Fast Microstructure and Phase Analyses of Nanopowders using Combined Analysis of TEM scattering patterns

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Supplementary Materials

We present here, supplementary informations that shall be useful for the reader willing to perform microstructure and phase analyses from EPD patterns using both MAUD [1] and FPSM [2].

1. EPD Intensity extraction in MAUD

The ImageJ plugins used to import 2-dimensional diffraction data coming from CCD or imaging plate detectors can be accessed in MAUD through the “Datasets/Datafiles” window by clicking on the “From images” button (Fig.1). In ImageJ, one should first open the image file (TIFF or JPEG) and edit the image properties to indicate the size of the CCD camera (in pixels) and the pixel size, if not properly loaded from the image file. The integration is handled using the plugin menu “Multi-spectra from normal transmission/reflection image” where few options are available. The diffraction geometry (Fig. 2) is considered so that at normal incidence ω, χ and φ angles are 90°, 0° and 0°, respectively while η varies from 0° to 360° along the ring. The intensity integration being performed by an azimuthal segmentation of the ring patterns, starting angle (η_0), final angle (η_f) and the number (n) of desired spectra are users' entries. Each segment of the EPD will thus represent the summation of intensities along arcs covering an angular range of (η_f- η_0)/n degrees. Using a circle displayed on the image, it is possible to estimate roughly the centre of the EPD (X and Y in mm) that will be later refined in the Rietveld procedure together with a correction for elliptical distortion coming from a non-perfectly perpendicular 2D detector with respect to the incident electron beam direction. These corrections are equal to the ones used for Rietveld texture analysis from synchrotron diffraction images [3] and we remind to that paper for further informations. It is recommended to calibrate/refine the error and positioning errors later during the Rietveld refinement rather than a priori relying on some calibrated values since such values can slightly shift from pattern to pattern due to e.g. χ rotation or microscope adjustments. This latter procedure gives a much better calibration than what can be done using any graphical routine on the 2D image. The distances from the EPD centre will thus be expressed in mm and the sample-detector distance will be handled directly in MAUD once the data are imported. To convert the distances in mm to 2θ scattering angles, the different camera lengths of the TEM shall be calibrated [4] using a nanopowder sample with known lattice parameters and space group. The spectra resulting from the integration procedure (sometimes called "caking") are used in MAUD as datafiles. If a beam stopper is used during data acquisition, affected spectra can simply be removed from this list, or corresponding areas in the diffraction 1D patterns excluded from the refinement procedure. MAUD allows an easy summation along the Debye rings, in order to provide a 1D pattern with low textural signature. Such a pattern exported as a simple 2-columns (2θ position, intensity) ascii file can be submitted straightforwardly to the FPSM internet tool.

2. Phase identification using the Full-Pattern Search-Match procedure

The Full-Pattern Search-Match (FPSM) approach operates an automated search/match procedure based on the full pattern fitting of the summed intensity along the EDP rings. FPSM can account for the existence of peaks broadening due to size, microstrain effects, background contribution, and is able to correctly index strongly overlapped peaks whose maxima can differ significantly from the position they would get if singled. This procedure is based on the Crystallography Open Database (COD) [5], which includes the American Mineralogist Crystal Structure Database (AMCSD) [6] and the International Zeolite Database [7]. It is already available on two dedicated servers [8]. Only little information such as a list of possible elements (obtainable from TEM by EDS or EELS analyses and used in order to decrease calculation times) and the instrumental profile function (which to a first approach can be given by the system for high- or middle-resolution instruments) are pre-requisites. They are used to match the experimental diffraction profile h(x) with the ones calculated for each possible structure found in the COD database resulting in a set of possible matching phases with a confidence factor. During the Full-Pattern calculation, phase fractions are also refined and returned in the case of multiphase samples. Regarding phase identification from EPD, we have tested with success this procedure on various nanocrystalline materials (TiO_2, Mn_3O_4, $CoFe_2O_4$, MgO, Pt, SiO_2, …). Importantly, we noticed that the approximation of scattered intensities from kinematic scattering is good enough to make the FPSM procedure effective, at least in the case of nanopowders (Fig. 3), even if deviations from observed intensities appear. The database scanning and matching proceeds within few minutes (mostly depending on the number and kind of chosen elements) and requires one single EPD for materials presenting no or low texture effects. For materials with a strong texture the search/match procedure is not efficient but this can be partly circumvented by summing EPD along the rings and/or taken at different tilt angles to “randomize” the pattern.

