TEM. This resolves a major constraint posed by X-ray methods.

Also, HREM has several limitations for resolving crystal structures: structure resolution depends on KV (higher voltage-higher resolution) and HREM image contrast is depending on defocus and thickness of sample.

The electron diffraction structure analysis (EDSA) in materials was originally developed by the Russian School of structure analysis in the 50's.

Many different structures of organic and inorganic substances have been determined up to now and gave a great contribution in the crystallography and crystal chemistry of solids. Recently, many structures of beam sensitive materials have been resolved successfully through the use of direct phasing of ED intensities. The method has been demonstrated to work well [6] both in theory and practice – using maximum entropy approach -even in bulk inorganic structures (over a wide range of thickness) and with conventional TEM probes size (100 nm) instruments.

The key for reliable atomic structure analysis is linked to the increasing of reliability and precision of the electron diffraction data. Speed of data acquisition is an issue, as radiation damage usually occurs (specially for organic compounds) for expositions larger than a minute. In fact, in order to resolve successfully a structure in electron crystallography we need to accurately (equal or better than 1 % precision) determine the intensity of all different spots (up to 200) present in an electron diffraction pattern and correct for dynamical diffraction contribution, especially for strong reflections.

In practice, in both light element detection and structure analysis is usually enough precise measurement of < 50-100 reflections to have accurate picture of the crystal structure, though in X-Ray several hundred of reflections have to be measured. Despite all these interesting features, electron diffraction was rarely used in the past as a standard tool for crystal identification mainly because the electron interactions with matter are about 10,000 times stronger than the ones observed with x-rays. In the simplest interpretation, in the X-ray case, the radiation incident upon the specimen is scattered by the atomic planes of the crystal when the Bragg condition,

$$\alpha = 2d \sin \theta_B \quad (1)$$

is satisfied. (d is the distance between scattering planes and θ_B is the Bragg angle). The ideal case for using direct methods is when intensity in a diffracted beam is a result of single scattering events from the scattering planes (kinematical diffraction). For X-rays, the probability of scattering is already low; therefore the probability for multiple scattering is vanishing small. The measured intensity is then related to structure factor according to the relationship,

$$I_g^{\text{exp}} = |F_g|^2 \quad (2)$$

Electrons, however, interact more strongly with matter than X-rays by 3-4 orders of magnitude. The intensities of scattered beams deviate from kinematical and upper equation no longer holds. This phenomenon, termed dynamical diffraction, is demonstrated in the next figure for two beams (Figure 1).

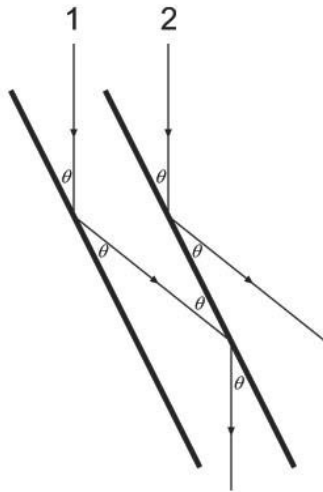


Figure 1. Diffracted beams that meet the Bragg condition (equation 1) are necessarily in the same condition to be rediffracted back into the incident beam. Demonstrated here for two beams, this is the origin of dynamical diffraction [3].

The probability for rediffraction is a function of specimen thickness; therefore as the electrons propagate through the specimen, intensity is continually exchanged between diffracted and transmitted beams. At the exit surface the diffracted beam intensity no longer represents the scattering strength as indicated by the structure factor.

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 complex dynamical calculations are undertaken.

4. Solution: Precession Electron Diffraction (Vincent- Midgley)

One new experimental approach to reducing dynamical effects in electron diffraction data is precession electron diffraction (PED) proposed by Vincent & Midgley [5]. In this technique, the incident beam is precessed in a hollow cone about a centred zone axis direction as the data are collected. The data show reduced dynamical effects because there are far fewer simultaneously excited reflections in the off-zone condition. In addition, the precession integrates the diffraction intensities through the Bragg condition, which provides a data set less subject to minor sample tilt, and makes interpretations of pattern symmetry more reliable. This technique is equivalent to the Buerger precession technique [4], 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 a very few reflections are simultaneously excited;
- much more reflections are visible in ED pattern;
- the diffracted intensity of the beams is the integrated intensity;
- the resulting diffraction pattern can be considered less dynamical;
- the resulting diffraction pattern intensities can be used directly for ab-intio structure determinations of unknown nanomaterials.

