

The maximum entropy method and charge flipping, a powerful combination to visualize the true nature of structural disorder from in situ X-ray powder diffraction data

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Introduction

Rietveld refinement is considered to recover the maximum amount of information that is contained in powder diffraction data. Nevertheless, this amount is smaller than that contained in a complete set of observed structure factor amplitudes. The correlations between the different crystallographic parameters as well as the application of constraints and restraints can often not be avoided in Rietveld refinement. In case of an ordered crystal structure, the refinement process is able to reconstruct the phases of structure factors with reasonable accuracy even if the structure model is not perfect. However, if the crystal is disordered, (except for simple cases) the refinement process is not easy, typically requiring the introduction of rigid bodies, constraints, restraints and anharmonic ADPs to reach convergence. In such cases the structural model obtained from Rietveld refinement needs to be verified and improved. This can be achieved by the Maximum Entropy Method (MEM), which can be used as a complementary method for deriving the most probable electron density from limited information by maximizing the entropy. Recent progress in synchrotron powder X-ray diffraction techniques, including third generation synchrotron sources, low-noise image plate detectors (IP), new optical systems, and analytical methods enables the extraction of structure factor amplitudes with high accuracy. These developments not only increase the success rate of crystal structure determination from powder diffraction data, but also (by determining the charge density distribution using the MEM) allow for the investigation of advanced structural features such as disorder, diffusion pathways in ionic conductors, electron density due to chemical bonds and nano-applications.

However, the reconstruction of the accurate electron density from the experimental data suffers from model biasing effects in addition to the artifacts caused by the incompleteness of the data set. The MEM electron densities depend on the lack of completeness of the underlying data set. Efforts have been undertaken to overcome these limitations, by introducing alternative weighting factors that force the distribution of the residuals of the final structure factors towards the required Gaussian distribution. In particular for powder diffraction data, heavily overlapping reflections (where only the sum of the individual intensities of the overlapping peaks is available) can be handled using so called G-constraints, thus avoiding a model bias due to the separation of the measured intensity into contributions from the reflections belonging to this overlap group. The combination of the MEM and Rietveld methods was introduced in 1995 and is called the REMEDY-cycle, after the name of the computer program. In this method, the structure model is iteratively improved by replacing the values of the calculated structure factors (F_{calc}) from Rietveld refinement by the corresponding values of the observed structure factors F_{obs} obtained from MEM calculations.

Here we present a *new combination* of the MEM and the method of charge flipping (CF). Reflection phases from CF were introduced for two purposes: Firstly, to improve the accuracy of the phases obtained from the Rietveld method and secondly as a fast method to visualize the type of disorder independent of the Rietveld model. This approach not only succeeded in revealing the basic features of the crystal structure, but also fine details as the type

of disorder (rotational and/or conformational disorder), and the type of thermal vibrations. In general, different types of structure factor amplitudes and phases imposing different types of constraints were subjected to the MEM with the aim of acquiring the least biased electron density.

Results and discussion

Six types of MEM-electron density maps have been calculated for ordered δ - $K_2C_2O_4$, disordered α - $Rb_2C_2O_4$ and disordered α - Rb_2CO_3 so as to visualize and understand the disorder in the latter two compounds. The MEM ordered densities vary in the amount of bias towards the structure models, which affects the amplitudes and phases of the structure factors. The completely biased densities $\rho_{(calc)}^{MEM}$ (Fig. 87) give an indication of the amount of information that

can be extracted by the MEM from the data. Comparison of $\rho_{(calc)}^{MEM}$ (Figs. 88(a1), (b1), (c1)) with the corresponding model densities shows that the latter are much more structured than the former, especially in the cases of the oxalates. This strongly suggests that the highly-structured densities of the models actually are artifacts. A smooth character is also found for the MEM-densities based on the experimental data (Figs. 88 and 89). Differences with $\rho_{(calc)}^{MEM}$ can be analyzed on the basis of difference densities

$$\Delta\rho_{(I)}^{MEM} = \rho_{(I)}^{MEM} - \rho_{(calc)}^{MEM}, \quad (28)$$

where (I) stands for one of the six types of maps: obs, obs + G, LeBail + G, obs + CF, obs + CF + G and LeBail + CF + G (Fig. 87).

