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Limits of the Patterson method for the determination of one-dimensionally modulated structures

BY BERNARD DOUDIN AND GERVAIS CHAPUIS

Université de Lausanne, Institut de Cristallographie, BSP Dorigny, 1015 Lausanne, Switzerland

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Abstract. The Patterson function can reveal the modulation of a basic structure if its summation terms include only satellite reflections. Examples of Patterson summations for various types of modulated structures illustrate the difficulties of interpretation and the bias occurring in the determination of the amplitudes and phases of the modulation. The opportunity to use the Patterson function to determine modulated structure is discussed.

Introduction. The Patterson synthesis has been shown to be useful to study the structure of one-dimensionally modulated crystals (Steurer, 1987, and references therein). It provides a straightforward means to determine directly from the observations the relative amplitudes and phases of correlated atoms. However, the width of the maxima, the various types of disorder and the limits of observability are factors which seriously affect the method.

Examples will illustrate how summations including low intensities (this is often the case for satellite reflections) create systematic errors and lead to large deviations of the information deduced from (3 + 1)-dimensional Patterson maps. Summations including only satellite reflections reveal the deviations from the basic structure. They are, however, affected by the width of the atomic electronic peaks.

Definitions. If we consider a reciprocal lattice generated by the vectors $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, $\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*$, where at least one of the α, β, γ is 'irrational' (large superstructure), the Fourier and Patterson summations are direct extensions of the three-dimensional cases (Steurer, 1987):

$$P(UVWT) = (1/V_c) \sum_{hklm}{}' I_{hklm} \times \cos 2\pi(hU + kV + lW + mT)$$

$$\rho(xyzt) = (1/V_c) \sum_{hklm}{}' F_{hklm} \times \exp 2\pi i(hx + ky + lz + mt).$$

The real crystal in R^3 is defined by the hyperplane:

$$t = \alpha x + \beta y + \gamma z.$$

If the sum is restricted to satellite reflections only, the corresponding (3 + 1)-dimensional Fourier or Patterson will be called the difference function, abbreviated (3 + 1)FDF and (3 + 1)PDF.

Examples. In what follows, we shall use difference functions only. This restriction is guided by practical reasons: we consider modulated structures showing small deviations from the basic structure as is mostly the case (and implicit in their definition). Such deviations of the electronic densities will lead to full Patterson summations with maxima, proportional to the square of the electron densities, too small to be observed.

The modulated phase of $(C_3H_7NH_3)CdCl_4$ [abbreviated C3CD (Doudin & Chapuis, 1988)] and two hypothetical structures will be used to calculate Patterson and Fourier functions. Their characteristics are given in Table 1.

(*a*) *Displacive modulation.* A (3 + 1)FDF may be interpreted as the difference between a density modulated with the phase t and a density independent of t, corresponding to the average structure. It is clear that the largest difference occurs when the amplitude is maximal (Figs. 1, 2). Peaks appearing in a (3 + 1)FDF have:

(i) a phase ϕ_{max} at which the displacement from the average position d_0 is maximal;

(ii) a position $d_0 + \kappa A$ where A is the amplitude of the modulation and $\kappa \geq 1$ reaches one when A increases (Fig. 2).

The value of κ higher than one is due to the space extension of the atomic peaks. This effect

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Table 1. *Characteristics of the test structures*

