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Direct Methods in Superspace. I. Preliminary Theory and Test on the Determination of Incommensurate Modulated Structures

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Abstract

The validity of the Sayre equation [Sayre (1952). *Acta Cryst.* **5**, 60-65] for $(3+n)$-dimensional periodic structures is examined. A practical procedure is proposed for the determination of incommensurate modulated structures; this is an extension of the direct method previously proposed for solving superstructures [Fan Hai-fu, He Lao, Qian Jin-zi & Liu Shi-xiang (1978). *Acta Phys. Sin.* **27**, 554-558]. With the newly proposed method, the phase problem for the main as well as the satellite reflections can be solved directly without making particular assumptions about the modulation. A known incommensurate modulated structure, γ-Na_2CO_3, was used in the test. Satisfactory results were obtained.

Introduction

Incommensurate modulated phases are often found in inorganic solids (minerals, alloys, *etc.*) and organic solids. In many cases, the transition to the modulated structure corresponds to a change of certain physical properties. Hence it is essential to know the structure of incommensurate phases in order to understand the mechanism of the transition and properties in the modulated state. Up to the present, methods used in the determination of incommensurate modulated structures, such as the least-squares method of Yamamoto (1982), rely on some assumption about the modulation and on a preliminary knowledge of the main (average) structure. In this paper a method is described which starts by handling X-ray diffraction data and ends in a $(3+n)$-dimensional electron density map revealing the details of the modulated structure objectively. This method is proposed not to replace but to combine with the least-squares method in a way like that for solving ordinary small molecular structures.

$(3+n)$-dimensional description of modulated structures

A modulated structure is a kind of crystal structure in which the atoms suffer from certain occupational and/or positional fluctuations according to a periodic modulation. In the case that all the wave vectors of the modulation wave are commensurate with unit vectors of the reciprocal cell, a superstructure results, while in the case that the wave vectors are incommensurate with unit vectors of the reciprocal cell, an incommensurate structure is obtained. An n-dimensional ($n = 1, 2, \ldots$) periodic modulation corresponds to an n-dimensional modulated structure. In this section, the descriptions of modulated structure by de Wolff (1974) and by Yamamoto (1982) are briefly reviewed.

For an n-dimensional modulated structure, the reciprocal vector $\mathbf{H}$ of a main or satellite reflection can be expressed in three-dimensional space as

$$\mathbf{H} = h_1\mathbf{a}^* + h_2\mathbf{b}^* + h_3\mathbf{c}^* + \sum_{i=1}^{n} h_{3+i}\mathbf{k}^i, \qquad (1)$$

where

$$\mathbf{k}^i = k_1^i\mathbf{a}^* + k_2^i\mathbf{b}^* + k_3^i\mathbf{c}^*.$$

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$\mathbf{k}^i$ is the ith wave vector of the n-dimensional modulation wave function. In the case of incommensurate modulation, at least one of k_1^i, k_2^i, k_3^i should be irrational. Define a $(3+n)$-dimensional reciprocal lattice with unit vectors

$$\mathbf{b}_1 = \mathbf{a}^*, \quad \mathbf{b}_2 = \mathbf{b}^*, \quad \mathbf{b}_3 = \mathbf{c}^*,$$
$$\mathbf{b}_{3+i} = \mathbf{k}^i + \mathbf{d}_i \quad (i = 1, 2, \ldots, n), \tag{2}$$

where the $\mathbf{d}_i$ are the unit vectors perpendicular to the usual three-dimensional space. A reciprocal-lattice vector in the $(3+n)$-dimensional space can then be written as