3. Blackman correction implemented in MAUD

One problem in electron diffraction arises from the dynamical diffraction nature that cannot be represented correctly using the kinematical approximation. In the program we implemented the 2-beam or Blackman correction [9] to give a better approximation in between the pure kinematical approximation and a more sophisticated multi-slice calculation [10, 11]. In the usual practice it is possible to insert the electron scattering factors in Rietveld program and refine electron diffraction powder patterns, but as all the available programs but MAUD use analytical derivatives, they cannot use the Blackman correction that requires a numerical integration. Recently Palatinus [12] have developed an analytical solution using the Bloch-wave method to permit a dynamical calculation and refinement of the structure factors. But if the latter is possible in the single crystal case with a decent calculation speed, the same solution cannot be used in the powder case at the moment.

MAUD uses numerical derivatives, so it was possible to include the full Blackman formulation with the usual approximations into the refinement. We briefly report here the final formulas as used in the program. The formulas were derived using the theory and equations reported in [9,11] and are very similar to what is used in PCED [13] for the simulation of polycrystalline electron diffraction pattern. So the ratio between the dynamical and kinematical intensity of a hkl reflection is given by:

$$\frac{I_{hkl}^{dyn}}{I_{hkl}^{kin}} = \frac{1}{A} \int_{-\pi/4}^{\pi/4} \int_{0}^{A/\cos\theta_2} J_0(2x) dx \, d\theta_2$$

where

$$A = \frac{F_{hkl} \pi H}{V_c K}$$

with

$$K = \sqrt{\frac{2me}{h^2}\left(E + \frac{F_{000}}{V_c}\right)}$$

and J_0 is the zero order Bessel function, Fhkl is the kinematical structure factor calculated using electron scattering factors [14], H is the thickness in Angstrom of the crystallite, Vc the cell volume, m and e are respectively the mass and charge of the electron, h the Planck constant and E the acceleration voltage of the microscope in Volts.

The correction is a little different from the one proposed by Blackman [9] as the division by A in the first formula implies that we are dividing by the thickness (same formulation is reported in [13]. This is necessary to preserve the proportionality of the intensity to the volumetric amount of the phase. It is not strictly necessary when dealing with only one phase, as it is a common factor for all intensities, but it assures the possibility of a phase quantification when dealing with more phases. Again, the thickness factor H, in principle should be the effective thickness in the [hkl] direction for an anisotropic crystallite but the Blackman correction is not sufficiently accurate to appreciate this anisotropic influence in the dynamical correction. In MAUD the dynamical correction is activated in the options panel of the electron radiation along with the option to use the same anisotropic crystallite used for the line broadening calculation. Otherwise a thickness value can be refine instead and the parameter is located in the phase microstructure panel options where also the anisotropic crystallite model is available.

