Reconstruction of electron density by the Maximum Entropy Method from X-ray powder diffraction data based on incomplete crystal structure models: a case study of apatites with different intercalated metal atoms

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Conventional Fourier analysis is one of the most commonly used methods for localization of missing atoms in crystal structures from powder diffraction data. A "perfect" Fourier map would require a complete set of structure factors up to a resolution of at least $\sin\theta/\lambda = 5.0$ Å^{-1}. In the case of powder diffraction, accessible information is limited, as compared to single crystal diffraction, mainly due to the projection of three-dimensional reciprocal space onto the one dimensional 2θ axis, resulting in intrinsic and accidental peak overlap. In addition, the resolution of powder diffraction data measured on laboratory instruments is generally limited to $\sin\theta/\lambda \approx 0.6$Å^{-1}. As a result, the Fourier transform is affected by series termination errors (e.g., spurious peaks of positive electron densities that do not correspond to atoms in the structure and unphysical local minima with negative densities). The concept of informational entropy was introduced in the field of crystallography to handle series termination effects in Fourier maps. The Maximum Entropy Method (MEM) allows to maximize the information extracted from the intrinsically limited experimental X–ray powder diffraction data. It has been demonstrated that MEM can be successfully used with powder diffraction data for localization of missing atoms with high occupancies in incomplete crystal structures [1, 2], for revealing the true nature of structural disorder [3, 4] and for determination of integrated atomic charges [5]. On the other hand, the capability of the MEM to locate missing atoms with low occupancies and to reconstruct their accurate electron density distribution is not fully investigated. This holds in particular true in case of commonly used high-resolution laboratory X-ray powder diffraction data.

In the present work, the possibilities and limitations of the MEM for localization of missing intercalated metal atoms in apatites (general formula is $Ae_5(PO_4)_3M_xOH_{1-x}$, Ae = Sr or Ca, M = Cu, Ni or Zn) with intercalated copper, nickel or zinc metal atoms were evaluated.

