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Structure solution of zeolites by automated electron diffraction tomography – Impact and treatment of preferential orientation

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ABSTRACT

In this paper the reliability of structure solution of nano-crystalline porous compounds with preferred orientation based on automated electron diffraction tomography (ADT) is discussed. It will be shown that the limitations of the data acquisition geometry can be overcome by completing the missing diffraction data with additional diffraction information. Apart from different ways of sample preparation, data merging with either additional ADT data sets or intensities derived from X-ray powder diffraction comprise an effective way to improve the accuracy of the structure solution.

1. Introduction

Properties of porous materials are strongly driven by their atomic structure. Pore size, shape and connectivity, as well as the position of acidic and vacant metal sites, trigger the material behavior more than the amount of total empty volume. Many porous materials for advanced applications are synthesized in form of nano-grains, either because it is not possible to grow larger coherent crystalline domains, or the nano-crystalline product has physical and chemical properties that are lost in the bulk material. Due to their high technological impact, the structure characterization of such materials is an important challenge for modern crystallography.

X-ray powder diffraction (XRPD) is a well-established technique that allows fast identification of known phases and structure refinement of unknown phases if a reliable starting model is available. It is not always possible to derive such an ab initio structural model from XRPD data alone, as the overlapping of reflections at medium–high resolution hampers a proper measurement of reflection intensities. This problem is accentuated when (1) peaks are broadened due to the nanoscopic size of the crystallites, (2) the structure is characterized by long cell parameters and eventually pseudosymmetry, (3) crystals have marked preferential orientation able to ruffle reflection intensity ratio and (4) more phases are present in the sample. In order to overcome these limitations and to determine structural models ab initio, external information can be used for supporting XRPD data, such as (1) knowledge derived from structurally related phases [1]; (2) nuclear magnetic resonance (NMR) and other structural spectroscopies [2,3]; (3) a priori information about atomic and molecular connectivity, as implemented in simulated annealing [4,5] and in zeolite-specific algorithms (FOCUS) [6,7]; (4) high resolution TEM images and related Fourier transforms which deliver insights about crystal symmetry and the crystallographic phases of strong reflections [8–10].

Electron diffraction, in contrast to XRPD, is able to sample single crystals a few tens of nanometres in size, regardless from eventual surrounding other phases. Diffraction patterns taken with a transmission electron microscope are close to planar cuts through reciprocal space and usually show no problem with reflection overlap, allowing for a more easy determination of crystal symmetry and reflection intensities. In this respect, electron diffraction data has been successfully used to support XRPD for pre-partitioning of overlapping peaks in XRPD patterns and for cell parameter and symmetry determination [8,9]. It was also possible to determine ab initio zeolitic structures using only electron diffraction data collected on several crystals with different orientation [11,12], but this method has been often thwarted by the difficulty of recognizing the correct solution (that normally is not the one with the lowest structural residual) and the impossibility of localizing oxygen and other light atoms [13].

In the last years automated diffraction tomography (ADT) emerged as a new approach able to speed up electron diffraction data acquisition and at the same time to provide improved data

