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MULTI-DIMENSIONAL DIRECT METHODS

FAN HAI-FU
Institute of Physics, Chinese Academy of Sciences
Beijing 100080, P.R. China

1. Introduction

In single crystal structure analysis, it is usually assumed that crystals are ideal 3-dimensional periodic objects. However real crystals are never perfect. What we obtained under this assumption is not the real structure but just an averaged structure over a large number of unit cells. Unfortunately a knowledge on the averaged structure is often not enough for understanding the properties of many solid state materials. Therefore an important task for methods of solving crystal structures is to extend from ideal periodic crystals to real crystals which contain various kinds of defects. Modulated crystal structures belong to a kind of crystal structures containing periodic defects, i.e. the atoms in which suffer from certain occupational and/or positional fluctuation. If the period of fluctuation is commensurate with that of the three-dimensional unit cell then a superstructure results, otherwise an incommensurate modulated structure is obtained. Incommensurate modulated phases can be found in many important solid state materials. In many cases, the transition to the incommensurate modulated structure corresponds to a change of certain physical properties. Hence it is important to know the structure of incommensurate modulated phases in order to understand the mechanism of the transition and properties in the modulated state. Up to the present many incommensurate modulated structures were solved by using some kind of trial-and-error methods. With these methods it is necessary to make assumption on the property of modulation before we can solve the structure. This often causes difficulties and leads easily to errors. In view of diffraction analysis, it is possible to phase the reflections directly and solve the structure objectively without relying on any assumption about the modulation wave. Multi-dimensional direct methods have been developed for this purpose. The theoretical background and practical applications will be discussed in detail.

2. Incommensurate modulated structures

A modulated structure can be regarded as the result of applying a periodic modulation to a regular structure. *Figure* 1 shows two examples. The modulation wave in *figure* 1a represents the fluctuation of atomic occupancy. When it is applied to the background regular structure, the 'heights' of the atoms are modified. A commensurate modulated structure (superstructure) will result (*figure* 1b), if the period **T** of the modulation function is commensurate with the period **t** of the structure, i.e. **T**/**t** = n, where n is an integer. The resulting superstructure now has a true period **T** and a pseudo period **t**,

respectively corresponding to a true unit cell and a pseudo unit cell. On the other hand, if **T** is incommensurate with **t** (*figure* 1c), i.e. **T**/**t** = r, where r is not an integer, we obtain an incommensurate modulated structure, in which no exact periodicity can be found although **t** remains a pseudo period. A modulation function can also represent the fluctuation of atomic positions and the positional modulation can also be either commensurate or incommensurate. In practice a modulated structure can simultaneously include different kinds of occupational and/or positional modulations.

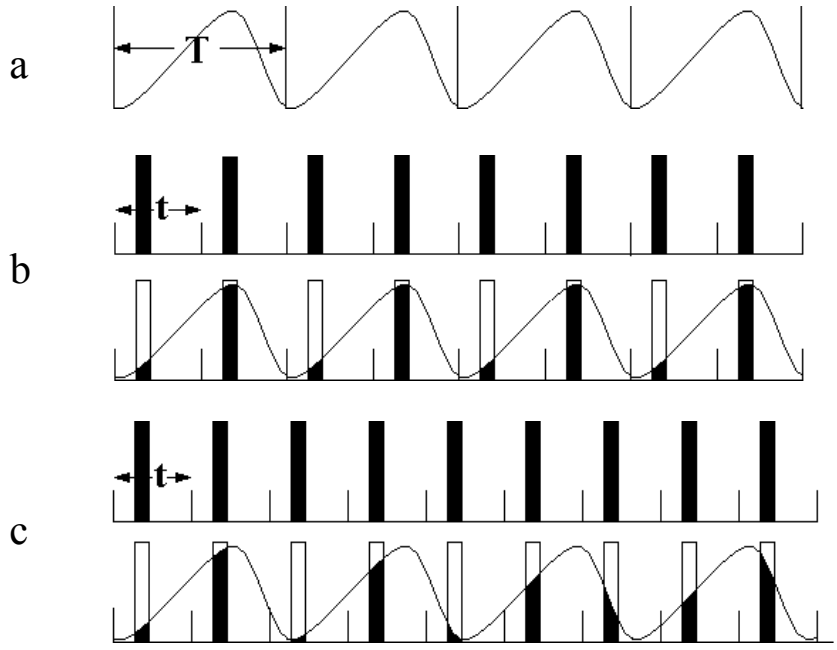

Figure 1. Occupational modulation of a one-dimensional structure
(a) modulation wave with a period equal to **T**; (*b*) upper row: one-dimensional regular structure with atoms shown as thick vertical lines and with a period equal to **t**; lower row: the resulting commensurate modulated structure; (*c*) upper row: one-dimensional regular structure; lower row: the resulting incommensurate modulated structure

In the reciprocal space an incommensurate modulated structure produces a 3-dimensional diffraction pattern, which contains satellites round the main reflections. An example of a section of such a 3-dimensional diffraction pattern is shown schematically in *figure* 2.

