Structure of incommensurately modulated chromium pyrophosphate studied by Maximum Entropy Method (MEM)

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Abstract. A general discussion is given of the Maximum Entropy Method (MEM) as a method to determine the electron density in superspace from X-ray diffraction data. The MEM has been used to determine the electron density in superspace of incommensurately modulated chromium pyrophosphate from X-ray diffraction data published by Palatinus et al. [Acta Crystallogr. B 62, 556]. Chromium pyrophosphate, Cr$_2$P$_2$O$_7$, contains ordered regions (83% of the volume) and regions with disorder. Analysis of the MEM density has allowed us to determine the displacive modulation functions within the ordered regions. The disordered regions can be described as the alternate occupation of two conformations of the pyrophosphate unit and two positions of the chromium atom. Both the conformations and the occupational probabilities of them depend continuously on the phase of modulation $t$.

1. Introduction

A long-standing problem in aperiodic crystallography is the true shapes of modulation functions of modulated crystals. In principle, modulation functions are defined by an infinite number of parameters, but only a limited number of parameters can be varied in structure refinements, because additional parameters would lead to dependencies among them. Usually modulation functions are described by truncated Fourier series with one or a few harmonics or by a special function, like a block-wave or saw-tooth-shaped function. In all these cases the outcome of the refinement is biased by the choice of the model for the modulation functions, and it cannot be guaranteed that the true functions will be found.

A model-independent reconstruction of the electron density in the unit cell can be obtained from the Maximum Entropy Method (MEM) applied to the integrated intensities of Bragg reflections in X-ray diffraction [1]. Local maxima in the density are identified with atomic positions. In this way the crystal structure can be derived from the reconstructed density. For aperiodic crystals the MEM can be used to determine the generalized electron density in the superspace unit cell [2, 3, 4]. Local maxima in $t$-sections (physical-space sections) of the generalized density then provide the atomic positions in physical space. Positions as a function of $t$ for one period $0 \leq t < 1$ then give the modulated atomic positions from which the modulation functions can be derived.

Chromium pyrophosphate Cr$_2$P$_2$O$_7$ has an incommensurately modulated structure at room temperature. The superspace symmetry is $C/m(\sigma_1 0 \sigma_3)\bar{1}$s with lattice parameters of the basic-structure unit cell of $a = 7.019$, $b = 8.406$, $c = 4.626$ Å and $\beta = 108.61^\circ$. The modulation
wavevector is $\mathbf{q} = (-0.361, 0, 0.471)$. Structure refinements of a superspace model against X-ray diffraction data have been published in [5]. Palatinus et al. [5] have shown that a structure model based on simple modulation functions is insufficient to describe the diffraction data. Instead a model was proposed that involved disorder over two configurations for a small range of $t$-values (designated model B).

We have recently re-analyzed the diffraction data of $\text{Cr}_2\text{P}_2\text{O}_7$ by the MEM [6]. Based on the interpretation of the generalized MEM-electron density, we have obtained an accurate description of the modulation functions within the ordered regions and we could develop a description of the modulation of the lack of order in the disordered regions. Here we present a summary of these results, after discussing the principles of the application of the MEM in superspace. The final section is devoted to a critical discussion of modulation functions as they can be determined by X-ray diffraction experiments.

2. The Maximum Entropy Method

The generalized electron density $\rho_s(x_s)$ in $(3+d)$-dimensional superspace is discretized on a $(3+d)$-dimensional grid over the superspace unit cell. This results in $N_{\text{pix}} = N_1 \times N_2 \times N_3 \times N_4$ pixels for $d = 1$. The entropy of the discrete generalized electron density is defined as [7]

$$S = - \sum_{k=1}^{N_{\text{pix}}} \left\{ \rho_k \log \left( \frac{\rho_k}{\rho_k^{\text{prior}}} \right) - \rho_k + \rho_k^{\text{prior}} \right\}, \quad (1)$$

where $\rho_k = \rho_s(x_{sk})$ is the electron density at the grid point with coordinates $x_{sk}$ and $\rho_k^{\text{prior}}$ is the corresponding value of the reference density or prior. The electron density $\{\rho_k\}$ as well as the prior are normalized to reflect the total number of electrons $N_e$ in the unit cell of volume $V$, according to

$$\frac{V}{N_{\text{pix}}} \sum_{k=1}^{N_{\text{pix}}} \rho_k = N_e \quad (2)$$

The principle of maximum entropy defines the optimal electron density as the electron density $\{\rho_k\} = \{\rho_k^{\text{MEM}}\}$ which maximizes the entropy $S$ (Eq. 1). It is a simple exercise to show that $S$ assumes its maximum value if $\rho_k^{\text{MEM}} = \rho_k^{\text{prior}}$ for all points $k$. Information about the electron density can be incorporated into the procedure, if they can be expressed as constraints on the density. Constraints of the form $C = 0$ can be incorporated by the method of undetermined Lagrange multipliers. Then the maximum is determined of

$$Q = S + \lambda C \quad (3)$$

for variation of all $\{\rho_k\}$ and the Lagrange multiplier $\lambda$. At convergence $C = 0$ is identically fulfilled.

