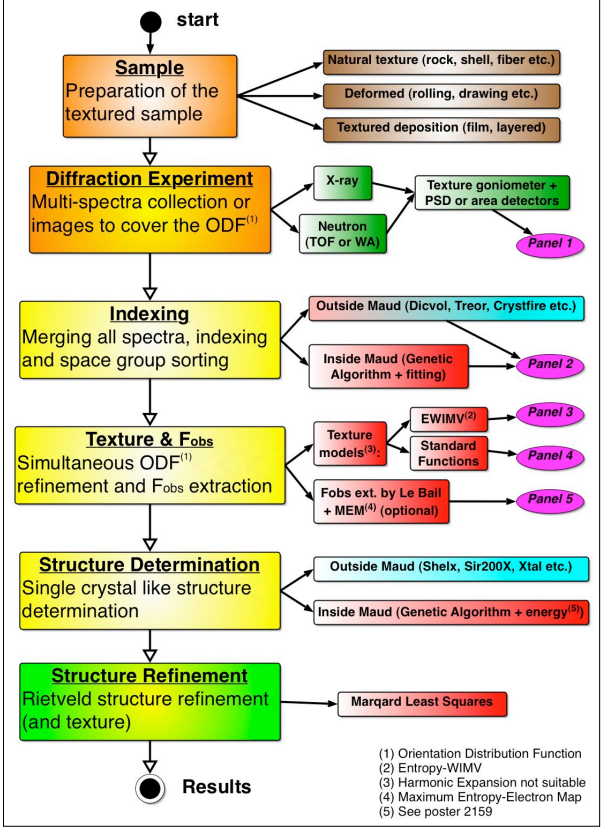
Algorithms for Solving Crystal Structure using Texture

Luca Lutterotti, Mauro Bortolotti - E-mail: luca.lutterotti@ing.unitn.it, mauro.bortolotti@ing.unitn.it
Department of Materials Engineering and Industrial Technologies, University of Trento.

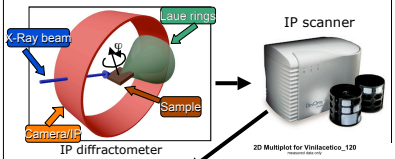
Abstract
Texture is generally considered a nightmare for crystal structure solving or refinement. Wessels et al. [1] have demonstrated as texture can be used successfully to help the extraction of reliable structure factors from powder data to employ single crystal like structure solution methods. The methodology has been extended a little further and some new algorithms will be presented to simplify the procedure in a unique improved step. Using an approach derived from Rietveld Texture Analysis [2] the simultaneous texture determination and structure factors extraction can be done. This was possible by introducing a new texture algorithm (EWIMV) and a texture aware extraction algorithm to combine the two procedures. By this method it is possible to extract structure factors from really highly overlapped pattern and use only one single experiment. An alternative method uses instead a Maximum Entropy Electron Map fitting approach to apply some constraints to the structure factors extraction.The algorithms were implemented in the software Maud [3] along with other ab-initio structure solution routines for peak finding and indexing (through evolutionary algorithms), space group sorting and refinement constraints (energy computation, fragments etc.). Some examples of application of the methodology will be presented as well.

Structure solution by texture (using Maud)



Panel 1

Experiment: *only one experiment for everything*.
Several spectra must be collected at different tilting conditions of the sample. The number of spectra should be sufficient to ensure the ODF (Orientation Distribution Function) determination. The diffraction range and intensities should be sufficient for indexing and structure determination. As an example a curved image plate (IP) diffractometer as in the figure collecting 6 images in reflection at 0, 60, 120, 180, 240, 300° in φ with an incident (ω) angle of 5° ensures the feasibility of the entire analysis.



IP diffractometer

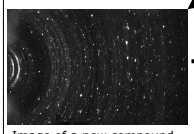
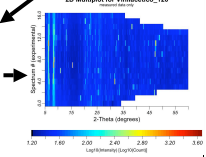
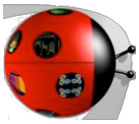


Image of a new compound with graininess (treated as texture) at 120° in φ



Same image converted in spectra by Maud for analysis

As you can see, potentially overlapping reflections are resolved by texture.



