

**m15.o01****The Role of Electron Diffraction in Zeolite Structure Determination.**

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Because electron diffraction can sample individual microcrystals, it is clear that this single crystal method can facilitate, in at least two ways, structure determination for inorganic materials, such as zeolites, that are preferentially microcrystalline. First, in a qualitative application, three-dimensional tilts of individual small crystals, to map the reciprocal lattice, greatly facilitates unit cell and space group determination when powder diffraction indexing programs fail. If incoherent multiple scattering leads to violation of systematic absences, these absences can be restored by collection of precession diffraction patterns based on the Vincent-Midgley method [1], as demonstrated recently [2]. The second, quantitative application, i. e. *ab initio* structure determination from electron diffraction intensity data, also seems to be feasible. In the auspicious case of thin layered zeolite crystals in the MWW framework, the three-dimensional structure was determined by direct methods based on maximum entropy and likelihood [3], the only difficulty arising from the 'missing cone' of structural information imposed by the goniometric tilt limit. Possible methods for restoration of the missing information, although approximately provided by phase and amplitude prediction (Sayre equation), include alternate crystallization of the desired crystal projection by appropriate structure directing agents, or, simply, by sectioning the desired view of the structure in available samples. Multiple scattering perturbations include both n-beam dynamical and secondary scattering; collection of precession data greatly reduces the latter influence [2], facilitating *ab initio* analyses via direct methods (e. g. tests on LTA, ITQ-1, ITQ-7, ZSM-10, MOR, MCM-68), while systematic dynamical diffraction is still observed (even at 300 kV). Improved collection of intensity data via imaging plates, exploiting a much greater linear response to intensity, is also recommended. One other, largely unexplored, possibility is to collect zero loss electron diffraction intensities in electron microscopes with in-line 'omega' energy filters. Generally, for unknown zeolite structures, electron diffraction analyses have been carried out in parallel with the usual powder determinations, not only to provide needed symmetry information but also to detect structural details of important zones, e. g. the location of porous channels to guide the powder determination; in some cases, the crystal structure would not have been solved without this electron crystallographic information. Whether or not true *ab initio* electron crystallography can ever exist as an independent structural tool for zeolites remains a question to be answered by ongoing research.

[1] Vincent, R.; Midgley, P., *Ultramicroscopy* 1994 53, 271.[2] Dorset, D. L., *Ultramicroscopy*, in press.[3] Dorset, D. L., et al., *Acta. Cryst.* 2005 A61, 516.**m15.o02****Quantified electron diffraction on pigments**

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Institute of Physical Chemistry, Johannes Gutenberg-University, Welderweg 11, 55099 Mainz, Germany, E-mail: kolb@uni-mainz.de, URL: <http://www.uni-mainz.de/~kolb>.**Keywords: electron diffraction, computer simulation, structure analysis**

Organic pigments are normally insoluble and nanocrystalline materials which form several polymorphs. Unfortunately, they are often of such low crystallinity that single crystal x-ray diffraction can not be applied. X-ray powder diffraction as an alternative path to crystal structure analysis suffers from preferred orientation, impurities and peak overlap. Electron diffraction (ED) is for many organic pigments the only pathway to structural characterisation. The 3-dimensional data sets which can be achieved via several tilts of an appropriate crystal around selected axes are comparable in size to those from x-ray powder diffraction and the combination of both methods turned out to be the most successful path. [1-3]

Dependent on the habit of the crystals sample holders with different flexibility can be used. Nanodiffraction (by using a 10  $\mu\text{m}$  C2 aperture) allows a beam diameter of approx. 10-20 nm and comprises combined with scanning mode imaging a gentle way to sample the reciprocal space of beam sensitive compounds. Electron diffraction data was collected at 300 kV with a FEI Tecnai F30 ST. Unit cell parameters from ED were subsequently refined by x-ray powder data if available. Subsequently, it is possible to index the zones on-line and to use a cryo holder in order to reduce the beam damage. [4]

Structure analysis has been performed through simulation methods taking only kinematic diffraction into account. Models needed for simulation methods based on single crystal x-ray data of comparable compounds taken from CSD and partial charges have been calculated using ESP charges from DFT [4]. For kinematical approach R-values of approx. 20-30% can be achieved, whereas the application of dynamical effects including the refinement of the centre of Laue circle and the crystal thickness leads to values about 5% [5]. Refinement of the structure based on x-ray powder diffraction data was performed using Rietveld approach.

Different from x-ray powder diffraction there is no fully automated routine developed to collect electron diffraction data and to process respectively analyse the collected data in advance. Improvements have been made at different stages of the structure analysis path which lead to a significant acceleration of the process. This allowed us now the structure analysis of polymorphic small organic molecules such as laked azo-pigments and Cu-Phthalocyanines.

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[4] MaterialStudio 4.0 and Cerius 2 version 4.2 MS, Accelrys Inc., 9685 Scranton Road, San Diego, CA 92121 - 3752, USA.

[5] Jansen, J.; Tang, D.; Zandbergen, H.W. and Schenk, H., *Acta Cryst.*, A54, (1998) 91-101.