Superspace group	$P^{P\bar{1}}_{\bar{1}}(0,\beta,0)$ with $\beta=0.3$
Cell dimensions	$10\times10\times10$ Å $a_1=a_2=a_3=90°$
Number of reflections	13 962 (satellites of first and second order)
$(\sin\theta)/\lambda_{max}$	0.65 Å^{-1}
Test structure 1	
	Cl in (0.1,0.2,0.3) with occupancy $P=0.5$
	$u_x=0.3\cos2\pi[t+(1/8)]$
	$u_y=0.4\cos2\pi t$
	$u_z=0.1\cos2\pi[t+(1/4)]$
	Cl in (−0.1,−0.2,−0.3) with $P=0.5$
	$u_x=0.3\cos2\pi[t+(3/8)]$
	$u_y=0.4\cos2\pi[t+(1/2)]$
	$u_z=0.1\cos2\pi[t+(1/4)]$
Test structure 2	
	Cl in (0.1,0.2,0.3) with $P=0.5-0.2\sin2\pi t$
	$u_x=0.3\cos2\pi[t+(1/8)]$
	$u_y=0.4\cos2\pi t$
	$u_z=0.1\cos2\pi[t+(1/4)]$
	Cl in (−0.1,−0.2,−0.3) with $P=0.5+0.2\sin2\pi t$
	$u_x=0.3\cos2\pi[t+(3/8)]$
	$u_y=0.4\cos2\pi[t+(1/2)]$
	$u_z=0.1\cos2\pi[t+(1/4)]$

was seriously underestimated in the article cited previously. The author considered examples with fictitious and very narrow atomic peaks.

A (3+1)PDF can be easily interpreted as an autocorrelation function concerning peaks defined with the (3+1)FDF function (Fig. 3). In this case, a multiplicative factor $\kappa(A_1)+\kappa(A_2)$ has to be taken into account to determine the sum of the amplitudes A_1, A_2 of the modulations concerning correlated atoms. This factor is only approximately one if the sum of the amplitudes is higher than 0.5 Å. The modulated structures

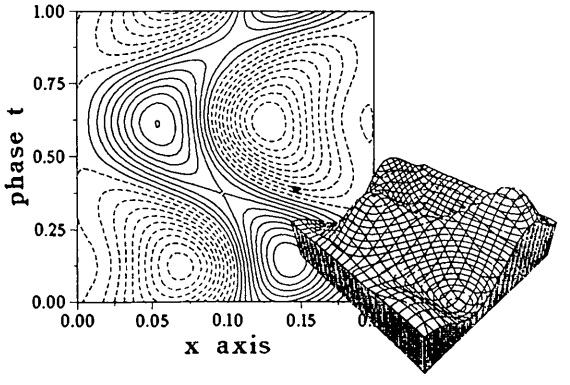

Fig. 1. (3+1)FDF of the test structure 1. The Fourier summation is integrated along y and z within the limits $0.05\le y\le0.35$, $0.2\le z\le0.4$.