Panel 2

Indexing: *the steps*
- Merging the spectra to randomize
- Peak finding by second derivative
- Peak fitting and revision (Fig. 1)
- Results exported (dicvol91 format)

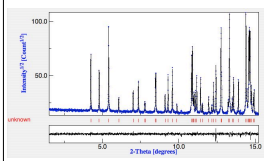


Fig. 1: Peak location and fitting for sample 2 of the sdpdrr-2

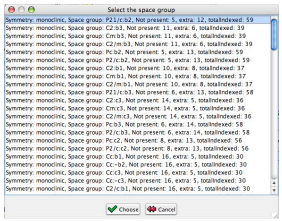


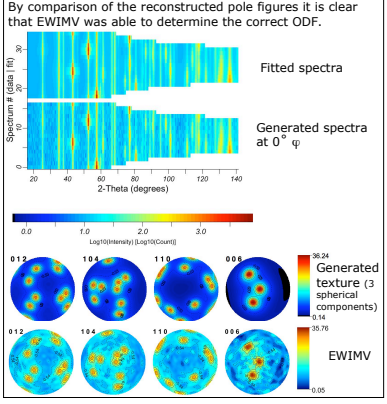
Fig. 2: sorting of space groups on dicvol91 results

The results of dicvol91 can be imported in Maud and for each solution chosen a scan over all space groups is done to sort them by an index computed as the sum of the number of non indexed and extra reflections of the space group not located in the spectrum. An example of the sorting for the sample 2 of the sdpdrr-2 after importing dicvol91 results applied to the peaks located as for Fig. 1 is reported in Fig. 2. It is easy to recognize as this simple sorting correctly identify the P21/C as first.

Genetic Algorithm (GA) indexing in Maud
Two approaches:
- The internal GA library of Maud determine the best individual (cell parameters) respect to the list of located peaks.
- A second approach (slower) uses directly the spectrum without prior peaks location. Each individual in the GA define its fitness by a Le Bail fit of the spectrum. It is useful for a highly overlapping pattern. The best individual selected proceed then to a Le Bail + Least Squares fit of the cell parameters for a refinement of the cell.

Panel 3

Texture model: *EWIMV*
EWIMV (derived from WIMV) is part of the discrete texture methods. The ODF space described in the three eulerian angles is divided in small cells each one defining the value of the ODF in its volume. The pole figure value for each peak of each spectrum is computed by a numerical integral throughout the ODF space considering a tube projection or averaging over adjacent cells.
In Maud an external cycle performed once every refinement cycle extracts the pole figure values from the spectra using a tuned Le Bail algorithm and computes the ODF through an entropy method. The ODF is used in the subsequent fitting or refinement cycle to compute the texture intensities (pole figure values) for each peak/point.
The entropy algorithm ensures the smoothest positive solution for the ODF. A positive ODF is always guaranteed.
To show the potentiality of the method a collection of spectra in the same geometry and conditions as in the Panel 1 has been simulated for corundum adding statistical noise and a sharp texture generated with three spherical components (see Panel 4 for the standard functions in texture). The analysis has been done using EWIMV for texture and the MEM (Panel 5) for the crystal structure.
By comparison of the reconstructed pole figures it is clear that EWIMV was able to determine the correct ODF.

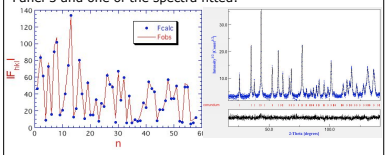


Panel 5

F_{obs} extraction:
F_{obs} are extracted using a Le Bail method after each texture cycle at the end of each iteration step of the minimizing routine (either a Least squares or Genetic Algorithm or Simulated Annealing can be used as minimizing routine in the fitting of spectra). The extracted structure factors for each spectrum j are weighted over their texture to obtain the overall F_{obs}:

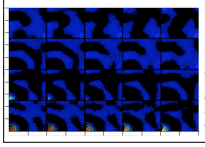
$$\left|F_{hkl}^{obs}\right|^2 = \frac{\sum_{j=1}^{Nspectra} \left|F_{hkl}^{obs}\right|^2 \sqrt{P_{hkl,j}}}{\sqrt{P_{hkl,j}}}$$