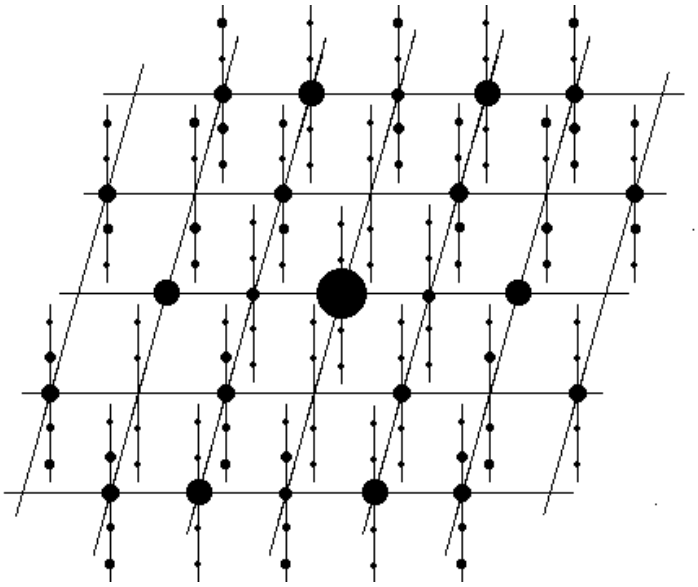

Figure 2. Schematic diffraction pattern of an incommensurate modulated structure
The vertical line segments indicate projected lattice lines parallel to the fourth dimension

The main reflections are consistent with a regular 3-dimensional reciprocal lattice although the satellites do not fit the same lattice. On the other hand, while the satellites are not commensurate with the main reflections, they have their own periodicity. Hence, it can be imagined that the 3-dimensional diffraction pattern is a projection of a 4-dimensional reciprocal lattice, in which the main and the satellite reflections are all regularly situated at the lattice nodes. From the properties of the Fourier transform the incommensurate modulated structure here considered can be regarded as a 3-dimensional "section" of a 4-dimensional periodic structure. This representation was first proposed by de Wolff [1] in 1974 to simplify the structure analysis of the incommensurate modulated structure of γ-Na_2CO_3.

The above example corresponds to a one-dimensional modulation. For an n-dimensional (n=1,2, …) modulation, it needs a (3+n)-dimensional description. A (3+n)-dimensional reciprocal vector is expressed as

$$\mathbf{h} = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3 + \ldots + h_{3+n}\mathbf{b}_{3+n} \qquad (n = 1,2,\ldots) \qquad (1)$$

where $\mathbf{b}_i$ is the i^{th} translation vector defining the reciprocal unit cell. The structure factor formula is written as

$$F(\mathbf{h}) = \sum_{j=1}^{N} f_j(\mathbf{h}) \exp[i2\pi\,(h_1\bar{x}_{j1} + h_2\bar{x}_{j2} + h_3\bar{x}_{j3})] \qquad (2)$$

where

$$f_j(\mathbf{h}) = f_j(h)\int_0^1 d\,\bar{x}_4 \ldots \int_0^1 d\,\bar{x}_{3+n}\, P_j(\bar{x}_4, \ldots, \bar{x}_{3+n}) \times$$
$$\exp\left\{i2\pi\,[(h_1U_{j1} + h_2U_{j2} + h_3U_{j3}) + (h_4x_{j4} + \ldots + h_{3+n}x_{j(3+n)})]\right\} \qquad (3)$$

The $f_j(h)$ on the right-hand side of (3) is the ordinary atomic scattering factor, P_j is the

occupational modulation function and U_j describes the deviation of the j^{th} atom from its average position $(\bar{x}_{j1}, \bar{x}_{j2}, \bar{x}_{j3})$. For more details on (2) and (3) the reader is referred to the papers by de Wolff [1], Yamamoto [2] and Hao, Liu & Fan [3]. What should be emphasised here is that, according to (2) a modulated structure can be regarded as a set of 'modulated atoms' situated at their average positions in 3-dimensional space. The 'modulated atom' in turn is defined by a 'modulated atomic scattering factor' expressed as (3).