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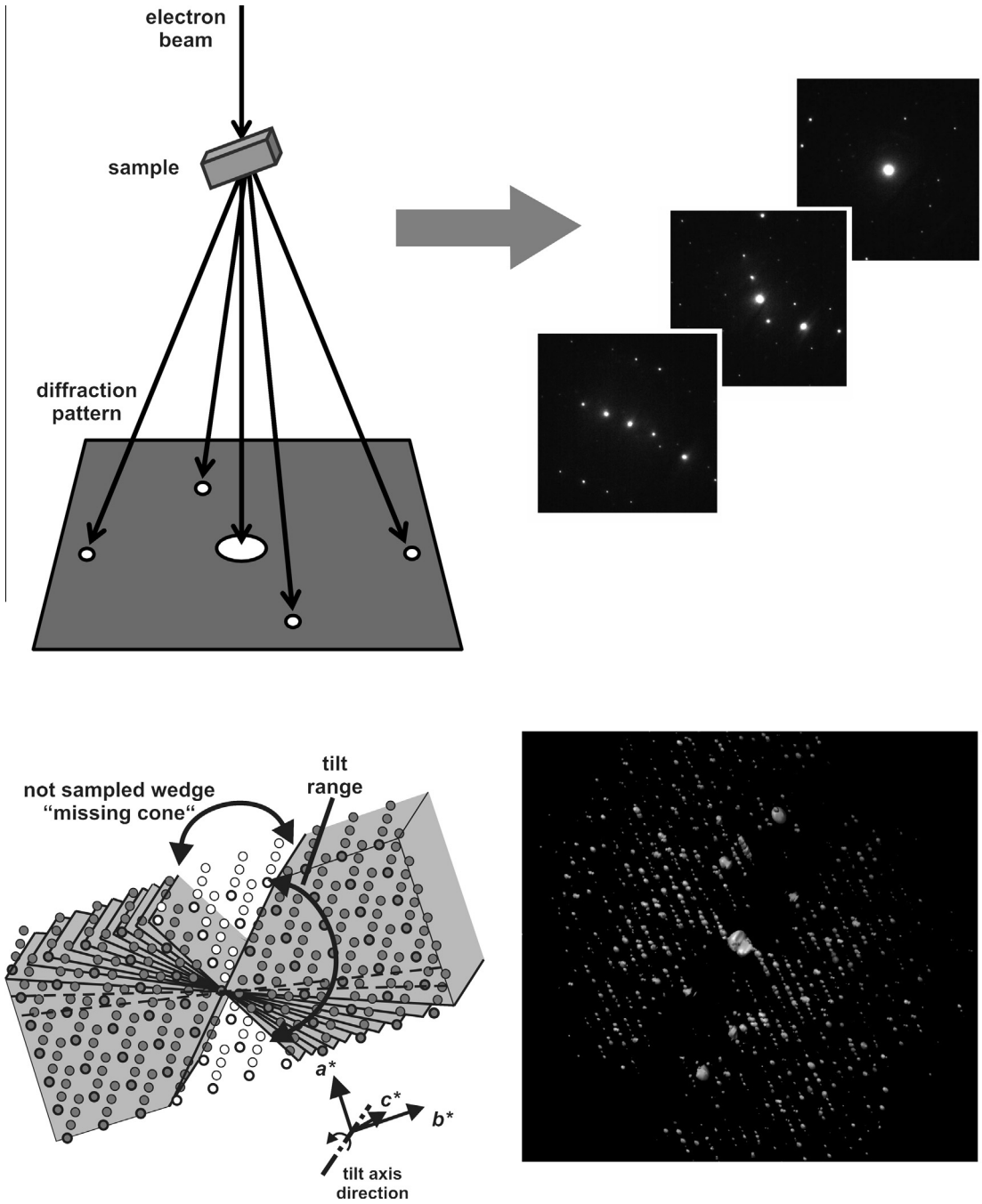

Fig. 1. ADT data acquisition: scheme showing the sequential collection of electron diffraction patterns and exemplary off-zone diffraction patterns (top); scheme showing three-dimensional diffraction reconstruction and the missing cone volume (bottom left); exemplary reconstructed diffraction space (bottom right).

sets with a significant higher completeness and less dynamical effects, thus able to deliver full and immediately interpretable ab initio structure solutions [14–17]. As shown in Fig. 1 (top), ADT data acquisition is based on a homogenous sampling of the reciprocal space by tilting a crystal around an arbitrary axis in fixed tilt steps of about 1°. This allows a complete scan of the reciprocal space within the tilt range of the microscope goniometer (commonly referred to as tilt α), with a significant increment of sampled independent reflections.

Differently from traditional electron diffraction patterns, collected along oriented crystallographic zones, ADT data cannot be directly interpreted. The acquired patterns have to be converted into a three-dimensional diffraction volume by a dedicated software package as shown in Fig. 1 (bottom). From the three-dimensional reconstruction, cell parameters and orientation matrix can be directly extracted using automated routines based on clustering of difference vectors [18]. Diffuse scattering, non-merohedral twinning and polycrystallinity can also be immediately detected by visual inspection, and related to cell parameters and crystal shape.

When cell parameters and orientation matrix have been determined, all recorded reflections can be indexed and integrated. Because each diffraction pattern is acquired off-zone, there is a significant reduction of dynamical effects that normally allows treating the data with a simple kinematical approximation (i.e., the intensity I of a given reflection hkl is directly proportional to the squared structure factor F^2_{hkl}, as for X-ray diffraction).