Direct Methods for Incommensurate Intergrowth Compounds. II. Determination of the Modulation using only Main Reflections

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Abstract

A modified Sayre equation for incommensurate intergrowth compounds is presented. With this equation, both magnitude and phase for structure factors of satellite reflections can be estimated quantitatively through the observed intensities of main reflections, provided their phases are already known. Modulation functions can then be revealed by the Fourier synthesis calculated using the observed main reflections and the estimated satellites. The method has been tested with the known structures of two inorganic misfit layer compounds, $(LaS)_{1.14}NbS_2$ and $(PbS)_{1.18}TiS_2$. Satisfactory results were obtained.

Introduction

Incommensurate intergrowth compounds can be considered as coherent combinations of two or more modulated structures (Janner & Janssen, 1980; van Smaalen, 1992). In a diffraction experiment, they give Bragg reflections at the nodes of the reciprocal lattices of the basic structures of the subsystems (main reflections). Additional, satellite, reflections are found owing to the incommensurate modulations. In paper I of this series (Fan, van Smaalen, Lam & Beurskens, 1993), the multidimensional direct method proposed by Hao, Liu & Fan (1987) has been extended for use in the determination of modulations in composite structures. Experimentally observed intensities of both main and satellite reflections are needed in this procedure. However, since intensities of main reflections contain information on the modulation, it could be possible to determine the modulation in a composite structure by measuring only the intensities of main reflections. For this purpose, a new modified Sayre equation is derived,

with which the magnitudes and phases for structure factors of satellite reflections can be estimated quantitatively, provided the magnitudes and phases of the main reflections are known. A least-squares method has been used to determine the modulation of composite structures using only the observed structure-factor magnitudes of main reflections (Kato, 1990). Our method differs from the least-squares method in that the structure factors of satellites can be estimated before the modulation model has been established. This means that with our method the modulation waves can be measured directly from the resultant Fourier map while no preliminary assumption about the modulation is needed.

The method

1. Modified Sayre equations for composite structures

According to the structure-factor formula for a composite structure of incommensurate intergrowth compounds (Petricek, Maly, Coppens, Bu, Cisarova & Frost-Jensen, 1991; van Smaalen, 1992; Yamamoto, 1992), we can define the structure factor for a composite structure, $\mathcal{F}(\mathbf{H}_s)$, as

$$\mathcal{F}(\mathbf{H}_s) = \sum_{\nu} F_{\nu}(\mathbf{H}_s W^{\nu, -1}) / V_{\nu}, \qquad (1)$$

where V_{ν} and $F_{\nu}(\mathbf{H}_s)$ are, respectively, the unit-cell volume and the structure factor of the νth substructure; $\mathbf{H}_s = (h_1,...,h_{3+d})$ is the $(3+d)$-dimensional scattering vector; and the matrices W^{ν} take care of the fact that the role of main-reflection indices and satellite indices is different for the different subsystems ν (van Smaalen, 1992). As a single unit cell is not defined, the structure factor (1) is normalized to scattering per unit volume of material, *e.g.* per Å^3. If

$H_s^\nu = H_s W^{\nu,-1}$, then $F_\nu(H_s^\nu)$ can be expressed as (Yamamoto, 1982)

$$F_\nu(H_s^\nu) = \sum_{(R_s^\nu | \tau_s^\nu)} \sum_\mu mt_\mu \int_0^1 dt_1 ... \int_0^1 dt_d \, P^\mu(t) f_\mu(H_s^\nu)$$

$$\times \exp\{2\pi i[H_3^\nu R_3^\nu x^o(\mu) + H_d^\nu M_{d3}^\nu x^o(\mu)$$

$$+ H_s^\nu \cdot \tau_s^\nu + H^\nu \cdot R_3^\nu u^\mu(t) + H_d^\nu \cdot R_d^\nu t]\}, \quad (2)$$

$$f_\mu(H_s^\nu) = f_\mu^o(|H^\nu|) \exp[-\tilde{H}^\nu \cdot \tilde{R}_3^\nu \underline{\beta}^\mu(t) R_3^\nu \cdot H^\nu]. \quad (3)$$