Diffraction data are incorporated in the form of the so-called $F$ constraint, $C_{F2} = 0$ [8]. The application of the MEM to X-ray diffraction data requires phased structure factors $F_{\text{obs}}(\mathbf{H}_i)$ of the $i = 1, \cdots, N_F$ reflections with scattering vectors $\mathbf{H}_i$. It thus relies on a previously solved crystal structure. We have argued that a structure model with a reasonable fit to the diffraction data already gives accurate values for the reflection phases, while the amplitudes of the structure factors come from the experiment [7]. With $\sigma_i$ the standard uncertainty of $|F_{\text{obs}}(\mathbf{H}_i)|$ and $\{F_{\text{MEM}}(\mathbf{H}_i)\}$ obtained by (3+1)-dimensional Fourier transform of the trial density $\{\rho_k\}$, the $F$-constraint is [8]

$$C_{F2} = -1 + \frac{1}{N_F} \sum_{i=1}^{N_F} w_i \left( \frac{|F_{\text{obs}}(\mathbf{H}_i)| - F_{\text{MEM}}(\mathbf{H}_i)|}{\sigma_i} \right)^2. \quad (4)$$
Useful weighting schemes include unit weights as well as weights inversely proportional to some power of the length of the scattering vector. The latter method has the effect of increasing the weight for low-angle reflections, which is necessary to obtain a Gaussian distribution of residuals

$$\frac{\Delta F(H_i)}{\sigma_i} = \frac{[F_{\text{obs}}(H_i) - F_{\text{MEM}}(H_i)]}{\sigma_i}$$

at convergence. It is particularly useful for periodic crystals, because intense reflections have short scattering vectors in those cases. Modulated crystals also have satellite reflections, which can be weak irrespective of the length of the scattering vector. Accordingly, we have found that weights proportional to some power of the structure factor amplitude [9],

$$w_i = |F_{\text{obs}}(H_i)|^n \left( \frac{1}{N_F} \sum_{i=1}^{N_F} |F_{\text{obs}}(H_i)|^n \right)^{-1}$$

provide better results, i.e. they lead to the best approximation to a Gaussian distribution of the residuals at convergence. These weights are denoted by $F_n$; $n = 2$ turned out to be optimal choice for $\text{Cr}_2\text{P}_2\text{O}_7$ [6].

An important issue is the choice of the number of pixels, $N_{\text{pix}}$ [7]. The grid needs to reflect the point symmetry of the lattice. For monoclinic symmetry this implies that each of the numbers $N_j$ ($j = 1, \cdots, 4$) must be an even number [7]. Secondly, the number $N_j$ need to be sufficiently large, in order to be able to compute the structure factors $\{F_{\text{MEM}}(H_i)\}$ with sufficient accuracy, and to obtain the atomic positions with sufficient accuracy. The resulting mesh should be smaller than 0.1 Å. Accordingly, we have chosen $72 \times 96 \times 48$ pixels along the first three axes, which correspond to a mesh of $0.097 \times 0.088 \times 0.096$ Å$^3$ in real space. The number of points along the fourth axes needs special attention. A minimum of four points is required for each expected harmonic of the modulation functions. Sharp features of modulation functions—as presently expected saw-tooth-shaped functions—require many more points. Therefore, we have chosen 48 points along the fourth axis in the present study. Even for this moderate number of points along each of the four axes, the computer program BAYMEM [7] uses several Gbyte of RAM.

The MEM of Eqs 1–4 has two fundamentally different applications. With a prior density defined by the independent atom model for the structure, the MEM can be used as an alternative method to the multipole model for charge-density studies [10]. With a uniform prior the resulting MEM-density appears slightly noisy, but it is still of sufficient quality to show local maxima that define the positions of the atoms. Since the present interest is the $t$-dependent positions of the atoms, we have used the uniform prior for the study on $\text{Cr}_2\text{P}_2\text{O}_7$ [6].