There is a special kind of incommensurate modulated structures called composite structures. The characteristic of which is the coexistence of two or more mutually incommensurate 3-dimensional lattices. Owing to the interaction of coexisting lattices, composite structures are also incommensurate modulated structures. Unlike ordinary incommensurate modulated structures, composite structures do not have a 3-dimensional average (basic) structure. The basic structure of a composite structure corresponds to a 4- or higher-dimensional periodic structure. For a detailed description of composite structures the reader is referred to the paper by van Smaalen [4].

Obviously crystal-structure analysis of incommensurate modulated structures would better be implemented in multi-dimensional space. For this purpose we need firstly a theory on multi-dimensional symmetry and secondly a method to solve directly the multi-dimensional phase problem. The first problem has been solved by Janner and co-workers [5 - 8]. Our work on multi-dimensional direct methods is aiming at the second problem.

3. Modified Sayre equations in multi-dimensional space

It has been proved by Hao, Liu and Fan [3] that the Sayre equation [9] can easily be extended into multi-dimensional space. We have

$$F(\mathbf{h}) = \frac{\theta}{V} \sum_{\mathbf{h'}} F(\mathbf{h'}) F(\mathbf{h} - \mathbf{h'}) \tag{4}$$

here **h** is a multi-dimensional reciprocal vector defined as (1). The right-hand side of (4) can be split into three parts, i.e.

$$F(\mathbf{h}) = \frac{\theta}{V} \left\{ \sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'}) F_{\mathrm{m}}(\mathbf{h} - \mathbf{h'}) + 2 \sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'}) F_{\mathrm{s}}(\mathbf{h} - \mathbf{h'}) + \sum_{\mathbf{h'}} F_{\mathrm{s}}(\mathbf{h'}) F_{\mathrm{s}}(\mathbf{h} - \mathbf{h'}) \right\} \tag{5}$$

Where subscript m stands for main reflections while subscript s stands for satellites. Since the intensities of satellites are on average much weaker than those of main reflections, the last summation on the right-hand side of (5) is negligible in comparison with the second, while the last two summations on the right-hand side of (5) are negligible in comparison with the first. Letting $F(\mathbf{h})$ on the left-hand side of (5) represents only the structure factor of main reflections we have to first approximation

$$F_{\mathrm{m}}(\mathbf{h}) \approx \frac{\theta}{V} \sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'}) F_{\mathrm{m}}(\mathbf{h} - \mathbf{h'}) \tag{6}$$

On the other hand, if $F(\mathbf{h})$ on the left-hand side of (5) corresponds only to satellites, it follows that

$$F_{\mathrm{s}}(\mathbf{h}) \approx \frac{\theta}{V} \sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'}) F_{\mathrm{m}}(\mathbf{h} - \mathbf{h'}) + \frac{2\theta}{V} \sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'}) F_{\mathrm{s}}(\mathbf{h} - \mathbf{h'}) \tag{7}$$

For ordinary incommensurate modulated structures the first summation on the right-hand side of (7) has vanished, because any three-dimensional reciprocal lattice vector corresponding to a main reflection will have zero components in the extra dimensions so that the sum of two such lattice vectors could never give rise to a lattice vector corresponding to a satellite. We then have

$$F_{\mathrm{s}}(\mathbf{h}) \approx \frac{2\theta}{V} \sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'}) F_{\mathrm{s}}(\mathbf{h}-\mathbf{h'}) \tag{8}$$

For composite structures on the other hand, since the average structure itself is a 4- or higher-dimensional periodic structure, the first summation on the right-hand side of (7) does not vanish. We have instead of (8) the following equation:

$$F_{\mathrm{s}}(\mathbf{h}) \approx \frac{\theta}{V} \sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'}) F_{\mathrm{m}}(\mathbf{h}-\mathbf{h'}) \tag{9}$$

Equation (6) indicates that the phases of main reflections can be derived by a conventional direct method neglecting the satellites. Equation (8) or (9) can be used to extend phases from the main reflections to the satellites respectively for ordinary incommensurate modulated structures or composite structures. This provides a way to determine the modulation functions objectively. The procedure will be in the following stages:

i) derive the phases of main reflections using Equation (6);
ii) derive the phases of satellite reflections using Equation (8) or (9);
iii) calculate a multi-dimensional Fourier map using the observed structure factor magnitudes and the phases from i) and ii);
iv) cut the resulting Fourier map with a 3-dimensional 'hyperplane' to obtain an 'image' of the incommensurate modulated structure in the 3-dimensional physical space;
v) parameters of the modulation functions are measured directly on the multi-dimensional Fourier map resulting from iii).