mt_μ is the multiplicity factor of the independent atom μ of subsystem ν. f_μ^o and β^μ are the three-dimensional atomic scattering factor and temperature factor of the μth atom, respectively. H is the projection of H_s onto physical space while H_3 and H_d represent, respectively, the first three and the last d components of H_s. The subsystem symmetry operators $(R_s^\nu | \tau_s^\nu)$ are derived from superspace symmetry operators $(R_s | \tau_s)$ by application of W^ν. They are composed of a 3×3 physical-space part (R_3^ν), a $d \times d$ part transforming the additional coordinates and the left lower $d \times 3$ part M_{d3}^ν. The right upper $3 \times d$ part contains only zeros. $\tilde{M}$ indicates the transpose of the matrix M. The atomic positions are divided into a basic structure position $x^o(\mu)$ and a modulation part $u^\mu(\bar{x}_{\nu s,4},...,\bar{x}_{\nu s,3+d})$, with arguments of the modulation functions $x_{\nu s,3+j} = \sigma_\nu[L + x^o(\mu)]$, where σ_ν is the matrix of modulation wave vectors for subsystem ν and L is a lattice vector of the basic structure. The occupational probability $P(\bar{x}_{\nu s,4},...,\bar{x}_{\nu s,3+d})$ and the temperature tensor may also be modulated. Equations (1)–(3) are easily generalized to include symmetry operators that map one subsystem onto another (van Smaalen, 1992).

Similarly to three-dimensional space, we have in multidimensional space

$$\rho_s(x_s) = \sum_{H_s} \mathscr{F}(H_s) \exp(-2\pi i H_s \cdot x_s) \quad (4)$$

$$\mathscr{F}^{sq}(H_s) = \sum_{H_s'} \mathscr{F}(H_s') \mathscr{F}(H_s - H_s'), \quad (5)$$

where $\mathscr{F}^{sq}(H_s)$ is the structure factor of the squared multidimensional structure in which atoms are squared while their positional parameters are left unchanged. Corresponding to (1), (2) and (3), we have

$$\mathscr{F}^{sq}(H_s) = \sum_\nu F_\nu^{sq}(H_s W^{\nu,-1})/V_\nu \quad (6)$$

$$F_\nu^{sq}(H_s^\nu) = \sum_{(R_s^\nu | \tau_s^\nu)} \sum_\mu mt_\mu \int_0^1 dt_1 ... \int_0^1 dt_d [P^\mu(t)]^2 f_\mu^{sq}(H_s^\nu)$$

$$\times \exp\{2\pi i[H_3^\nu R_3^\nu x^o(\mu) + H_d^\nu M_{d3}^\nu x^o(\mu)$$

$$+ H_s^\nu \cdot \tau_s^\nu + H^\nu \cdot R_3^\nu u^\mu(t) + H_d^\nu \cdot R_d^\nu t]\} \quad (7)$$

$$f_\mu^{sq}(H_s^\nu) = f_\mu^{sq,o}(|H^\nu|) \exp[-\tilde{H}^\nu \cdot \tilde{R}_3^\nu \underline{\beta}^{\mu,sq}(t) R_3^\nu \cdot H^\nu], \quad (8)$$

where $f_\mu^{sq,o}(|H^\nu|)$ and $\beta^{\mu,sq}$ denote the three-dimensional atomic scattering factor and temperature factor of the μth squared nonequivalent atom in subsystem ν, respectively.

Suppose that the crystal is composed of equal atoms and $P^\mu(\bar{x}_{\nu s,4},...,\bar{x}_{\nu s,3+d}) \simeq 1$. Also, assume that the temperature tensor is not modulated. Then, $f_\mu(H_s^\nu) = f(H_s)$ and $f^{sq}(H_s^\nu) = f^{sq}(H_s)$ and it follows from (1), (2) and (7) that

$$\mathscr{F}(H_s) = f(H_s) A(H_s) \quad (9)$$

$$\mathscr{F}^{sq}(H_s) = f^{sq}(H_s) A(H_s) \quad (10)$$

$$A(H_s) = \sum_\nu V_\nu^{-1} \sum_{(R_s^\nu | \tau_s^\nu)} \sum_\mu mt_\mu \int_0^1 dt_1 ... \int_0^1 dt_d$$

$$\times \exp\{2\pi i[H_3^\nu R_3^\nu x^o(\mu) + H_d^\nu M_{d3}^\nu x^o(\mu)$$

$$+ H_s^\nu \cdot \tau_s^\nu + H^\nu \cdot R_3^\nu u^\mu(t) + H_d^\nu \cdot R_d^\nu(t)]\}. \quad (11)$$