The MEM electron density $\rho_k^{\text{MEM}}$ has be determined with the computer program BAYMEM [7] applied to the diffraction data from [5]. Two-dimensional sections of the generalized electron density have been visualized with the computer program JANAD2006 [11]. Local maxima and other topological properties of three-dimensional, physical-space sections of the four-dimensional generalized density were obtained with the computer program EDMA for each of 100 $t$-sections in the interval $0 \leq t < 1$. This has resulted in the determination of the modulation functions of all atoms according to the procedure described in Section 1 and [7].

3. MEM-based modulation functions

The MEM was able to reproduce the modulation functions of model B within the ordered regions for all atoms except phosphorus [Fig. 1(a)]. A model M has been developed [6], in which the modulation function of atom P is accurately given by the positions derived from the MEM-density [Fig. 1(b)]. Model M gives a slightly better fit to the diffraction data than model B, and it avoids unphysically short interatomic distances P–O that were found for model B [6].
Figure 1. Modulation function of atom P. Displacements along x, y and z are given in Å. Filled circles give the values derived from the MEM-electron density. The full lines in the top panels (a) represent the modulation function of model B [5]. The full lines in the bottom panels (b) have been obtained after refinement of the first harmonic parameters of modulation functions fitted to the MEM-derived points (filled circles). They constitute model M. Figure 1(a) has been reproduced from [6].

The disordered regions involve intervals of width 0.084 in t. In model B the disorder is described by a split-atom model for atoms Cr, O2, O3 and P [e.g. see the modulation function around \( t \approx 0.12 \) and \( t \approx 0.62 \) in Fig. 1(a)]. The positions within the split-atom regions are not modulated in model B. Atom O1 is described by a continuous, smooth modulation function over the complete interval. The atoms Cr, O2, O3 and P exhibit smeared electron densities within the disordered regions in the MEM-density maps. Two maxima have only been found for atom O2, thus confirming the split-atom model. However, both the positions and the integrated number of electrons that can be assigned to each of the two maxima vary with \( t \). This implies a modulation within the disordered regions that affects the positions of the atoms and concomitantly the occupancies of the two conformations/orientations of the PO\(_4\) units [6]. Although in each t-section of the MEM-density only smeared, asymmetric maxima could be located near the positions of phosphorus, we have modeled the t-dependent position of atom P in the model M for the structure [Fig. 1(b)].

The positions of atoms in crystals are defined as the time-averaged positions of their nuclei. In case of harmonic movements, the time-averaged positions coincide with the local maxima in the electron density (which are time-averaged densities by virtue of the diffraction experiment). However, for anharmonic thermal movements, the local maxima and averaged atomic positions do not coincide. It might then be more accurate to identify the atomic positions with the center of charges of the electron density distribution around each maximum. Figure 2 shows the positions of the centers of charge in comparison to the positions of the local maxima of the MEM-electron density of atoms Cr and O3. They show a good match between local maximum and center of charge within the ordered regions, while the disordered regions are characterized by marked deviations between the two positions. This suggests that the modulated disorder might involve anharmonic motion of the atoms. Accordingly, model M includes third-order ADPs for
atom P.

4. Conclusions
The Maximum Entropy Method (MEM) in superspace has been applied to x-ray diffraction data of incommensurately modulated Cr$_2$P$_2$O$_7$. The MEM has lead to a description of the structure of Cr$_2$P$_2$O$_7$ that differs from the refined structure model B in [5] especially in the disordered regions. Positions of atoms are modulated, such that the CrO$_6$ and P$_2$O$_7$ units attain different positions and orientations, while deformations of these units lead to internal strain. The internal strain is released by the existence of disordered regions, which are characterized by the alternate occupation of one of two conformations/orientations of the CrO$_6$ and P$_2$O$_7$ units. Both the conformations and the occupational probabilities vary with the phase of the modulation.

Model M has been developed on the basis of the MEM-electron density map, but it gives only a slightly better fit to the diffraction data than model B does, while it does not capture the description as developed for the disordered regions of most atoms. Reasons for the failure to find a structure model that captures all features observed in the MEM-density include:

(i) The limited accuracy of $\sim 0.01\text{Å}$ of MEM-derived positions together with the impossibility to refine all the parameters that were necessary to construct a model based on $\rho^{MEM}(\mathbf{x}_s)$, due to interdependencies between these parameters. Nevertheless, we believe that the MEM has established the true nature of the modulations in Cr$_2$P$_2$O$_7$.

(ii) The failure to identify two positions in the disordered regions of most atoms. This is probably the result of a small distance between the two expected positions, but nevertheless prohibits the accurate determination of these positions.

(iii) The complex nature of the modulations, probably involving modulated anharmonic ADPs, that cannot be refined and neither directly be estimated from the MEM-densities.

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