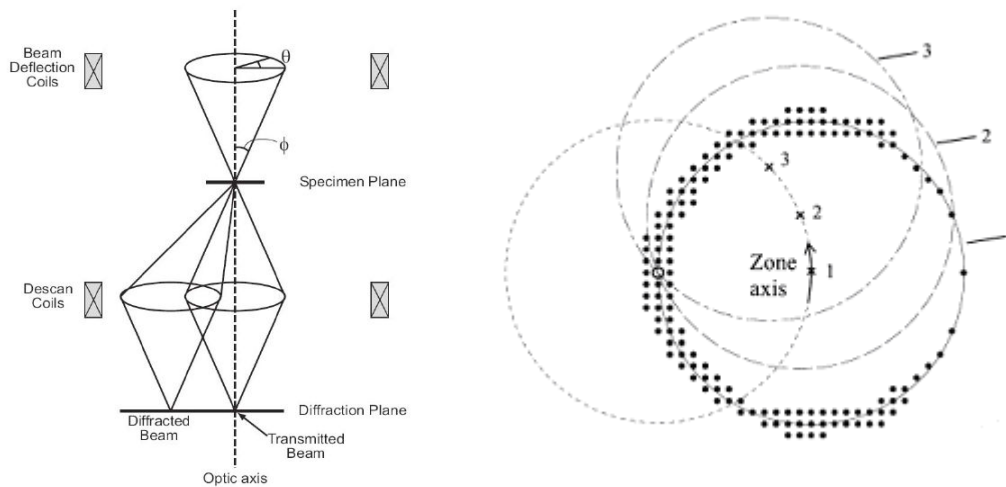


Figure 2. a) The schematic diagram of precession electron diffraction (PED). The beam is tilted off zone by angle ϕ using the beam tilt coils and serially precesses through an angle $\theta = 2\pi$. A complementary descans of the beam is provided below the specimen by using image shift TEM coils to restore the zone axis pattern. b) During precession, the Laue circle rotates about the zero beam and sweeps the zero Laue zone.

This means that kinematically forbidden reflections and multiple scatterings are greatly reduced making easier the space group identification. By using quasi-kinematical precession intensities, several mineral, catalyst, and complex oxide structures have already been ab-initio solved [7].

By precessing a focused incident beam at a constant angle around a zone axis in combination with a similar precession of the beam below the specimen one obtains the equivalent of the precession of the specimen (as in an X-ray precession camera). The reflections are swept successively through the Ewald sphere and the resulting integrated intensities are recorded as uniform discs on the photographic plate (Figure 2a). The diffraction conditions during the precession movement can be visualized in different ways: by movement of the central spot around a circle in the zero Laue zone, or by the equivalent rotation of the Laue circle about the central spot (Figure 2b). The integration will reduce the sensitivity to thickness; multiple beam dynamical effects are expected to be less than in the SAD patterns because the beam is of the zone axis [1,3].

The purpose of the precession technique is to acquire intensity data, which in the early stages of structure determination can be treated within a kinematical approximation.

This geometry yields several very interesting features [2]:

- The pattern may be indexed as a conventional diffraction pattern while the intensities have actually been gathered from off-zone reflection conditions.
- Inelastic dynamical effects such as Kikuchi lines and intensity variations in CBED spots are reduced by averaging over incident beam directions.
- Since the beam is entering the sample from an off-axis direction, much of the dynamical scattering that is particularly strong at the exact Bragg condition (or zone axis channeling condition) is avoided.

- Many more FOLZ reflections are excited, under more kinematical conditions, by the Ewald sphere allowing the acquisition of an increased number of intensities for use in structure solution techniques.
- More HOLZ reflections are illuminated, yielding expanded 3-dimensional data sets provided that spots from separate Laue zones do not overlap.