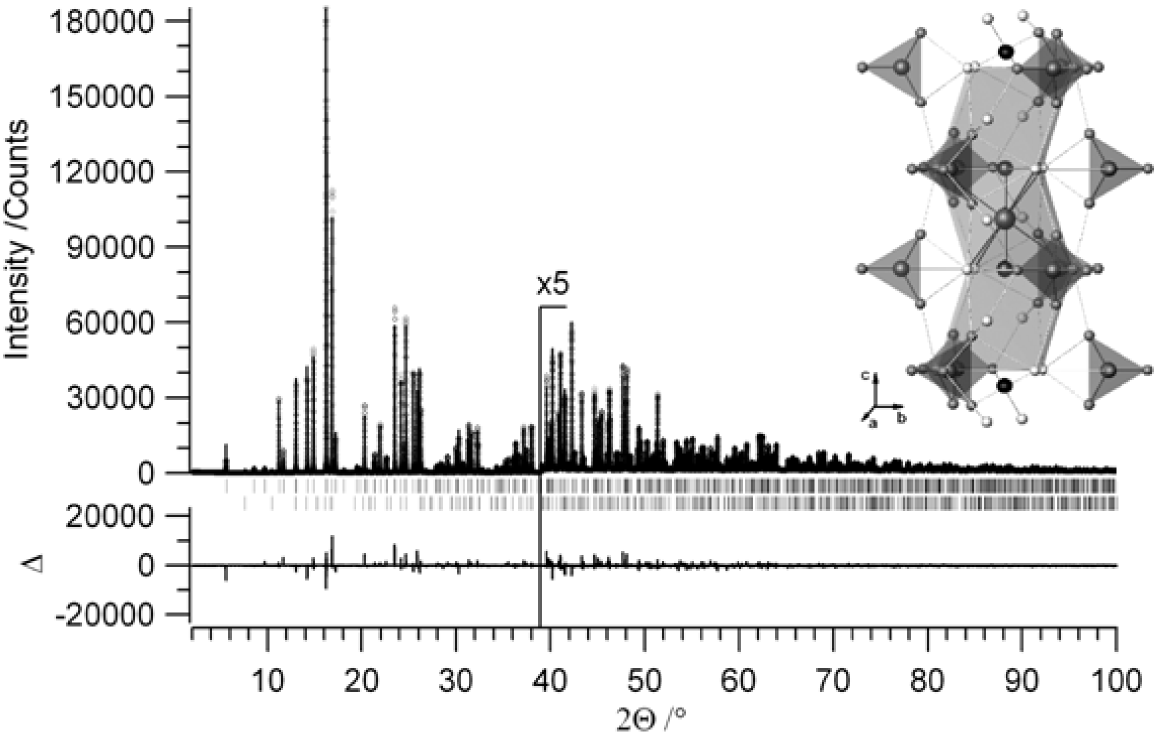

Figure 1: Rietveld refinement of laboratory X-ray powder diffraction data of apatite $Sr_5(PO_4)_3Cu_{0.1}OH_{0.9}$) without copper atoms $Sr(OH)_2 \cdot H_2O$ was refined as second phase (2%). Insert: channel structure of apatite with intercalated metal atoms (O-M-O linear unit along *c*-axes in the center).

X–ray powder diffraction data of all apatites with intercalated copper atoms were collected at room temperature on a laboratory powder diffractometer D8–Advance (Cu–Kα_1 radiation from a primary Ge(111) monochromator; Linx-Eye position–sensitive detector (PSD)) in Bragg-Brentano geometry (fig. 1). X–ray powder diffraction data of apatites with intercalated zinc and nickel atoms were collected at room temperature on a laboratory powder diffractometer STOE (Cu–Kα_1 radiation from a primary Ge(111) monochromator; Mythen PSD) in Debye-Scherrer geometry. X–ray powder diffraction data of one series of Sr–apatites were also measured at room temperature at the high-resolution powder diffractometer I11 (λ=0.8264(3) Å, Mythen PSD) at Diamond (Great Britain).

We found that the conventional Fourier maps based on F_{obs} (observed structure factors are calculated from the best incomplete model) contain a lot of spurious peaks with high electron density, making it impossible to locate the intercalated metal atoms unambiguously. Using difference-Fourier maps, copper atoms with occupancies of 0.3, 0.125 and 0.1 could be located, while for compounds with lower concentration of 0.05 the difference-Fourier map contained spurious peaks higher than the peaks at the presumed copper positions. MEM maps based on F_{obs}, F_{obs}+G and F_{LeBail}+G allowed unambiguous localization of copper atoms with occupancies down to 0.05, which corresponds to approximately 1.4 electrons per site (fig. 2).

The strong advantage of the MEM is the possibility to use G–constraints for overlapping reflections, thus avoiding the model-bias for observed structure factors (F_{obs}) values from Rietveld refinement [4, 5]. The amplitudes of structure factors can be received after a Le Bail fit (F_{LeBail}) without the need any structural information. They also can be used as experimental data for MEM calculations for centrosymmetric structures in combination with phases from Rietveld refinement and G-constraints for overlapping reflections. For non-centrosymmetric structures problems arise in dividing intensities between real and imaginary parts and in assigning phases. Another advantage of the MEM is the possibility to use so-called prior information on the system [6]. In the present work, prior information is provided by the electron density distribution corresponding to a refined independent spherical atom model (ISAM) using the same experimental data (procrystal density). The procrystal prior electron density clearly reduces artifacts and MEM reconstructions with this prior allow the visualization of fine features of the electron density.