$$\hat{\mathbf{H}} = \sum_{i=1}^{3+n} h_i \mathbf{b}_i. \tag{3}$$

Comparison of (1) and (3) shows that $\mathbf{H}$ is the projection of $\hat{\mathbf{H}}$ along directions $\mathbf{d}_i$ onto the three-dimensional space. In other words, the whole three-dimensional diffraction pattern from a modulated structure may be imagined as the projection of a hypothetical $(3+n)$-dimensional weighted reciprocal lattice along directions $\mathbf{d}_i$ onto the usual three-dimensional space. Accordingly, a modulated structure can be imagined as the section of a hypothetical $(3+n)$-dimensional periodic structure at a three-dimensional hyperplane perpendicular to directions $\mathbf{d}_i$. Unit vectors of the direct lattice reciprocal to (2) should be given as

$$\begin{aligned} \mathbf{a}_1 &= \mathbf{a} - \sum_{i=1}^{n} k_1^i \mathbf{d}_i, \\ \mathbf{a}_2 &= \mathbf{b} - \sum_{i=1}^{n} k_2^i \mathbf{d}_i \\ \mathbf{a}_3 &= \mathbf{c} - \sum_{i=1}^{n} k_3^i \mathbf{d}_i, \\ \mathbf{a}_{3+i} &= \mathbf{d}_i \quad (i = 1, 2, \ldots, n), \end{aligned} \tag{4}$$

where $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are reciprocal to $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$. A vector $\mathbf{x} = x_1\mathbf{a} + x_2\mathbf{b} + x_3\mathbf{c}$ in three-dimensional direct space can then be expressed in a $(3+n)$-dimensional description as

$$\mathbf{x} = \sum_{i=1}^{3+n} x_i \mathbf{a}_i, \tag{5}$$

where $x_{3+j} = k_1^j x_1 + k_2^j x_2 + k_3^j x_3$. Notice that x_1, x_2, x_3 with respect to $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are identical to those with respect to $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ since $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are the projections of $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ along directions $\mathbf{d}_i$ as shown in (4).

In the $(3+n)$-dimensional description, an atom will no longer be a sphere. It will be spun out continuously along the directions $\mathbf{d}_i$ of the extra dimensions with periodic variation in occupation and/or position (x_1, x_2, x_3). The main (average) structure is described by atoms with constant scattering power and constant coordinates x_1, x_2, x_3 over the extra dimensions. The deviation of the modulated structure from the average one occurs on a hyperplane, *i.e.* the usual three-dimensional space perpendicular to $\mathbf{d}_i$. Therefore the $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ components of the μth atom in the unit cell can be written as

$$x_i^\mu = \bar{x}_i^\mu + u_i^\mu \quad (i = 1, 2, 3), \tag{6}$$

where $\bar{x}_1^\mu, \bar{x}_2^\mu, \bar{x}_3^\mu$ are the $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ components of the atomic position of the μth atom in the average structure and $u_1^\mu, u_2^\mu, u_3^\mu$ are the corresponding displacements. The $\mathbf{a}_{3+i}$ components of the positional vector are given by

$$x_{3+i}^\mu = \bar{x}_{3+i} + u_{3+i}^\mu \quad (i = 1, 2, \ldots, n), \tag{7}$$

where $\bar{x}_{3+i}$ is the $(3+i)$th coordinate in the average structure which is a continuous parameter independent of μ,

$$u_{3+i}^\mu = \sum_{m=1}^{3} k_m^i u_m^\mu.$$

In the modulated structure, $u_1^\mu, u_2^\mu, u_3^\mu$ are periodic functions of $\bar{x}_{3+i}$. Now the scattering factor of the μth $(3+n)$-dimensional atom with respect to an origin at $(\bar{x}_1^\mu, \bar{x}_2^\mu, \bar{x}_3^\mu, 0, \ldots, 0)$ can be written as

$$f_\mu(\hat{\mathbf{H}}) = f_\mu(\mathbf{H}) \int_0^1 \mathrm{d}\bar{x}_4 \ldots \int_0^1 \mathrm{d}\bar{x}_{3+n} P_\mu \times \exp\left[i2\pi \left(\sum_{m=1}^{3} h_m u_m^\mu + \sum_{j=4}^{3+n} h_j x_j^\mu \right) \right], \tag{8}$$

where $f_\mu(\mathbf{H})$ is the usual atomic scattering factor and P_μ is the density modulation function. The structure factor in $(3+n)$-dimensional space is thus

$$\mathbf{F}(\hat{\mathbf{H}}) = \sum_\mu f_\mu(\hat{\mathbf{H}}) \exp\left(i2\pi \sum_{j=1}^{3} h_j \bar{x}_j^\mu \right). \tag{9}$$