Hence,

$$\mathscr{F}(H_s)/\mathscr{F}^{sq}(H_s) = f(H_s)/f^{sq}(H_s) = \theta(H_s). \quad (12)$$

Combining (5) and (12), we obtain

$$\mathscr{F}(H_s) = \theta(H_s) \sum_{H_s'} \mathscr{F}(H_s') \mathscr{F}(H_s - H_s'). \quad (13)$$

This is the multidimensional Sayre equation for composite structures. The right-hand side of (13) can be divided into three parts, then

$$\mathscr{F}(H_s) = \theta(H_s) \Bigg[\sum_{H_s'} \mathscr{F}_{main}(H_s') \mathscr{F}_{main}(H_s - H_s')$$

$$+ 2\sum_{H_s'} \mathscr{F}_{main}(H_s') \mathscr{F}_{sat}(H_s - H_s')$$

$$+ \sum_{H_s'} \mathscr{F}_{sat}(H_s') \mathscr{F}_{sat}(H_s - H_s') \Bigg], \quad (14)$$

where the subscript 'main' indicates main reflections and the subscript 'sat' indicates satellites.

First, consider H_s in (14) to be a satellite reflection. Since the intensity of satellites is much weaker than that of main reflections on average, the last two summations on the right-hand side of (14) are much smaller than the first. Neglecting those, we have the modifed Sayre equation relating satellite reflections to main reflections:

$$\mathscr{F}_{sat}(H_s) \simeq \theta_{sat}(H_s) \sum_{H_s'} \mathscr{F}_{main}(H_s') \mathscr{F}_{main}(H_s - H_s'). \quad (15)$$

On the other hand, if H_s corresponds to a main reflection, two of the three contributions to (14) are retained to give another modified Sayre equation:

$$\mathscr{F}_{main}(H_s) \simeq \theta_{main}(H_s) \Bigg[\sum_{H_s'} \mathscr{F}_{main}(H_s') \mathscr{F}_{main}(H_s - H_s')$$

$$+ 2\sum_{H_s'} \mathscr{F}_{main}(H_s') \mathscr{F}_{sat}(H_s - H_s') \Bigg]; \quad (16)$$

although the second term is small compared to the

first, it is retained to allow calculation of the influence of the satellite reflections on the main reflections.

2. Determination of the function $\theta(\mathbf{H}_s)$

Equation (15) implies that both the magnitude and phase of the structure factor for satellite reflections can be estimated from the whole set of structure factors of main reflections, of which magnitudes are measured from the experiment while phases can be calculated from the known basic structure. However, there remains the problem of determining the function $\theta(\mathbf{H}_s)$. For an equal-atom structure, $\theta(\mathbf{H}_s)$ can be calculated from (12) using the form factor of the squared structure, which is easily calculated by the convolution

$$f_o^{sq}(|\mathbf{H}|) = \int f_o(|\mathbf{H}'|)f_o(|\mathbf{H} - \mathbf{H}'|)\,d\mathbf{H}'. \qquad (17)$$

For nonequal-atom structures, $\theta(\mathbf{H}_s)$ is approximated by its weighted average:

$$\theta(\mathbf{H}_s) \simeq \left\{ \sum_\mu w_\mu [f_\mu^o(|\mathbf{H}|)]^2 \Big/ \sum_\mu w_\mu [f_\mu^{sq,o}(|\mathbf{H}|)]^2 \right\}^{1/2}, \qquad (18)$$

where the weights represent the amount of atom type μ present in the structure [e.g. for $(\mathrm{LaS})_{1.14}\mathrm{NbS}_2$ the weights are $w(\mathrm{La}) = 1.14$, $w(\mathrm{Nb}) = 1$ and $w(\mathrm{S}) = 3.14$].