A program package *DIMS* (Direct methods for Incommensurate Modulated Structures) has been written in Fortran for the implementation of steps i) and ii) [10, 11].

4. Examples

4.1. THE MODULATED STRUCTURE OF γ-Na_2CO_3

This is a one-dimensional displacive modulated structure with a = 8.904 Å, b = 5.239 Å, c = 6.042 Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 101.35^{\circ}$ and the modulation wave vector $\mathbf{q} = 0.182\,\boldsymbol{a}^* + 0.318\,\boldsymbol{c}^*$. The superspace group is $P^{C\,2/m}_{-1\;\;s}$. The modulated structure was originally solved by trial-and-error method [12] and was used to verify the multi-dimensional direct methods [3]. 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 in the test. Firstly according to equation (6) the phases of $F(h_1h_2h_30)$ were derived by an ordinary direct method. A default run of the program *SAPI* 85 [13] using only the main reflections led automatically to the correct average structure. The signs of 300 strongest main reflections were then calculated, 90% of which were correct. Based on this, phases of the first-order and second-order satellites were derived by using equation

(8). The results were sorted in descending order of the structure-factor magnitude and cumulated in Table 1. Reasonably good agreement between the result of direct methods

TABLE 1. Phase derivation for satellite reflections of γ-Na_2CO_3

Reflection group	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	

and that of the original authors can be seen. A 4-dimensional electron density map was calculated using all the above phased reflections. Without bias by any assumed model the modulation parameters were measured directly on the map. 2-dimensional sections of which revealing the modulation of the *Na* and *O*(1,3) atoms are shown in *figure* 3.

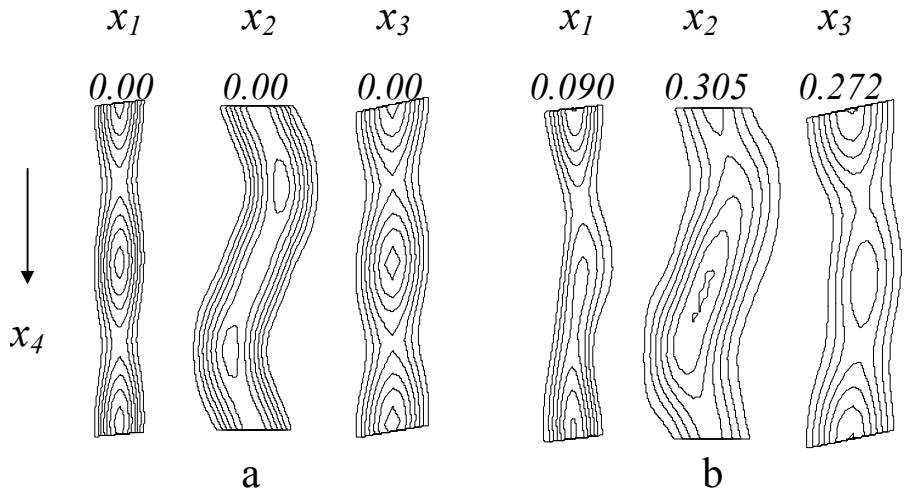

Figure 3. Sections of the 4-dimensional electron density map of γ-Na_2CO_3 showing the modulation of the *Na*(1) and *O*(1,3) atoms. (*a*) Sections through the average position of the *Na* atom. From left to right: $\rho(x_1, 0, 0, x_4)$, $\rho(0, x_2, 0, x_4)$ and $\rho(0, 0, x_3\ x_4)$; (*b*) Sections through the *O*(1,3) atom. From left to right: $\rho(x_1, 0.305, 0.272, x_4)$, $\rho(0.090, x_2, 0.272, x_4)$ and $\rho(0.090, 0.305, x_3\ x_4)$.