Accordingly, the $(3+n)$-dimensional electron density distribution can be obtained as

$$\rho(\mathbf{x}) = (1/V) \sum_{\hat{\mathbf{H}}} \mathbf{F}(\hat{\mathbf{H}}) \exp(-i2\pi \hat{\mathbf{H}}.\mathbf{x}), \tag{10}$$

where V is the volume of the unit cell of the average structure. It should be noticed that since in the incommensurate modulated structure the correspondence between $\hat{\mathbf{H}}$ and $\mathbf{H}$ is one-to-one, we have always $\mathbf{F}(\hat{\mathbf{H}}) = \mathbf{F}(\mathbf{H})$.

Use of the Sayre equation for an incommensurate modulated structure

1. *The Sayre equation in* $(3+n)$*-dimensional space*

In theory, the Sayre (1952) equation will be valid only when the following conditions are fulfilled: (*a*) the electron density should not be negative; (*b*) the atoms should not overlap each other; and (*c*) the

crystal should be composed of equal atoms. In practice, the third condition can rarely be fulfilled. However, the Sayre equation still gives satisfactory results in most cases.

For modulated structures the first two conditions can be satisfied as well as for ordinary structures. We can write in $(3+n)$-dimensional space that

$$\mathbf{F}^{sq}(\hat{\mathbf{H}}) = (1/V)\sum_{\hat{\mathbf{H}}'} \mathbf{F}(\hat{\mathbf{H}}')\mathbf{F}(\hat{\mathbf{H}}-\hat{\mathbf{H}}'), \qquad (11)$$

where $\mathbf{F}^{sq}(\hat{\mathbf{H}})$ is the structure factor of the squared modulated structure, in which the atoms are squared while their positional parameters are left unchanged. We have thus

$$\mathbf{F}^{sq}(\hat{\mathbf{H}}) = \sum_{\mu} f_{\mu}^{sq}(\hat{\mathbf{H}}) \exp\left(i2\pi \sum_{j=1}^{3} h_j \bar{x}_j^{\mu}\right), \qquad (12)$$

where

$$f_{\mu}^{sq}(\hat{\mathbf{H}}) = f_{\mu}^{sq}(\mathbf{H}) \int_0^1 \mathrm{d}\bar{x}_4 \ldots \int_0^1 \mathrm{d}\bar{x}_{3+n} P_{\mu}^2 \times \exp\left[i2\pi\left(\sum_{m=1}^{3} h_m u_m^{\mu} + \sum_{j=4}^{3+n} h_j \bar{x}_j^{\mu}\right)\right]. \qquad (13)$$

Suppose that the crystal is composed of equal atoms and $P \simeq 1$. The ratio between $\mathbf{F}(\hat{\mathbf{H}})$ and $\mathbf{F}^{sq}(\hat{\mathbf{H}})$ will then be independent of μ. From (13), (12), (9) and (8) we obtain

$$\mathbf{F}(\hat{\mathbf{H}})/\mathbf{F}^{sq}(\hat{\mathbf{H}}) = f(\mathbf{H})/f^{sq}(\mathbf{H}) = \theta(\mathbf{H}), \qquad (14)$$

where $f(\mathbf{H})$ is the usual atomic scattering factor in three-dimensional space and $f^{sq}(\mathbf{H})$ is the corresponding scattering factor of the 'square atom'. It follows from (11) and (14) that

$$\mathbf{F}(\hat{\mathbf{H}}) = [\theta(H)/V]\sum_{\hat{\mathbf{H}}'} \mathbf{F}(\hat{\mathbf{H}}')\mathbf{F}(\hat{\mathbf{H}}-\hat{\mathbf{H}}'). \qquad (15)$$