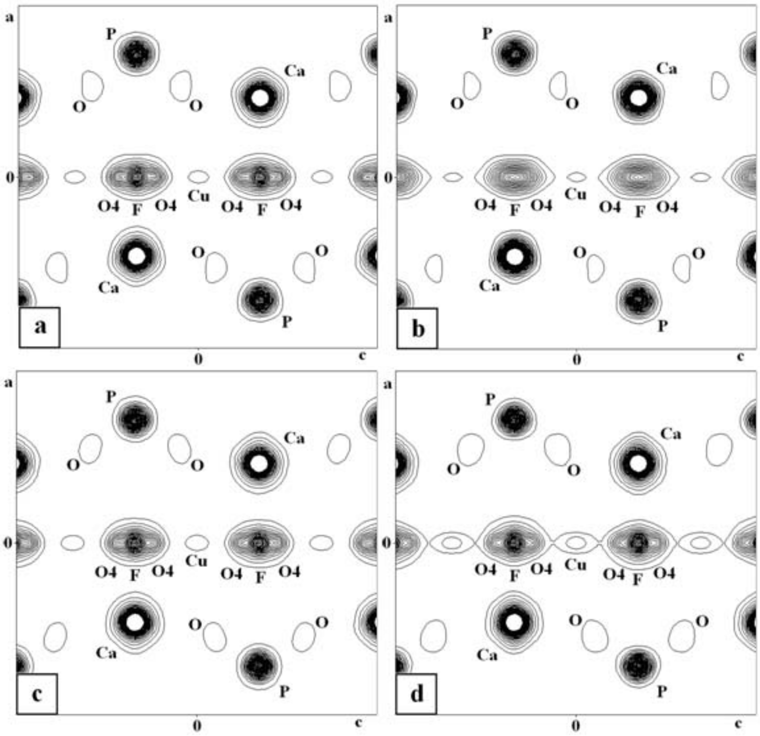

Figure 2: Two-dimensional electron-density maps at *y=0* of apatite $Ca_5(PO_4)_3Cu_{0.05}O_{0.5}H_{0.45}F_{0.5}$. Contour levels: from 1 to 50 e/Å^3, step 1 e/Å^3. High-resolution laboratory X-ray powder diffraction data with $\sin\theta/\lambda$= 0.55 Å^{-1}.
a) based on F_{obs} (with procrystal density for known atoms)
b) based on F_{obs} (with flat prior)
c) based on F_{obs}+G (with procrystal density for known atoms)
d) based on F_{LeBail}+G (with procrystal density for known atoms)

The value of the electron density at the position of missing intercalated metal atoms for the MEM maps based on F_{obs}+G were higher than for the MEM maps based on F_{obs} due to the better partitioning of the intensities between strongly overlapping reflections. The highest values of the electron density of missing intercalated atoms were obtained in case of MEM maps based on

F_{LeBail}+G and this value almost coincided with the value of the electron density of copper atoms for MEM calculations with intercalated copper atoms. In the case of MEM calculations based on F_{obs}+G and F_{LeBail}+G it was necessary to use the procrystal electron density for all known atoms, because of the reduced information content of group intensities as compared to individual reflections. The differences are mainly caused by different scale factors: the localization of missing atoms based on F_{LeBail}+G was performed with the scale factor from Rietveld refinement of the incomplete structure.

Two interesting examples of localization of missing metal atoms are the Sr–apatite with intercalated Zn atoms (fig. 3). A prominent feature of the powder diffraction data of this sample is the strong overlapping of the reflections in comparison to copper containing Sr– and Ca–apatites, which is caused by the change of the lattice parameters – only 9% of reflections are resolved, all other reflections are overlapped. For both samples all MEM maps were successful in localization of missing Zn atoms and the main features of the MEM maps were the same as in the case of Sr–apatite with missing copper atoms. The localization of missing copper atom in fluorine containing Ca–apatite was complicated by the presence of fluorine atoms, with the located copper atom showing a lower value of electron density as compared to fluorine free Ca–apatite.