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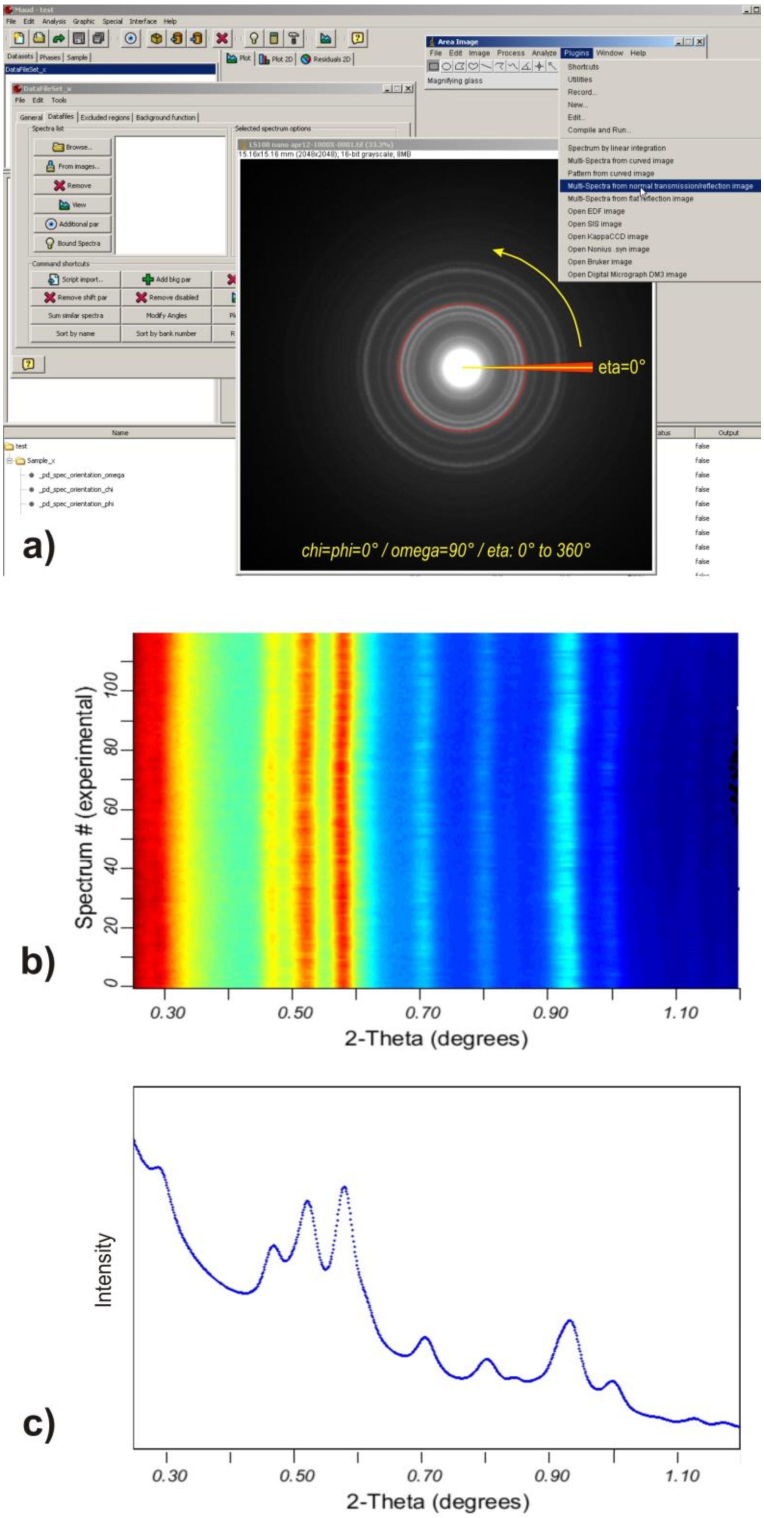

Figure SM1: a) EPD intensity integration is done using an ImageJ plugin via the MAUD user interface. An azimuthal segmentation of the ring patterns is performed resulting in a set of patterns used in MAUD as datafiles. b) 2D plot where all the segments are displayed on top of each other's with the η−azimuthal variation along the ordinate and colour-levelled scattered intensities. c) 1D plot where all the segments are summed.