This is the ordinary Sayre equation in $(3+n)$-dimensional space. It forms the foundation of the application of direct methods to modulated structures. If the structure contains unequal atoms or $P_{\mu} \neq 1$, we can still calculate $\theta(H)$ using the approximation

$$\theta(H) = \langle |F(\hat{\mathbf{H}})| \rangle_H / \langle (1/V) |\sum_{\hat{\mathbf{H}}'} \mathbf{F}(\hat{\mathbf{H}}')\mathbf{F}(\hat{\mathbf{H}}-\hat{\mathbf{H}}')| \rangle_H, \qquad (16)$$

where $\langle\ \rangle_H$ means the average over a shell having a mean radius of H.

2. *The Sayre equation on a three-dimensional hyperplane*

Usually in a modulated structure the modulation to the main (average) structure will not be very strong. Hence the total intensity of satellite reflections will be very weak in comparison with that of the main reflections. We can expect that a modified Sayre equation exists for only the main reflections, *i.e.*

$$\mathbf{F}(\hat{\mathbf{H}}_0) = [\theta(H)/V]\sum_{\hat{\mathbf{H}}_0'} \mathbf{F}(\hat{\mathbf{H}}_0')\mathbf{F}(\hat{\mathbf{H}}_0-\hat{\mathbf{H}}_0'), \qquad (17)$$

in which $\hat{\mathbf{H}}_0$ denotes the reciprocal vector with all components h_i $(i>3)$ equal to zero. This implies that the phases of main reflections can be obtained by ordinary direct methods.

3. *Modified Sayre equation linking main and satellite reflections*

Following Fan Hai-fu, He Lao, Qian Jin-zi & Liu Shi-xiang (1978) [see also Fan Hai-fu, Yao Jia-xing, Main & Woolfson, 1983) we can derive a modified Sayre equation which links the phases of satellite reflections with those of the main reflectins

A modulated structure can be described by superimposing a difference structure onto a main structure in $(3+n)$-dimensional space. We write

$$\rho(\mathbf{x}) = \rho_m(\mathbf{x}) + \Delta\rho(\mathbf{x}), \qquad (18)$$

where $\rho_m(\mathbf{x})$ denotes the electron-density distribution of the main structure. If both sides of (18) are squared and the term $\Delta\rho^2(\mathbf{x})$ is neglected it follows that

$$\rho^2(\mathbf{x}) = \rho_m^2(\mathbf{x}) + 2\rho_m(\mathbf{x})\Delta\rho(\mathbf{x}). \qquad (19)$$

Fourier transformation of (18) and (19) gives (20) and (21) respectively:

$$\mathbf{F}(\hat{\mathbf{H}}) = \mathbf{F}_m(\hat{\mathbf{H}}) + \Delta\mathbf{F}(\hat{\mathbf{H}}), \qquad (20)$$

$$\mathbf{F}^{sq}(\hat{\mathbf{H}}) = \mathbf{F}_m^{sq}(\mathbf{H}) + (2/V)\sum_{\hat{\mathbf{H}}'} \mathbf{F}_m(\hat{\mathbf{H}}')\Delta\mathbf{F}(\hat{\mathbf{H}}-\hat{\mathbf{H}}'). \qquad (21)$$

Here the subscript m stands for the partial contribution from the main structure. If $\hat{\mathbf{H}}$ is a vector corresponding to one of the satellite reflections then both $\mathbf{F}_m(\hat{\mathbf{H}})$ and $\mathbf{F}_m^{sq}(\hat{\mathbf{H}})$ equal zero. Hence from (20) and (21) we have

$$\mathbf{F}_s^{sq}(\mathbf{H}) = (2/V)\sum_{\hat{\mathbf{H}}'} \mathbf{F}_m(\hat{\mathbf{H}}')\mathbf{F}_s(\hat{\mathbf{H}}-\hat{\mathbf{H}}'), \qquad (22)$$