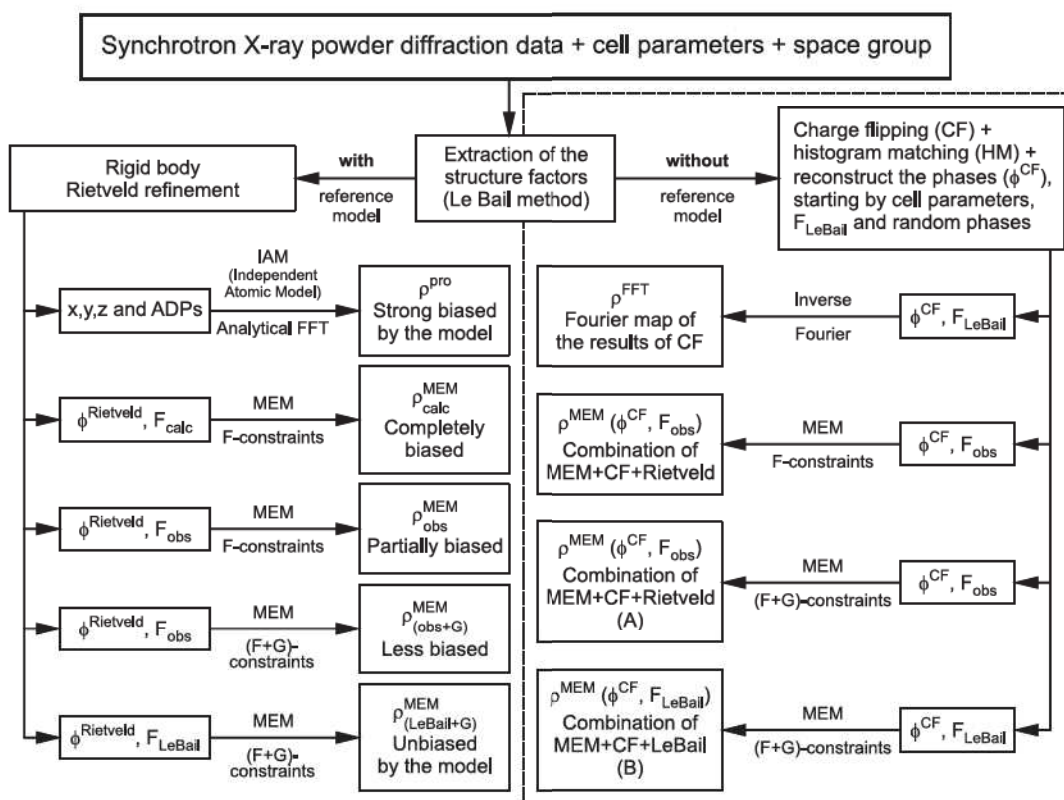


Figure 87: Flowchart, showing the procedure for extracting the different types of structure factors and phases used to reconstruct the different types of electron density maps from powder diffraction data. The procedures combining MEM and CF are framed by a dashed line.