$P_{hkl,j}$ is the texture (pole figure) value for the j_{th} spectrum.
If the EWIMV texture model is used (Panel 3), two successive Le Bail extractions are effectively performed, the first for the texture, using the structure factor values from the previous iteration, and the second for the new structure factors using the texture values computed from the last ODF. The procedure is based on the fact that the texture and structure correlation can be easily resolved if the number of data (spectra) is sufficient to cover the entire ODF. Comparison of some structure factors extracted by this procedure with generating values for the example in Panel 3 and one of the spectra fitted:



MEM-Le Bail F_{obs} extraction:
To improve the reliability of the structure factors extraction a MEM (Maximum Entropy-Electron Map) method can be used after the Le Bail extraction described before. The steps are:
- the F_{obs} extracted by Le Bail at iteration k are used to compute an electron map (normalized to the nominal electron density if available) using the MEM approach
- new F_{hkl} are computed from the map and used for the next refinement iteration
- after the refinement iteration the F_{hkl} are used for the next texture extraction/ODF computation
- the F_{hkl} are used as the starting point for the next Le Bail Fobs extraction (few Le Bail iterations to enforce memory)
- again MEM to compute the next electron map and so on.

The electron density map enforce a compatibility of the F_{obs} for highly overlapping reflections.
The MEM algorithm has been derived from the algorithm of MEED [4] applying some extra constraints to minimize the number of maxima and the background of the map.


Electron density map sections (on the c-axis) obtained by MEM for a tetragonal zirconia using one Cu-Xray spectrum and poorly crystallized phase mixed with corundum. By contours the Zr and O atoms are located correctly in the asymmetric unit

Panel 4

Standard functions in the ODF
In Maud there are two type of standard functions: a fiber component and a spherical component (linear combination of a Gauss and Lorentz standard function).
The Gauss spherical component is defined as:

$$f(S,\omega) = N(S)e^{S\cos\omega} \geq 0,\ 0 \leq \omega = \omega(g_0,g) \leq \pi,\ 0 \leq S \leq \infty$$

where: $N(S) = \left[I_0(S) - I_1(S)\right]^{-1}, I_j(x) = \frac{1}{\pi}\int_0^{\pi} e^{x\cos t}\cos(jt)dt$

I_j is the modified Bessel function.
The Lorentz spherical component is instead:

$$f(t,\omega) = (1-t^2)\frac{(1+t^2)^2 + 4t^2\cos^2(\omega/2)}{(1+t^2)^2 - 4t^2\left[\cos^2(\omega/2)\right]^2} > 0,\ t < 1$$

g_0 and g are the eulerian coordinates in the ODF space, the first being the position of the maximum of the spherical component.
A fiber component is obtained integrating a Gauss spherical component around the fiber axis n:

$$f(S,\vec{n},g_0,g) = N(S)I_0\left(S\frac{1+z}{2}\right)e^{S(z-1)/2},\ z = \left(\vec{n}\cdot g_0^{-1}\cdot g\cdot\vec{n}\right)$$

Advantages of the use of standard function in a Rietveld like fitting :
- the texture is described by refinable parameters
- very sharp textures
- few parameters for simple textures (fiber, single components)
- usable for defined textures with data not covering the entire ODF space
- very smooth textures obtainable, easy to interpret.

Disadvantages:
- number and locations of components must be manually defined at the beginning
- complex textures require several components, thus several parameters

A Genetic Algorithm approach can be used in Maud to avoid the manual location of the components, but still these cannot compete with the EWIMV black box mode of operation (no prior assumptions to be made).

References
[1] Wessels, T.: Baerlocher, Ch.: McCusker, L. B. *Science,* 1999, **284**, 477.
[2] Lutterotti, L.: Matthies, S.: Wenk, H.-R.: Schultz, A. S.: Richardson, J. W. Jr, *J. Appl. Phys.*, 1997, **81**, 594.
[3] http://www.ing.unitn.it/~luttero/maud
[4] Kumazawa, S.: Kubota, Y: Takata, M.: Sakata, M., *J. Appl. Cryst.*, 1993, **26**, 453.