where the subscript s stands for satellite reflections. From the substitution of (14) into (22) it follows that

$$\mathbf{F}_s(\hat{\mathbf{H}}) = [2\theta(H)/V]\sum_{\hat{\mathbf{H}}'} \mathbf{F}_m(\hat{\mathbf{H}}')\mathbf{F}_s(\hat{\mathbf{H}}-\hat{\mathbf{H}}'), \qquad (23)$$

where $\mathbf{F}_m(\hat{\mathbf{H}})$, the partial contribution from the main structure, can be taken as the total structure factor of a main reflection, since the contribution from $\Delta\rho(\mathbf{x})$ to a main reflection can be neglected. It should be noticed that the vectors $\hat{\mathbf{H}}'$ in (23) will have their components h_i $(i>3)$ all equal to zero, while all vectors $\hat{\mathbf{H}}-\hat{\mathbf{H}}'$ in (23) will have their components h_i $(i>3)$ equal to the corresponding components of $\hat{\mathbf{H}}$. With (23) the phase derivation for the satellite reflections can be greatly simplified, once the phases of the main reflections are known.

4. *Strategy for solving incommensurate modulated structures*

A two-step procedure in reciprocal space can be used to determine an incommensurate modulated structure. In the first step only the phases of main reflections are to be derived using (17) in a way similar to that for ordinary structures. However there is no need to calculate and interpret any E map or Fourier map. In the second step the phases of satellite reflections are to be derived from those of main reflections by making use of (23). Finally a $(3+n)$-dimensional Fourier map is calculated, which can reveal completely the modulated structure.

Test and results

All the test calculations were performed with a known incommensurate modulated structure, γ-Na_2CO_3 (van Aalst, den Hollander, Peterse & de Wolff, 1976). This is a one-dimensional displacive modulated structure with $a=8{\cdot}904(3)$, $b=5{\cdot}239(2)$, $c=6{\cdot}042(2)$ Å; $\beta=101{\cdot}35(2)°$; $k_1=0{\cdot}182(1)$, $k_2=0{\cdot}000$, $k_3=0{\cdot}318(1)$. The space group has the following eightfold general positions expressed in the coordinates x_1, x_2, x_3, x_4 in four-dimensional space:

$$(0\,0\,0\,0),\ (\tfrac{1}{2}\tfrac{1}{2}\,0\,0)+$$

$$\begin{array}{cccc} x_1 & x_2 & x_3 & x_4 \\ -x_1 & -x_2 & -x_3 & -x_4 \\ x_1 & -x_2 & x_3 & x_4+\frac{1}{2} \\ -x_1 & x_2 & -x_3 & -x_4+\frac{1}{2}. \end{array}$$

1. *Test for the reliability of modified Sayre equations*

The modified Sayre equations (17) and (23) are the fundamental formulae to be used in the two-step procedure for solving incommensurate modulated structures. Equation (17) includes only the $\sum_2$ relationships among the main reflections, *i.e.* it excludes relationships containing any satellite reflection. On the other hand, (23) excludes only those relationships involving three satellite reflections. The self-consistency of (17) and (23) was tested with the theoretical data of γ-Na_2CO_3 at about 0·7 Å resolution, which was calculated from the final atomic parameters. In each test the phases (signs) of the 300 largest structure factors were calculated and compared with the true values. The results were arranged in descending order of

$$\left|\sum_{\mathbf{H}'} \mathbf{F}_{\mathbf{H}}\mathbf{F}_{\mathbf{H}'}\mathbf{F}_{\mathbf{H}-\mathbf{H}'}\right|$$

and sorted into six groups as listed in columns 3 and 4 of Table 1 for (17) and (23) respectively. For comparison, the result from the ordinary Sayre equation (15) is listed in column 5. As can be seen, (15) gives the most accurate result, while (17) contains the largest error. However, it can still be concluded that both (17) and (23) are accurate enough for the purpose of phase derivation.

