

The EXPO package [1] is a computing program able to successfully provide the structure solution by starting from minimal information: the experimental powder diffraction pattern and the chemical formula of the compound to investigate. EXPO can be used for solving organic, inorganic, metalorganic structures for a large variety of applications. Automation and efficiency are suitably combined in EXPO for performing all the steps of the solution process: indexation, space group determination, intensity extraction, structure solution, model optimization, Rietveld refinement.

Automation. Default strategies, identified as the most effective, are selected for carrying out the solution process automatically and quickly. They may fail when the experimental data resolution is bad and/or the structure complexity is remarkable. In these cases, EXPO can promptly switch to appropriate strategies by profiting by a user friendly graphical interface.

Efficiency. Innovative theories and computing procedures aiming at making straightforward all the steps of the solution process are integrated in EXPO and widely tested. EXPO is continuously updated and optimized in terms of both computing efficiency and graphical performances.

In EXPO the two stages based *ab initio* approach (in the first stage the intensities are extracted; in the second, the reflections are phased by Direct Methods) [2] is the automatic choice. The model provided by Direct Methods is usually partial and approximate because of well known unavoidable problems in powder diffraction (overlapping, background, preferred orientation). It can be optimized by default [3], [4] and/or non-default strategies [5], [6] which are able to reduce the errors depending on the limited experimental resolution.

A very recent study has regarded a new and more effective figure of merit [7], alternative to the classical one. It is able to pick up the phasing trial corresponding to the best solution among several feasible ones.

Non ab initio method, requesting the knowledge of the expected molecular geometry and based on Simulated Annealing technique [8, 9], can optionally be attempted particularly in case of solution of organic compounds.

Examples of successful automatic runs by EXPO will be discussed in addition to available special strategies.

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Pushing the limits of powder charge flipping

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In 2004 Oszlányi and Sütö introduced a new way of determining

crystal structures from single-crystal diffraction data that they termed charge flipping [1]. The algorithm is an elegant one, based on a very simple perturbation (charge flipping) of electron-density maps that are generated during the structure solution process. Initially, this charge-flipping algorithm was viewed as a curiosity, but in a surprisingly short period of time the approach found application in areas where traditional methods flounder. One of these was X-ray powder diffraction (XPD).

The original algorithm was adapted to accommodate powder diffraction data by two different groups in 2006 [2] and 2007 [3]. The latter includes a second perturbation of the electron-density map based on histogram matching [4] prior to the repartitioning of the intensities of overlapping reflections, and has been implemented in the program *Superflip* [5]. Although diverse structures have been solved automatically with this program, its limits have not yet been reached. By including information from electron microscopy (EM) experiments in different ways, three particularly complex zeolite structures [6,7,8] could be solved. At least part of the algorithm's strength lies in the fact that it operates in both real and reciprocal space, so manipulation in both is possible.

In the first of the zeolite structures, starting phases for the charge-flipping algorithm were generated using an approximate (but incorrect) model derived from several high-resolution transmission electron microscopy (HRTEM) images. In the second case, a structure envelope [9] was generated from a single lower resolution HRTEM image and imposed in real space to enforce the channel system. In the third case, reflection intensities from selected area electron diffraction patterns were used to pre-partition the intensities of reflections overlapping in the powder diffraction pattern.

It has also been shown that precession electron diffraction (PED) data can be used to improve the quality of the intensities extracted from a powder diffraction pattern (by identifying and eliminating weaker reflections) and to generate some better starting phases (by applying charge flipping to 2-dimensional PED data) [10]. In light of the improvements arising from the use of 2-dimensional EM data to supplement the powder diffraction data, an alternative approach using 2-dimensional subsets of the XPD data has recently been devised [11].

Further automation incorporating some of these developments into the software can be easily envisioned.

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Algorithm and performance of a new powder indexing software *Conograph*

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At IUCr2008, we proposed a new rapid exhaustive search powder indexing algorithm that was obtained by developing the Ito algorithm from various aspects. Several amendments have been added to the algorithm after that, and it was implemented into a powder indexing software *Conograph*. At IUCr2011, the algorithm and its performance are presented. The name of the software is taken from a mathematician J. H. Conway and a graph he observed in [1]. The graph is utilized to detect zones having more possibility to correspond to a sublattice of the true crystal lattice (*cf.* [2]) and to describe a theorem about the distribution of unobserved reflections due to extinction rule. The theorem is found and confirmed by the first author and gives a theoretical foundation of our algorithm.