4.2. THE MODULATION IN THE 2:2:1:2 Bi-Sr-Ca-Cu-O SUPERCONDUCTOR

This is a one-dimensional incommensurate modulated structure with $a = 5.422$ Å, $b = 5.437$ Å, $c = 30.537$ Å, $\alpha = \beta = \gamma = 90^o$ and the modulation wave vector $\mathbf{q} = 0.22\,\boldsymbol{b}^* + \boldsymbol{c}^*$. The superspace group is $N^{B\ b\ m\ b}_{1\ -1\ 1\ 1}$. The structure has been extensively studied by different authors [14 - 18]. Among the published results there exist some discrepancies, especially on the modulation of oxygen atoms of the Bi-O layer. Based on the known average structure, a default run of the program *DIMS* with 543 main reflections, 867 first-order and 469 second-order satellite reflections resulted in a

4-dimensional Fourier map [19]. The map is then cut by the 3-dimensional physical space to give the modulated structure, the projection of which along the ***a*** axis is shown in *figure* 4. A 2-dimensional section through the 4-dimensional Fourier map shows the sawtooth-like displacive modulation of the O(4) atom (*figure* 5), which is in consistent with the result by Coppens and co-workers [15, 18].

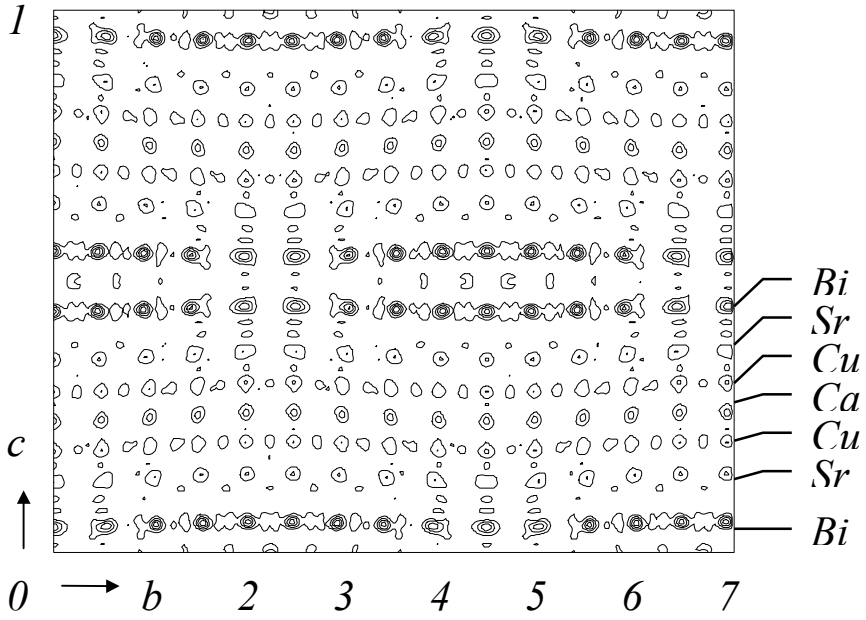

Figure 4. [100] projection of the 3-dimensional electron density map of the modulated structure 2:2:1:2 Bi-Sr-Ca-Cu-O: a region of 7×1 unit cells of the average structure were plotted along the ***b*** and ***c*** axes respectively .

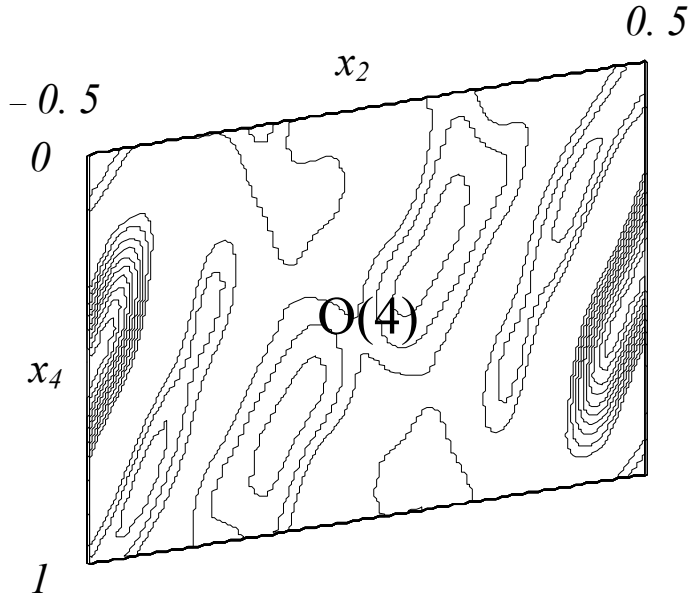

Figure 5. X_2 - X_4 section on the 4-dimensional electron density map of 2:2:1:2 Bi-Sr-Ca-Cu-O through the average position of the O(4) atom (x_1 = 0.145, x_3 = 0.0584) showing the sawtooth-like positional modulation.