Table 1. *Results on testing the self-consistency of the modified Sayre equations*

Group number	Number of reflections	Percentage of reflections with their phase (sign) correctly determined (I)	(II)	(III)
1	50	98	100	100
2	100	98	100	100
3	150	97	100	100
4	200	94	99	99
5	250	92	98	99
6	300	87	96	97

(I) Results from (17) on calculating 300 largest $F(h_1h_2h_30)$.
(II) Results from (23) on calculating 300 largest $F(h_1h_2h_31)$ using 300 $F(h_1h_2h_30)$ and 300 $F(h_1h_2h_31)$.
(III) Results from (15) on calculating 300 largest $F(h_1h_2h_31)$ using 300 $F(h_1h_2h_30)$, 300 $F(h_1h_2h_31)$ and 300 $F(h_1h_2h_32)$.
The inconsistency shown in (III) is due to the truncation effect and the existence of unequal atoms.

Table 2. *Atomic coordinates in the average structure of* γ-Na_2CO_3

	(I)			(II)		
	x	y	z	x	y	z
Na(1)	0	0	0	0	0	0
Na(2)	0	0	0·5000	0	0	0·5000
Na(3)	0·1689	0·5000	0·7404	0·1706	0·5000	0·7478
C	0·1654	0·5000	0·2388	0·1641	0·5000	0·2496
O(2)	0·2856	0·5000	0·1750	0·2897	0·5000	0·1771
O(1,3)	0·0902	0·3050	0·2723	0·1016	0·2940	0·2855

(I) Obtained from a default run of the *SAPI*85 program.
(II) From Table 1(*a*) of van Aalst, den Hollander, Peterse & de Wolff (1976).

2. *Test on solving an incommensurate modulated structure*

The 300 largest $|F(h_1h_2h_30)|$, 250 largest $|F(h_1h_2h_31)|$ and 150 largest $|F(h_1h_2h_32)|$ from the experimental data of γ-Na_2CO_3 were used. Firstly the phases of $F(h_1h_2h_30)$ were derived by an ordinary direct method. The program *SAPI*85 (Yao Jia-xing, Zheng Chao-de, Qian Jin-zi, Han Fu-son, Gu Yuan-xin & Fan Hai-fu, 1985; Fan Hai-fu, 1986), run with default control, gave automatically the correct average structure. The atomic parameters are listed in Table 2 in comparison with those obtained by Dubbeldam & de Wolff (1969). From the atomic parameters listed in Table 2 (I), the signs of the 300 largest $F(h_1h_2h_30)$ were calculated, 90% of which were correct. It should be emphasized that there is no need to calculate and interpret an E map at this stage. The phases obtained from an ordinary tangent refinement can be passed on to the second step directly. In the second step, a simple symbolic addition procedure was used to derive the phases of satellite reflections by making use of (23). The phases of $F(h_1h_2h_30)$ obtained in the first step were kept

Table 3. *Results on the phase derivation of satellite reflections*

Group number	Number of reflections	Percentage of reflections with their phase (sign) correctly determined $F(h_1h_2h_31)$	$F(h_1h_2h_32)$
1	50	100	100
2	100	92	90
3	150	81	82
4	200	73	
5	250	70	

fixed. The result is summarized in Table 3. Finally, a four-dimensional Fourier series was calculated using 300 main reflections and 400 satellite reflections. Two-dimensional sections of the Fourier series parallel to the fourth direction $\mathbf{x}_4$ and passing through the average position of Na(1) are shown in Fig. 1. Sections through O(1, 3) are shown in Fig. 2. We can conclude immediately from Fig. 1 that, within the experimental error, the modulation to Na(1) is pure displacive with components on $\mathbf{a}_1$ and $\mathbf{a}_3$ equal to zero. The modulation function is nearly a sinusiodal curve; its parameters can easily be read from Fig. 1(*b*). On the other hand, Fig. 2 shows that the modulation function of O(1, 3) is a helical curve in four-