In practice, $\theta(\mathbf{H}_s)$ will not be given by (12). The functions that enter the Sayre equation [(13)–(16)] depend on the temperature factors, which are not known. Furthermore, series-termination effects heavily influence the values of the summations and the Σ_2 relationships involved are different for (15) and (16). Therefore, $\theta_{sat}(\mathbf{H}_s)$ in (15) is not equal to $\theta_{main}(\mathbf{H}_s)$ in (16) and they both need to be determined from experimental data. The combination of (15) and (16) gives

$$\mathscr{F}_{main}(\mathbf{H}_s) \simeq \theta_{main}(\mathbf{H}_s)\left\{ \sum_{\mathbf{H}_s'} \mathscr{F}_{main}(\mathbf{H}_s')\mathscr{F}_{main}(\mathbf{H}_s - \mathbf{H}_s') \right.$$

$$+ 2\sum_{\mathbf{H}_s'} \left[\mathscr{F}_{main}(\mathbf{H}_s')\,\theta_{sat}(\mathbf{H}_s - \mathbf{H}_s') \right.$$

$$\left. \left. \times \sum_{\mathbf{H}_s''} \mathscr{F}_{main}(\mathbf{H}_s'')\mathscr{F}_{main}(\mathbf{H}_s - \mathbf{H}_s' - \mathbf{H}_s'') \right] \right\}. \qquad (19)$$

Equation (19) can be used to estimate $\theta_{sat}(\mathbf{H}_s)$ and $\theta_{main}(\mathbf{H}_s)$ since it involves only structure factors of main reflections, which are assumed to be known in advance. $\theta_{sat}(\mathbf{H}_s)$ and $\theta_{main}(\mathbf{H}_s)$ are each in fact some kind of atomic form factor. They may be expressed as the sum of Gaussian functions. We write accordingly

$$\theta_{main}(\mathbf{H}_s) = \sum_i A_i^{main} \exp(-B_i^{main}|\mathbf{H}|^2) + C^{main}, \qquad (20)$$

$$\theta_{sat}(\mathbf{H}_s) = \sum_i A_i^{sat} \exp(-B_i^{sat}|\mathbf{H}|^2) + C^{sat}, \qquad (21)$$

Table 1. *Coefficients of the function θ_{main}*

Sample	A_1^{main} $\times 10^{-6}$	A_2^{main} $\times 10^{-6}$	B_1^{main}	B_2^{main}	C^{main} $\times 10^{-6}$
$(\mathrm{LaS})_{1.14}\mathrm{NbS}_2$	2.956	8.871	0.2550	−0.2518	−2.176
$(\mathrm{PbS})_{1.18}\mathrm{TiS}_2$	4.773	−0.2279	0.2426	4.9440	−1.234

Table 2. *Coefficients of the function θ_{sat}*

Sample	A_1^{sat} $\times 10^{-6}$	A_2^{sat} $\times 10^{-6}$	B_1^{sat}	B_2^{sat}	C^{sat} $\times 10^{-6}$
$(\mathrm{LaS})_{1.14}\mathrm{NbS}_2$	98.98	107.7	0.2233	0.1357	106.2
$(\mathrm{PbS})_{1.18}\mathrm{TiS}_2$	60.13	3.033	0.3101	2.0549	0.3021

where only terms with $i = 1, 2$ have been used. All the parameters A_i^{sat}, B_i^{sat}, C^{sat}, A_i^{main}, B_i^{main} and C^{main} can be obtained by a least-squares refinement based on (19). It should be noted that, if $\theta_{sat}(\mathbf{H}_s)$ and $\theta_{main}(\mathbf{H}_s)$ are determined by a fit to (19), using $|F_o|$, their absolute values represent the scale of the experimental data and thus have no physical meaning. Only the angle dependence and their relative values can have some meaning.

Test and results

The method was tested with experimental X-ray diffraction data of $(\mathrm{LaS})_{1.14}\mathrm{NbS}_2$ and $(\mathrm{PbS})_{1.18}\mathrm{TiS}_2$ (van Smaalen, 1991; van Smaalen, Meetsma, Wiegers & de Boer, 1991). Both structures can be described as an alternating stacking of two types of layers (Wiegers & Meerschaut, 1992; van Smaalen, 1992). For $(\mathrm{LaS})_{1.14}\mathrm{NbS}_2$, there are in total 860 unique reflections with 584 main reflections and 276 satellites; while for $(\mathrm{PbS})_{1.18}\mathrm{TiS}_2$, 1652 unique reflections, including 1462 main reflections and 190 satellites, are available.