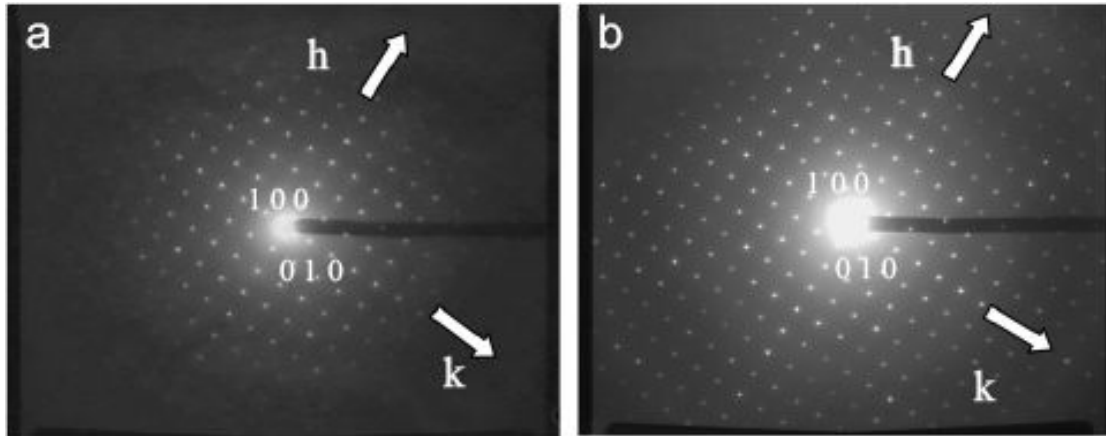


Figure 3. ED pattern of cubic LTA zeolite ($Pm\bar{3}m$, $a=12\text{\AA}$) at 200 kV before (a) and after applying precession (b).

The improved quality of the precession data over that of conventional ED has been demonstrated experimentally (Vincent and Midgley 1994; Own et al. 2004), and a small number of structures have been solved via the technique, some a priori (Gjønnnes et al. 1998a; Gemmi et al. 2003; Own and Marks 2005b), and others by a combination of simulation and/or correction using forward calculations (Vincent and Midgley 1994; Gjønnnes et al. 1998b). Additionally, precession has been used to derive Debye-Waller temperature factors from monatomic specimens using Wilson plots with good accuracy (Midgley et al. 1998).

Some of the capabilities demonstrated by the technique are listed below:

- Pseudo-kinematical intensities are available under some experimental conditions as will be seen below;
- 3-dimensional datasets can be acquired under appropriate conditions from a single zone axis pattern. Low electron energy or large cell dimension in the optic axis are necessary, and Laue zone overlap must be avoided;
- Decreased intensity oscillation with thickness is observed (also occurs with thickness averaging);
- Greater tolerance to orientation errors, and specimens do not have to be perfectly on-zone to obtain symmetric patterns;
- Consistency of intensity values among different projections allows more accurate merging of multiple 2D projections into 3D datasets;
- Enhancement of fine detail in the solution of a large structure over that of conventional TED (Gemmi et al. 2003);
- If some structure factors are known, precession can be used to gain crystal thickness information with reasonable accuracy (within 10-15 nm).

5. Development and characteristics of the new universal precession device "Spinning Star"

First electron diffraction precession experiments were performed with some beam precession instruments fitted to Philips EM430 and CM30T microscopes. However, we must stress here that in those early instruments although beam scanning was not a problem (at least for those instruments having STEM) descanning of the beam was not correct, so as a result precession electron diffraction pattern was not completely stationary. The reason for this is the poor precision in the digitalization of scan and descann signals by the electron microscope CPU unit. Moreover, the CPU unit cannot control TEM coils simultaneously for precession and descanning. In all those early instruments probe size was approximately 100 nm, mainly due to optical distortions. Recently, Own reported design of a precession device fitted in a Hitachi TEM working with parallel illumination mode at a frequency of 60 Hz. The same author has reported the fitting of a more recent version to a JEOL TEM resulting in high-quality precession patterns obtained with a probe of up to 25nm for very well aligned TEM experiments.

For beam precession, a special universal interface "Spinning Star" has been developed with some important built-in characteristics [2]:

- Precession device can be adapted independently to any TEM.
- Precession device is designed with a proper interface to work in combination with an electron diffractometer.
- Beam precession is possible with either parallel or convergent beam while keeping beam size as small as possible.
- Precession angle can be varied continuously (without need of any further alignment) in order to achieve maximum usable electron diffraction area and best compromise to avoid FOLZ and ZOLZ reflections overlapping with increasing precession angle.
- During precession the tilted beam precesses, tracing out a circuit of theta $(0, 2\pi)$; ZOLZ reflections can potentially be recovered as partial scans of $(0, \pi)$ tilt avoiding problems of FOLZ-ZOLZ overlapping at high precession angles.