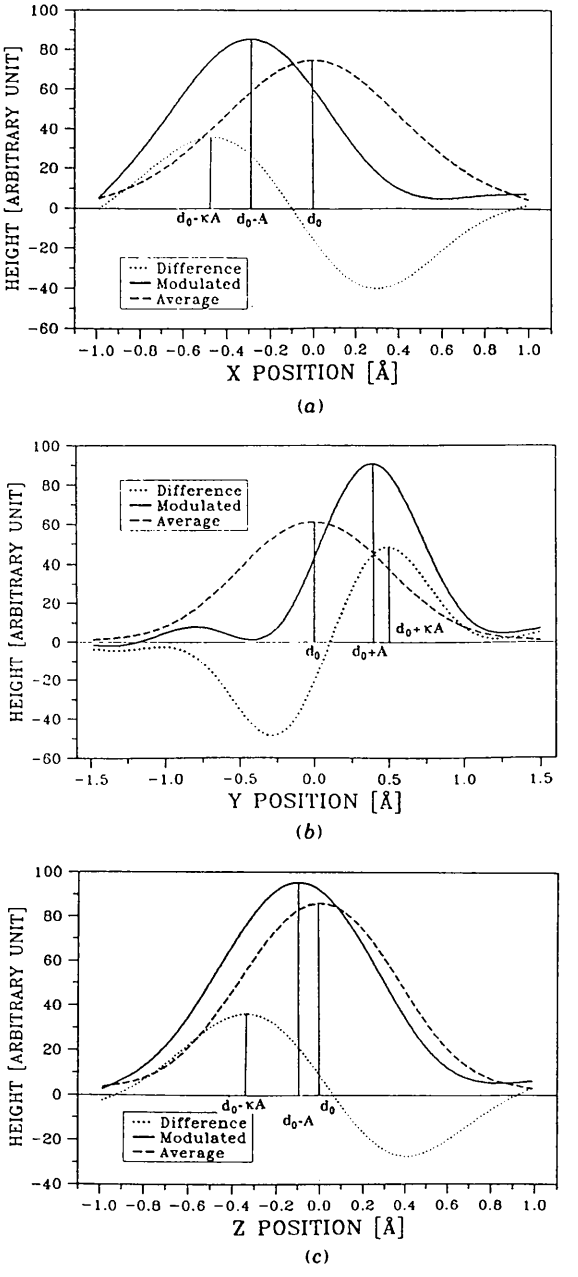

Fig. 2. Comparison between the average electronic density of the Cl atom (test structure 1) and the displaced density at a phase ϕ_{max}. (*a*) Along x with $\phi_{max}=1/8$; (*b*) along y with $\phi_{max}=0$; (*c*) along z with $\phi_{max}=1/4$.

rarely show such large values. Table 2 reveals the differences between estimated amplitudes and refined values for C3CD.

(*b*) *Displacive and occupational modulation.* In a displacive modulation case, the information for the differences of phases concerning the correlated atoms remains. However, difficulties will appear if an occupational contribution to the modulation exists (test structure 2). In this case, maxima appearing in a (3+1)FDF may be wider (Fig. 4*a*): the decrease of the difference between the displaced and the average electronic densities (moving the phase away from ϕ_{max}) can be reduced (or increased) by the change of the peak height corresponding to the modulation of occupation.

Interpretation difficulties arise furthermore from differences of transformation of a scalar (amplitudes of the occupational modulation) and a vector quantity (amplitudes of a displacive modulation) under an element of the superspace group. In our test example the only non-translational element is the inversion center at the origin. The occupational part of the correlated atoms creates a maximum at $T = \frac{1}{2}$. The displacive part has maxima at $T = 2\phi_0$ and $2\phi_0 + \frac{1}{2}$ [the modulation has the form $A\cos 2\pi(t + \phi_0)$]. Thus the Patterson summation will be strongly dependent on the phase ϕ_0 (see Figs. 4*b*, 5). Even in a simplified case, the deduction of any information about the amplitudes and phases will be difficult.

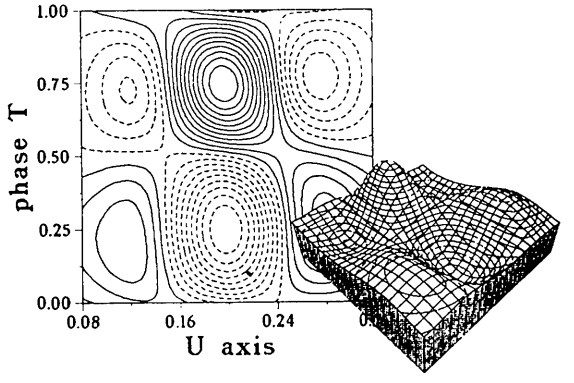

Fig. 3. (3+1)PDF of the test structure 1. Maxima appear at $U = 2d_0 = 0.2$, $T = 2\phi_0 + 1/2$ and $U = 2d_0 \pm 2A$, $T = 2\phi_0$ ($0.2 \le V \le 0.6, 0.5 \le W \le 0.7$).