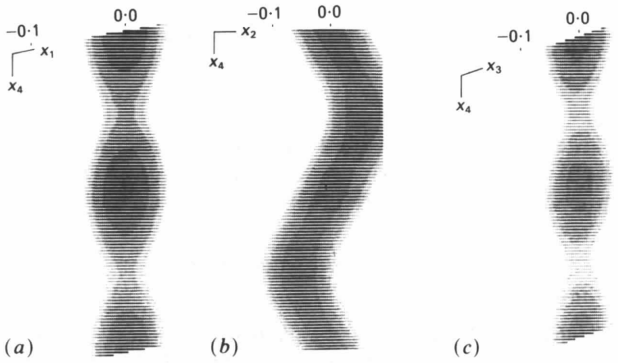

Fig. 1. Fourier sections through the centre line of Na(1). (*a*) $\rho(x_1, 0, 0, x_4)$; (*b*) $\rho(0, x_2, 0, x_4)$; (*c*) $\rho(0, 0, x_3, x_4)$.

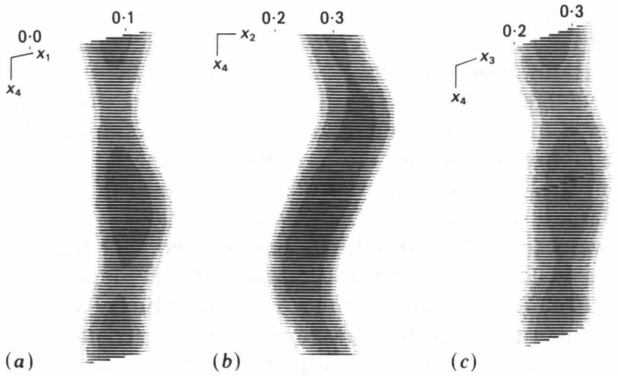

Fig. 2. Fourier sections through the centre line of O(1, 3). (*a*) $\rho(x_1, 0{\cdot}305, 0{\cdot}272, x_4)$; (*b*) $\rho(0{\cdot}090, x_2, 0{\cdot}272, x_4)$; (*c*) $\rho(0{\cdot}090, 0{\cdot}305, x_3, x_4)$.

Table 4. *Modulation parameters of* γ-Na_2CO_3

	(I) V (Å)	β (°)	(II) V (Å)	β (°)
Na(1)	0·32		0·297	
Na(2)	0·34		0·340	
Na(3)	0·30	−2·3	0·361	−4·8
C	0·35	−1·8	0·308	0·9
O(2)	0·11	−20·6	0·134	−17·7
O(1, 3)	U = 0·14	α = −108·6	U = 0·295	α = −146·2
	V = 0·27	β = 7·2	V = 0·405	β = 5·2
	W = 0·15	γ = −80·2	W = 0·260	γ = −119·8

(I) Obtained from three direct-method phased Fourier sections through the centre line of the corresponding atoms.
(II) From Table 1(*b*) of van Aalst, den Hollander, Peterse & de Wolff (1976).

dimensional space. Careful inspection of the Fourier series in the whole four-dimensional space is essential to find out the modulation parameters for O(1, 3). Table 4 lists the modulation parameters found from the Fourier sections compared with those from van Aalst *et al.* (1976). Good consistency between the two sets of parameters can be observed except for O(1, 3), of which the parameters cannot be accurately determined from only three sections like those in Fig. 2. The accuracy can be improved by using more Fourier sections or by making use of partial Fourier projections.

Concluding remarks

The present work points out the possibility of applying direct methods in multi-dimensional space to solve incommensurate modulated structures. The method is straightforward, easy to automate and there is no need to make assumptions about the modulation before the Fourier map is obtained. It is reasonable to use this method first to derive an initial model and then use a least-squares method [*e.g.* that of Yamamoto (1982)] to obtain the final structure. While the procedure used in this paper was very efficient, it is by no means optimized. Hence there is still room for improvement.

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