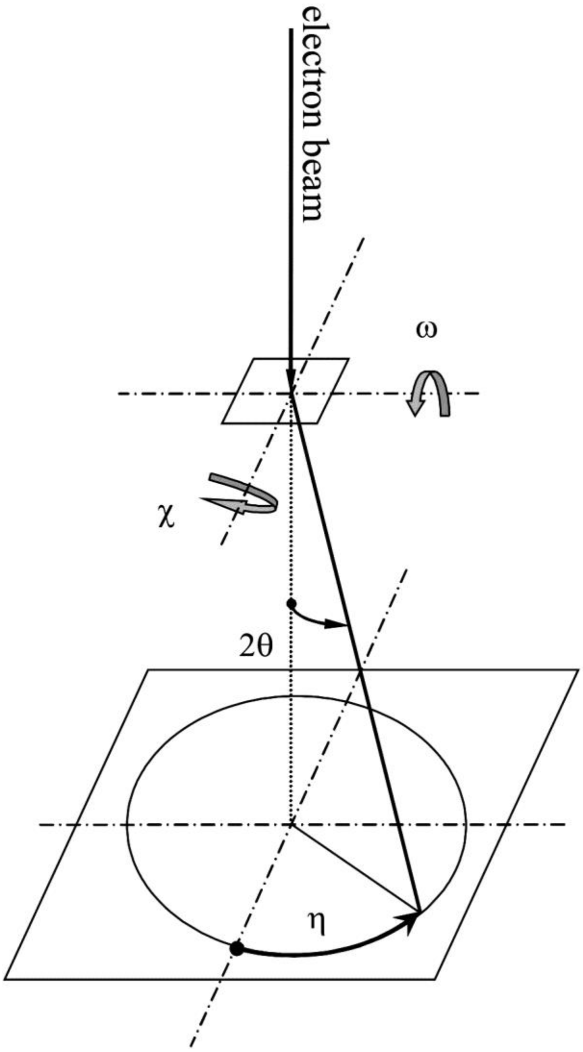

Figure SM2: Transmission geometry for TEM scattering experiments with the nomenclature used in MAUD.

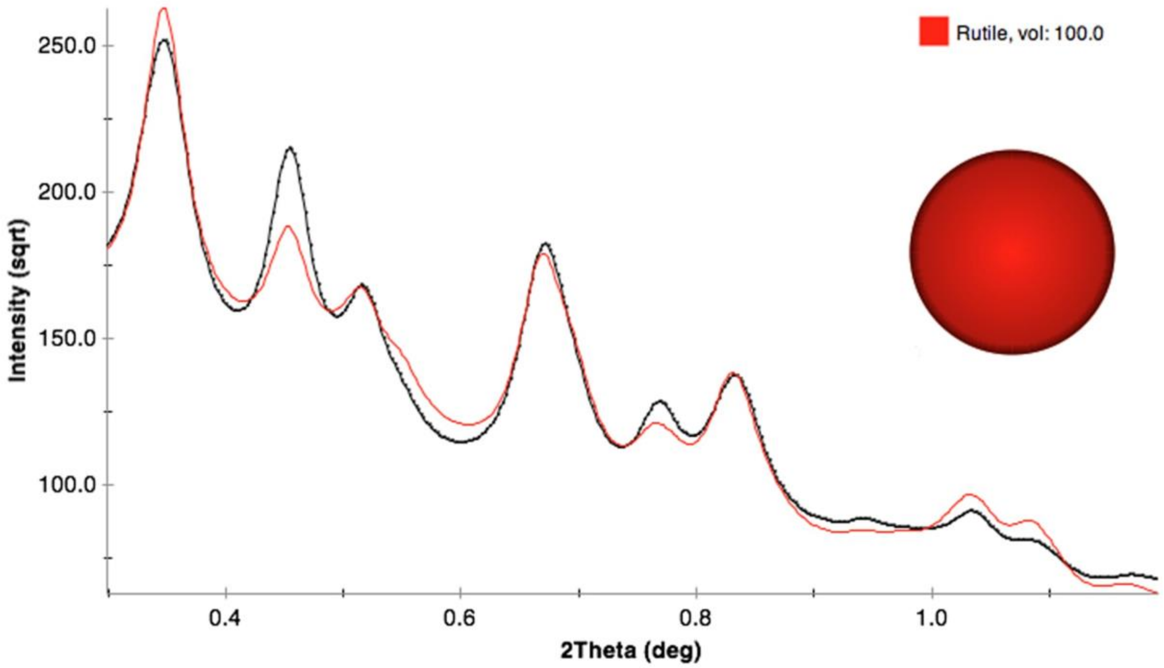

Figure SM3: FPSM-indexed rutile nanopowder Electron Powder Diffraction pattern within an isotropic crystallite shape hypothesis.