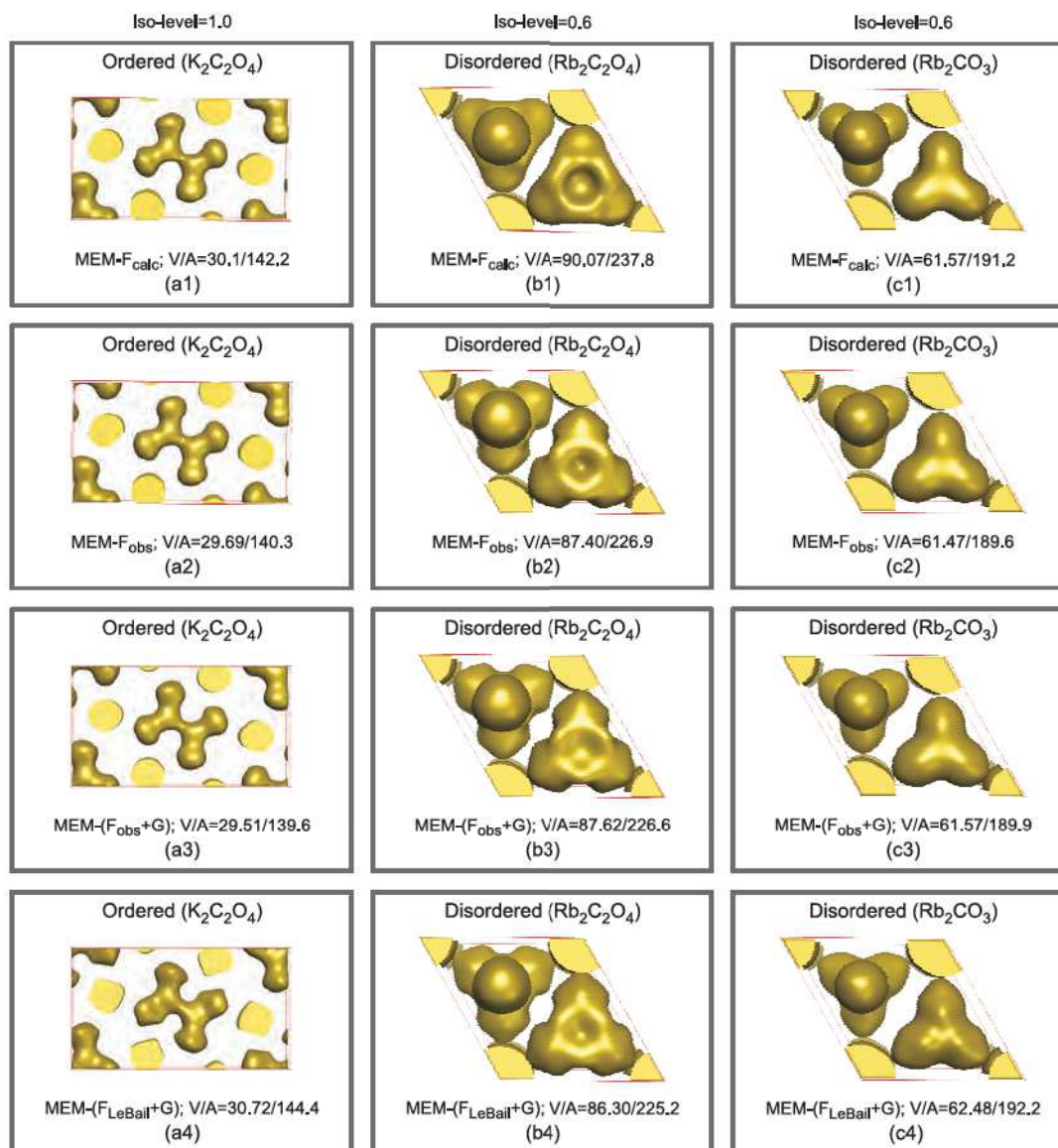


Figure 88: MEM-electron density maps for the crystal structures of ordered δ - $K_2C_2O_4$ in (a) and disordered α - $Rb_2C_2O_4$, α - Rb_2CO_3 in (b) and (c) respectively with different data subsets of F_{calc} (a1,b1,c1), F_{obs} (a2,b2,c2), $F_{obs} + G$ -constraints (a3,b3,c3) and $F_{LeBail} + G$ -constraints (a4,b4,c4). The iso-levels and the values of volume and area of the special iso-surfaces are displayed.

Figure 88 presents comparative considerations of the electron densities of the three compounds with different data subsets as calculated above; the enclosed volume and area of the iso-surfaces are indicated in the maps. For each compound all four maps have similar appearances. Nevertheless differences are found between any MEM density and the corresponding reference MEM density based on F_{calc} . These differences can be visualized by difference maps. Phases from CF are combined with either the observed

structure factors from Rietveld refinements or the observed structure factors obtained by the Le Bail procedure (Fig. 87). The first conclusion is that for all three compounds the main features of the densities are also reproduced by these two maps (Figs. 88 and 89). Turned around, this implies that the completely model-free approach of charge-flipping with LeBail-fitting provides a reasonable to good description of the crystal structure, including features due to disorder.