4.3. THE MODULATED STRUCTURE OF (Perylene)Co(mnt)$_2$(CH_2Cl_2)$_{0.5}$

The modulated structure (Perylene)Co(mnt)$_2$(CH_2Cl_2)$_{0.5}$ was solved straightforwardly by the multi-dimensional direct method [20]. The lattice parameters are a = 6.544 Å, b = 11.717 Å, c = 16.425 Å, α = 90.09°, β = 95.34°, γ = 94.67° and the modulation wave vector **q** = 0.211***a**** - 0.137 ***b**** - 0.368***c****. The superspace group is *P*[*P-1*]-*1*. Based on the known average structure, two default runs of the program *DIMS* were performed, one assuming the superspace group *P*[*P-1*]-*1* while the other using *P*[*P1*]*1*. The two resulting phase sets are nearly the same. This confirmed the superspace group *P*[*P-1*]-*1* and strengthened the reliability of the resultant phases. The 4-dimensional Fourier map so obtained reveals the correct modulated structure, which is characterised by the sawtooth-like displacive modulation of the *Co* and *S* atoms.

4.4. THE COMPOSITE STRUCTURE OF $(PbS)_{1.18}TiS_2$

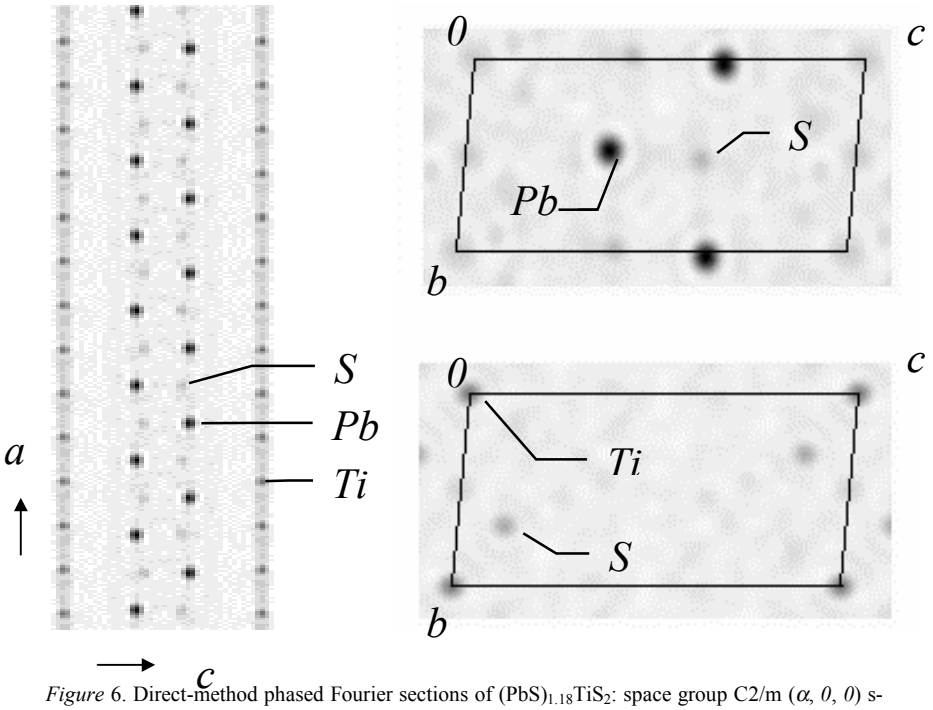

Figure 6. Direct-method phased Fourier sections of $(PbS)_{1.18}TiS_2$: space group C2/m (α, *0*, *0*) s-1; sub-system TiS_2: *a*=3.409, *b*=5.881, *c*=11.760 α=95.28°; sub-system *PbS*: *a*=5.800, *b*=5.880, *c*=11.759 α=95.28°. Left: $\rho(x_1, 0, x_3, 0)$ showing the 'chimney-ladder' structure; Top-right: $\rho(0.25, x_2, x_3, 0.25)$ showing the *PbS* layer; Bottom-right: $\rho(0, x_2, x_3, 0)$ showing the TiS_2 layer.

$(PbS)_{1.18}TiS_2$ is a composite structure [21], of which the basic structure is also a 4-dimensional one. A default run of *DIMS* in a test [22] using Equation (6) was able to reveal directly the basic structure (*figure* 6). Determination of the modulation by multidimensional direct methods was also successful [23].

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