First, coefficients for the expressions of $\theta_{main}(\mathbf{H}_s)$ and $\theta_{sat}(\mathbf{H}_s)$ were determined by a least-squares refinement based on (19) using the known phases and experimentally measured structure-factor magnitudes of main reflections. Results are listed in Tables 1 and 2. The reliability of these coefficients was checked by calculating the R factors

$$R = \sum ||\mathscr{F}_o| - |\mathscr{F}_c|| \Big/ \sum |\mathscr{F}_o|, \qquad (22)$$

where $|\mathscr{F}_o|$ is the structure-factor magnitude of main reflections derived from the experiment satisfying the definition of (1), $|\mathscr{F}_c|$ is that calculated from (19). We found that the final R factor for 584 main reflections of $(\mathrm{LaS})_{1.14}\mathrm{NbS}_2$ is 0.233, while that for 1462 main reflections of $(\mathrm{PbS})_{1.18}\mathrm{TiS}_2$ is 0.399.

Phases and moduli of satellite reflections were then calculated by phases and moduli of main reflections and $\theta_{sat}(\mathbf{H}_s)$ input into (15). For $(\mathrm{LaS})_{1.14}\mathrm{NbS}_2$, the average phase error with the phases from the refinement of the modulated structures is the same as obtained with the phase-extension procedure (Fan,

Table 3. *Comparison of satellite structure factors obtained by direct methods [(15)] with measured amplitudes of the satellites and phases from the modulated structure refinement*

R is defined in (22).

Sample	Number of reflections	Average phase error (°)	R
$(LaS)_{1.14}NbS_2$	276	17.05	0.300
$(PbS)_{1.18}TiS_2$	190	8.84	0.197

van Smaalen, Lam & Beurskens, 1993). For $(PbS)_{1.18}TiS_2$, the average phase error is slightly larger (Table 3). Comparing observed magnitudes with the calculated magnitudes of the satellites gives a higher R factor than the partial R factor in the refinement. It is to be determined whether the calculated satellites can be used in a refinement procedure. Nevertheless, Fourier maps do show the usefulness of the calculated satellite structure factors. The Fourier synthesis at the position of lanthanum using main reflections only does not show the modulation (Fig. 1). The additional inclusion of the calculated satellite structure factors (15) gives a Fourier map that is indistinguishable from the Fourier map obtained with measured magnitudes and phases from the refinement (Figs. 2 and 3).

Concluding remarks

It was shown previously that satellite reflections are an essential ingredient to make the modulations vis-ible in a Fourier synthesis of the reflections of an incommensurate intergrowth compound (Fan, van Smaalen, Lam & Beurskens, 1993). In this paper, it is shown that both the magnitudes and the phases of the satellite reflections can be derived from the structure factors of the main reflections. For the latter, measured amplitudes are combined with phases obtained from, for example, a basic structure
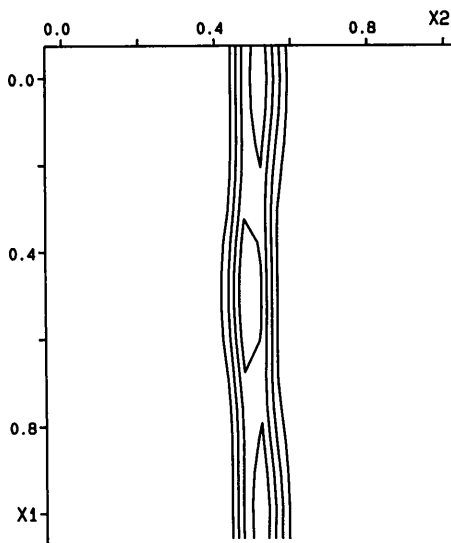

Fig. 2. The same section of the four-dimensional Fourier synthesis as in Fig. 1. Experimental main reflections with phases from the basic structure refinement are combined with both magnitudes and phases of satellite reflections obtained with the direct-methods procedure [(15)].
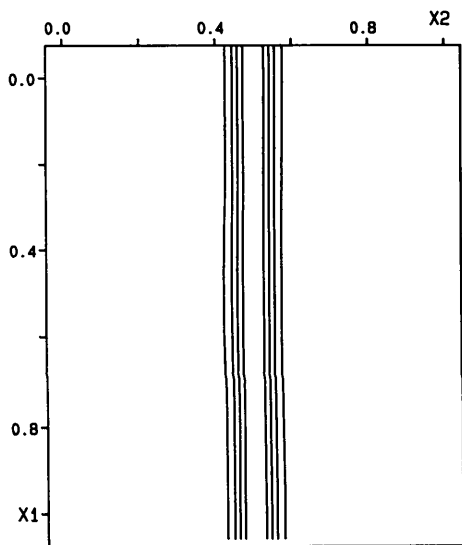