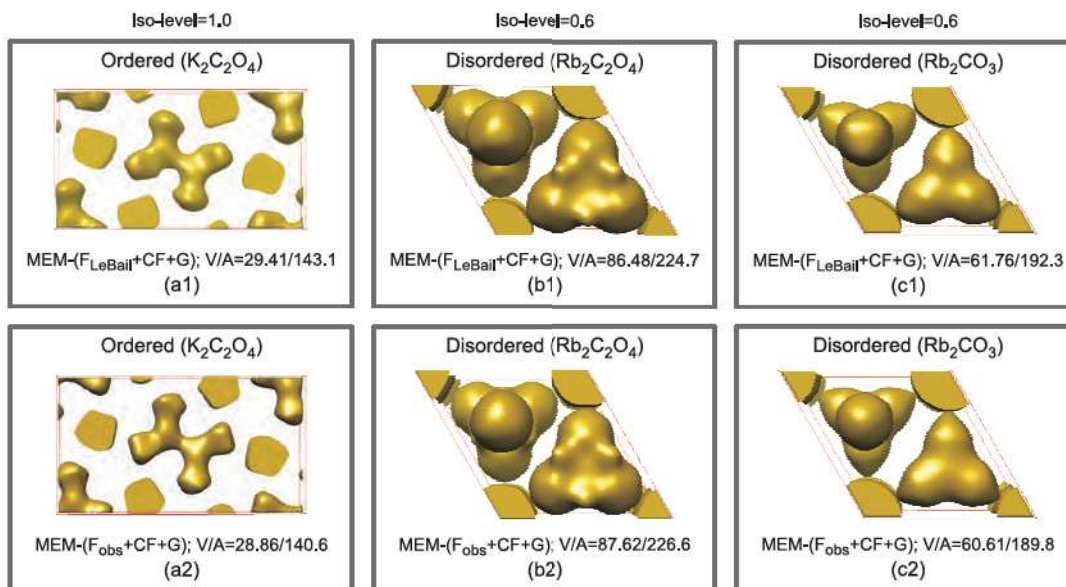


Figure 89: MEM-electron density maps for the crystal structures of ordered $\delta\text{-K}_2\text{C}_2\text{O}_4$ in (a) and disordered $\alpha\text{-Rb}_2\text{C}_2\text{O}_4$, $\alpha\text{-Rb}_2\text{CO}_3$ in (b) and (c) respectively based on reflection phases from Charge Flipping with two different types of amplitudes. (a1), (b1), (c1) $|F_{\text{LeBail}}|$, and (a2), (b2), (c2) $|F_{\text{obs}}|$.

The electron densities of ordered $\delta\text{-K}_2\text{C}_2\text{O}_4$, disordered $\alpha\text{-Rb}_2\text{C}_2\text{O}_4$, and $\alpha\text{-Rb}_2\text{CO}_3$ have successfully been reconstructed from X-ray powder diffraction data by the maximum entropy method (MEM). The MEM has been applied in a series of calculations ranging from calculations completely biased by the model to model-free calculations. The first observation is that for each compound all MEM calculations lead to similar densities, which give good representations of the crystal structure including disorder and anharmonic atomic displacements (Figs. 88 and 89). In particular this implies that crystal structures including positional and orientational disorder of functional groups can be determined from X-ray diffraction data without the intervention of a structure model: Structure factor amplitudes are obtained by Le Bail fits to the diffraction data and structure factor phases are determined by charge flipping with histogram matching.

The MEM employs phased structure factors as input (F constraint), while part of the diffraction information can be available as sums of intensities of groups of overlapping reflections (G constraint) typically obtained from powder diffraction. The MEM with F_{obs} as ‘experimental data’ (structure factor phases from the model

and structure factor amplitudes by LeBail decomposition biased by the model) leads to densities that differ by the least amount from the model. Stepwise replacing more of the models by experimental-based information leads to increasing differences to the model densities. Part of these differences will be due to inaccurate values for amplitudes or phases of reflections or to intrinsic features of the MEM related to the use of the G constraint. However, for another part these differences will reflect anisotropic ADPs (ordered $\delta\text{-K}_2\text{C}_2\text{O}_4$) not used in the model, and they indicate better representations of the disorder in $\alpha\text{-Rb}_2\text{C}_2\text{O}_4$ and $\alpha\text{-Rb}_2\text{CO}_3$ by the MEM than is given by the models.

The most important result is that completely *ab initio* electron-density distributions have been obtained by the MEM applied to the combination of structure factor amplitudes from Le Bail fits with phases from charge flipping. This new combination of the MEM and the method of charge flipping can thus be used for the determination of partially-ordered crystal structures from powder diffraction data.

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