The main function of *Conograph* consists of primitive unit-cell determination, lattice symmetry determination and lattice parameter refinement. In these procedures, observed errors of peak-positions are utilized to check the equality of equations including the Ito equation $2(q_1+q_2) = q_3 + q_4$ [3], to calculate propagated errors of lattice constants for lattice symmetry determination, and as weights in least squares method to refine lattice constants.

Conograph is already equipped with a graphic user interface to help users find the most plausible candidates easily. Several figures of merit (FOM) are prepared to sort the candidates: the de Wolff FOM [4], a symmetric FOM we propose as a natural extension of the de Wolff FOM, the number of lattice candidates detected in the neighbor of each candidate, and the unit-cell volume. For further improvements in the usability of the software, *Conograph* is planned to be distributed free including among users of Japan Proton Accelerator Research Complex (J-PARC).

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Chemical selectivity in structure determination by modulation enhanced X-ray diffraction

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X-ray diffraction methods in general allow only a limited chemical selectivity. In this contribution we show that structural information on a subset of atoms can be selectively obtained in a diffraction experiment, where the sample is subjected to a periodically varying external stimulus (temperature, pressure, concentration, light etc). This technique is called modulation enhanced diffraction (MED) [1]. In MED, the periodically varying data are averaged and post-treated by phase sensitive detection (PSD). PSD is a demodulation technique exploited in modulation excitation spectroscopy (MES) to obtain information on active species diluted into a spectator inactive matrix. In analogy to MES, MED extracts crystallographic information on a subset of atoms responding to an external stimulus, thus introducing

selectivity in diffraction. Simulated and experimental MED data were produced by using a TS-1 zeolite sample as spectator, in which Xe (acting as active species) is adsorbed and desorbed by a periodic temperature change. For both simulated and experimental data, MED yielded the powder diffraction pattern of the active subset, called the "demodulated pattern". The demodulated pattern was used to solve the crystal structure of the active species exclusively, demonstrating the chemical selectivity of MED and envisaging wide applications in the structure analysis of periodically changing materials (magnetic information storage systems, electrochemical systems such as batteries, solar cells, etc).

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Polarized Neutron and Light Scattering from Magnetic Nanostructures under AC-field

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Complementarity of Polarized Neutron and Soft X-rays Reflectometry (PNR and SXRR) has experimentally been demonstrated in a number of studies in which these methods were combined to refine static magnetic structures in thin films, superlattices and lateral nano-patterns [2]. Both methods use similar principles [1] of the data acquisition, theoretical description and analysis providing a comparable resolution in layer-by-layer vector magnetometry. The effect of spin birefringence in PNR is dual to the X-ray magnetic circular dichroism (XMCD) so that the depth sensitivity of PNR is well complemented by the element specificity of SXR. Furthermore, off-specular PNR probes lateral magnetic structures over micrometer scale reciprocal to that accessed with the direct space photoemission electron microscopy (PEEM) with resonant circular polarized light (RCPL). Smaller scales probed by polarized neutron grazing incidence small angle scattering (PN GISAS) can also be approached with RCPL GISAS.

Both methods, PNR and SXRR, have recently shown potentials to probe not only static properties of magnetic nano-structures, but also their evolution under time-dependent external field. Nearly instant X-ray response for a magnetization variation allows to access fast spin kinetics in individual nano-elements. In contrast, PNR can, as was recently demonstrated [3], records collective response of magnetic nano-structures to AC field varied over a broad range of amplitudes and frequencies (up to a few MHz). This, as will be thoroughly discussed, opens up new perspectives to experimentally distinguish between various re-magnetization scenarios in ensembles of lateral nano-patterns. First results on domain kinetics in continuous and periodically patterned magnetic films and heterostructures deduced from AC PNR experiments are reported. Further developments, including application of the time modulation of the incident neutron beam synchronized with AC field at the sample position will be outlined. Feasibility of magnon spectrometry with inelastic PNR under condition of ferromagnetic resonance is theoretically examined.

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