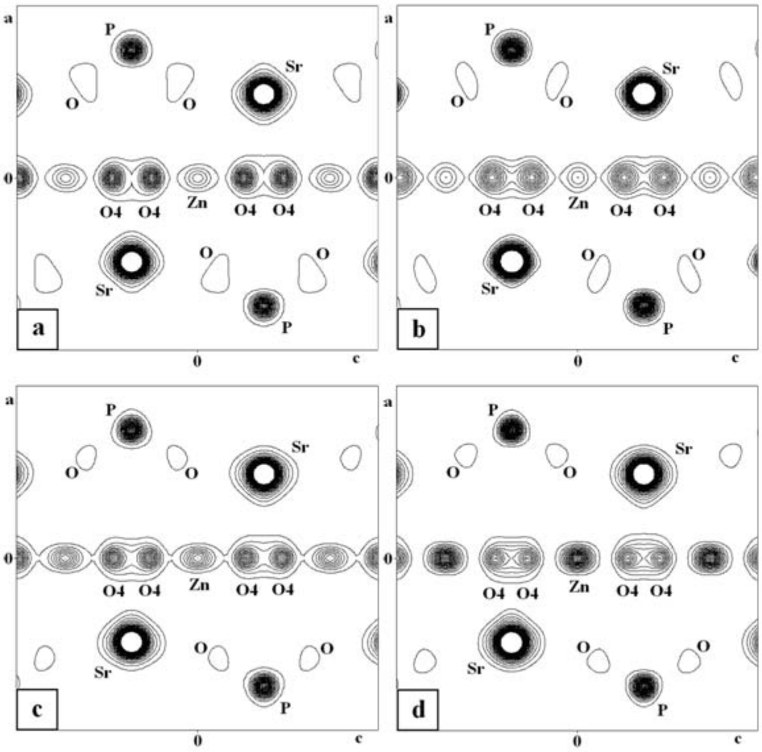

Figure 3: Two-dimensional electron-density maps at *y=0* of apatite $Sr_5(PO_4)_3Zn_{0.15}OH_{0.8}$. Contour levels: from 1 to 50 e/Å^3, step 1 e/Å^3. High-resolution laboratory X-ray powder diffraction data with $\sin\theta/\lambda$= 0.55 Å^{-1}.
a) based on F_{obs} (with procrystal density for known atoms)
b) based on F_{obs} (with flat prior)
c) based on F_{obs}+G (with procrystal density for known atoms)
d) based on F_{LeBail}+G (with procrystal density for known atoms)

For confirmation of the reliability of the results received from high-resolution laboratory X-ray powder diffraction data, the high-resolution synchrotron X-ray powder diffraction data were used for the MEM calculations of the Sr-apatite with intercalated copper atoms. Three different values of resolution $\sin\theta/\lambda$=0.55 Å^{-1}, $\sin\theta/\lambda$=0.65 Å^{-1}, and $\sin\theta/\lambda$=0.93 Å^{-1} were considered. The electron density distribution at resolution $\sin\theta/\lambda$=0.55 Å^{-1} from synchrotron data is very similar to the electron density distribution with the same resolution from laboratory data, but the value of the electron density in the position of the in-channel atoms is higher in case of synchrotron data. With increasing the resolution from $\sin\theta/\lambda$=0.55 Å^{-1} to $\sin\theta/\lambda$=0.93 Å^{-1} for synchrotron powder data, the value of the electron density of the located copper atoms is increased for all MEM maps. These results confirmed that the MEM can be successfully used for the determination of the accurate electron density distribution from high-resolution laboratory X-ray powder diffraction data. The difference between MEM maps from laboratory and synchrotron sources are caused primarily by different instrumental peak profiles and different resolution $\sin\theta/\lambda$.

As a common tendency it was confirmed that the MEM map based on F_{obs} is the most biased by the model, and the MEM map based on F_{LeBail}+G is the least biased by the model. For the MEM maps calculated with procrystal density for known atoms, the value of the electron density of located metal atoms is increased in the order of maps based on F_{obs}, F_{obs}+G, and F_{LeBail}+G. The MEM map based on F_{obs} with flat prior often contained small noise, and all MEM maps calculated with procrystal density for known atoms were basically free from noise.

The use of a structural model without intercalated metal atoms leads to many falsely assigned phases of weak reflections. Applying G–constraints for a sum of intensities of groups of overlapping reflections decreases the model bias not only through the absence of the model-biased partitioning of the overlapping intensities but presumably also through the decrease of the number of reflections with incorrect phases in the F–constraints.

The limits in the application of this powerful method for powder diffraction data still have not yet been determined.

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