Fig. 1. Section of the four-dimensional Fourier synthesis of $(LaS)_{1.14}NbS_2$ at the position of the La atom ($x = 0$ and $z = 0.174$). Contours are plotted at intervals of 1/5 of the maximum density. Main reflections are used, with experimental magnitudes and phases from the basic structure refinement.
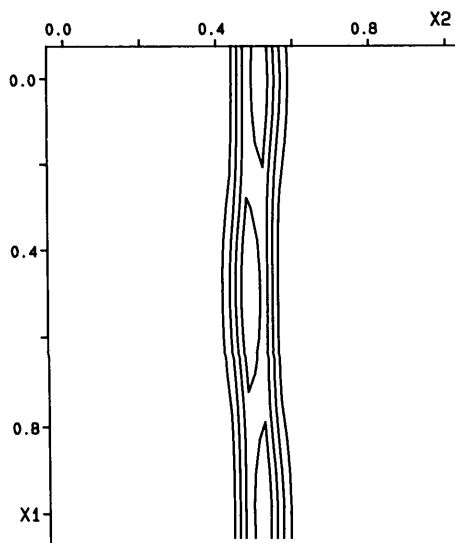

Fig. 3. The same section of the four-dimensional Fourier synthesis as in Fig. 1. For both main reflections and satellites structure factors are used with experimental magnitudes and phases from the modulated structure refinement.

refinement or a direct-methods procedure independent of the satellite reflections. This, at first sight surprising, result can be understood from the special nature of intergrowth compounds. The two subsystems coexist in a single thermodynamic phase and part of the satellite intensity due to the modulation is already contained in the main reflections. This information allowed the refinement of modulation parameters on main reflections only (Kato, 1990), but it is insufficient to reveal the modulation amplitudes in a Fourier synthesis (Fig. 1). The method proposed here allows one to calculate the satellite structure factors from the main reflections with sufficient accuracy to determine the modulation from a Fourier map (Fig. 2).

Phases of the satellite reflections can be obtained as described earlier (Fan, van Smaalen, Lam & Beurskens, 1993). For their magnitudes to be determined, a crucial step is that the functions $\theta_{sat}(H_s)$ and $\theta_{main}(H_s)$ can both be determined from the main reflections alone [(15), (16) and (19)]. Applications are given to the inorganic misfit layer compounds $(LaS)_{1.14}NbS_2$ and $(PbS)_{1.18}TiS_2$. The Fourier map calculated with the main reflections and the satellite reflections generated in the direct-methods procedure is found to be indistinguishable from the Fourier synthesis using experimental amplitudes for all reflections combined with phases from the refinement (Figs. 2 and 3). This shows the structure factors of the satellite reflections calculated with (15) to be sufficiently accurate to determine the modulations in these composite crystals.

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Quasicrystals and their Approximants: Dodecahedral Local Ordering *Versus* Canonical-Cell Description

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Abstract

Two models of icosahedral quasicrystals are compared and connected. These are canonical-cell ordering (CCO) over medium-length scales (about 10 Å and more) and dodecahedral local ordering (DLO), which describes interatomic arrangements. In the DLO model, each atom is surrounded by closest neighbours positioned at several vertices of a regular pentagon-dodecahedron; of the 20 vertices of any dodecahedron, only a few can be occupied simultaneously without conflict (eight at most). Some icosahedral quasicrystals and their crystalline approximants exhibit DLO as the main structure motif at atomic scales. DLO networks are formally described using an unconventional projection of a six-dimensional lattice. It is shown that most DLO configurations (but not all of them!) can be constructed from small atomic size canonical cells that are a factor of τ^3 smaller than the original ones. Two of the small canonical cells have the forms of distorted tetrahedra. It is also shown that DLO produces naturally the two most popular decorations of the Ammann rhombohedra: the edge decoration and the vertex-face decoration. Moreover, both decorations can be identified inside the same approximant. For medium-range distances, DLO leads to CCO with special decorations of the canonical cells. Therefore, the ordering in quasicrystals and in their approximants can be constructed as a hierarchy of dodecahedral ordering (or a hierarchy of canonical cells). It is shown that within the DLO model there may be an additional ordering of closest neighbours that leads to the transition between quasicrystals with primitive and face-centred lattices. The DLO-based duality between α-AlMnSi and Al_5Li_3Cu approximants is demonstrated. Possible physi-