"Spinning star" has been interfaced successfully to several TEMs (such as Philips EM4xx, Philips CM, FEI Tecnai, JEOL, Topcon); its function being independent from the presence (or not) of an STEM unit on the TEM. "Spinning star" can be adapted to any type of TEM be it either a digitally controlled microscope or an older analog instrument. The unit is also designed to be connected to an electron diffractometer device.



Front panel



Rear panel

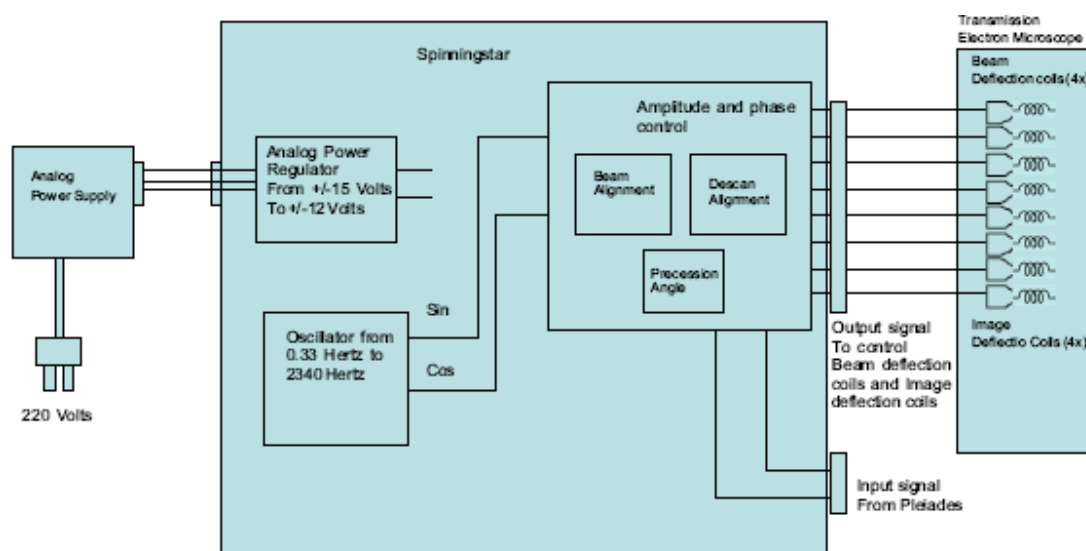


Figure 4. Front and back face and block scheme of the Spinning Star device

6. References

- [1] B.S. Berg, V. Hansen, P.A. Midgley, J. Gjønnnes. **Measurement of three-dimensional intensity data in electron diffraction by the precession technique.** Ultramicroscopy 74 (1998) 147-157.
- [2] A. Avilov, K. Kuligina, S. Nicolopoulos, M. Nickolskiya, K. Boulahyad, J. Portillo, G. Lepeshova, B. Soboleva, J.P. Collettef, N. Martinf, A.C. Robinsg, P. Fischione. **Precession technique and electron diffractometry as new tools for crystal structure analysis and chemical bonding determination.** Ultramicroscopy 107 (2007) 431-444.
- [3] Christopher Su-Yan Own, Ph.D. thesis, **System Design and Verification of the Precession Electron Diffraction Technique.** 2005, PDF <http://www.numis.northwestern.edu/Research/Current/precession.shtml>, EV ANSTON, ILLINOIS.
- [4] J.-L. Staudenmann, R.D. Horning and R. D. Knox. **Buerger precession camera and overall characterization of thin films and flat-plate crystals.** Journal of Applied Crystallography 20 (1987) 210-221
- [5] R. Vincent, P.A. Midgley. **Double conical beam-rocking system for measurement of integrated electron diffraction intensities.** Ultramicroscopy 53 (1994) 271.
- [6] W. Sinkler, L. D. Marks. **Dynamical direct methods for everyone.** Ultramicroscopy 75 (1999) 251-268.
- [7] A. Avilov, K. Kuligin, S. Nicolopoulos, M. Nickolskiya, K. Boulahya, J. Portillo, G. Lepeshov, B. Sobolev, J.P. Collette, N. Martin, A.C. Robins, P. Fischione. **Precession technique and electron diffractometry as new tools for crystal structure analysis and chemical bonding determination.** Ultramicroscopy 107 (2007) 431-444.