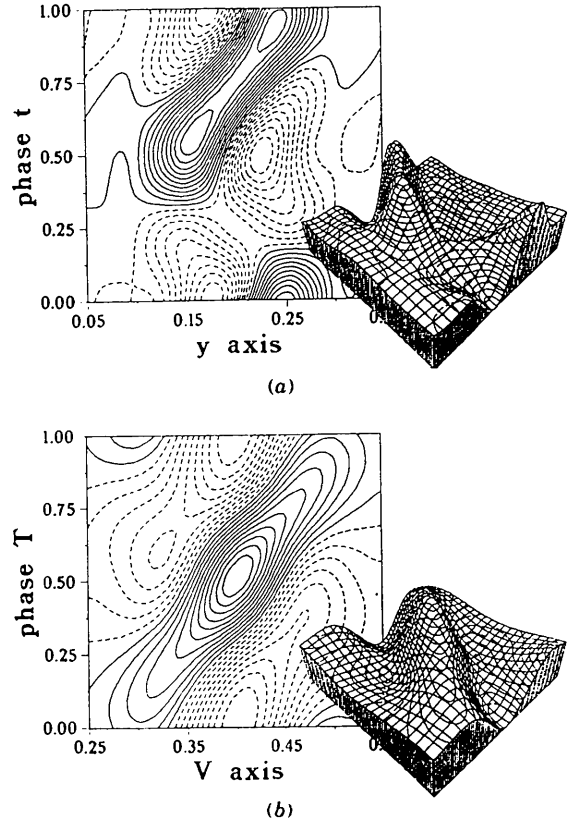

Fig. 4. (*a*) (3+1)FDF of the test structure 2 ($0.0 \le x \le 0.2$, $0.2 \le z \le 0.4$). (*b*) (3+1)PDF of the same atom correlated with that generated by the inversion center ($0.05 \le U \le 0.35$, $0.5 \le W \le 0.7$).

Table 2. *Comparison between amplitudes of modulation deduced from the Patterson maps and the refined values for C3CD*

Atoms		Sum of amplitudes	Refined value	Absolute value (Å)
Cl_a–Cl_a	ΔV	0.085	0.0596(8)	0.338(8)
Cl_a–Cl_a	ΔW	0.023	0.0118(1)	0.296(6)
Cl_a–Cd	ΔW	0.025	0.0122(1)	0.303(4)
Cl_a–Cl_e	ΔW	0.027	0.0140(1)	0.351(4)

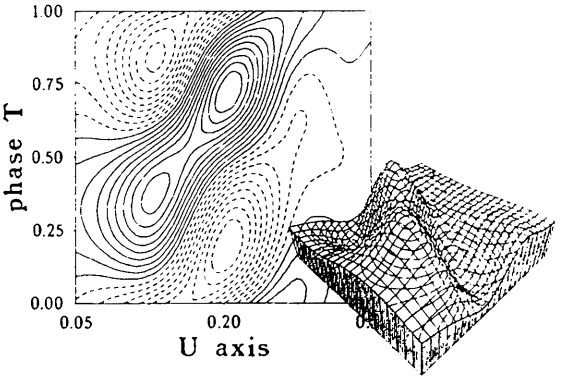

Fig. 5. (3+1)PDF of the test structure 2 ($0.2 \le V \le 0.6$, $0.5 \le W \le 0.7$).

Conclusion. In most cases, Patterson summations will not characterize in a precise way modulated structures. Even in simplified cases involving only a few atoms, the interpretation of (3 + 1)-dimensional Patterson maps can be complicated. The question remains, however: is the Patterson method useful for the determination of modulated structures?

The answer is affirmative if we wish to determine the type of modulation occurring (displacive, occupational, or both): the width and the position of maxima represent characteristic factors. The answer is different if we need information about the amplitudes and the phases. The Patterson method is useful if a 'trial-and-error' procedure does not yield results. This occurs when the structure does not exhibit any atom with large amplitudes or if many atoms are involved in the resolution of the structure. This case corresponds to the problems presented in the preceding paragraphs whereas the second creates interpretation problems for the Patterson owing to the large number of overlapping maxima. Thus the contribution of the Patterson method isrestricted. In our opinion, a reasonable balance should be found between the interpretation of complicated Patterson maps and the time dedicated to more careful measurements of low-intensity reflections.

References

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