DIRECT METHODS FOR MODULATED STRUCTURES

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INTRODUCTION

Modulated structures belong to that kind of crystal structure, in which the atoms 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. Modulated phases have been found in many important inorganic and organic solids. In many cases, the transition to the modulated structure corresponds to a change of certain physical properties. Hence it is important to know the structure of modulated phases in order to understand the mechanism of the transition and properties in the modulated state. Up to the present most procedures used for solving modulated structures, especially those for solving the incommensurate ones, depend on some preliminary assumption to the form of modulation. It is worthwhile to find a straightforward way to solve this important kind of structures. Both commensurate modulated structure (superstructure) and incommensurate modulated structure possess pseudo-translational symmetry. They have a corresponding subcell-structure called average structure or main structure, which is often relatively simple. In the reciprocal space, there will be two subsets of reflections: one includes the 'main reflections' contributed mainly from the average structure; the other includes the 'systematically weak reflections' which are due to the modulation. The phases of main reflections can easily be solved by traditional direct methods, however phases of the systematically weak reflections are rather difficult to determine. Special direct method procedures have been developed to extend phases from the main (strong) subset to the weak one. Unlike the others, direct methods do not rely on any assumption about the form of modulation. They solve the phase problem for the systematically weak reflections directly and reveal the modulation objectively. In this paper, theoretical and practical aspects on solving superstructures and incommensurate modulated structures are described.

WHAT IS A MODULATED STRUCTURE

A modulated structure can be regarded as the result of applying a periodic modulation to a regular structure. Fig. 1 shows two simplified

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with peaks shown in Table 1(b). The top six peaks correspond to the six independent atoms with positional shifts consistent with those in Table 1(a).

Table 1. Atomic positions of Freielebenite. (a) Results by Ito (1973); (b) results by a default run of SAPI.

(a)

Atom	Average position			True position			Shift		
	X	Y	Z	X	Y	Z	dX	dY	dZ
Pb	0.375	0.417	0.250	0.350	0.415	0.253	-0.025	-0.002	+0.003
Ag	0.375	0.750	0.250	0.378	0.760	0.212	+0.003	+0.010	-0.038
Sb	0.375	0.083	0.250	0.365	0.087	0.272	-0.010	+0.004	+0.022
S_1	0.125	0.250	0.250	0.138	0.219	0.346	+0.013	-0.031	+0.096
S_2	0.125	0.583	0.250	0.135	0.622	0.131	+0.010	+0.039	-0.119
S_3	0.125	0.917	0.250	0.148	0.942	0.266	+0.023	+0.025	+0.016

(b)

Peak No	Height	Atom	Position X	Y	Z	Shift dX	dY	dZ
1	4134	Pb	0.358	0.416	0.256	-0.017	-0.001	+0.006
2	3502	Ag	0.390	0.752	0.216	+0.015	+0.002	-0.034
3	2957	Sb	0.366	0.084	0.284	-0.009	+0.001	+0.034
6	1161	S_1	0.132	0.213	0.362	+0.007	-0.037	+0.112
5	1196	S_2	0.131	0.621	0.139	+0.006	+0.038	-0.111
4	1247	S_3	0.145	0.944	0.257	+0.020	+0.027	+0.007

Hwangheite. (Qian Jin-zi, Fu Ping-qui, Kong You-hua & Gong Guo-hong, 1982). Formula: $BaCeF(CO_3)_2$; space group: R3; unit cell: a=5.070, c=38.408 A and Z=6. This is a superstructure with 14 independent atoms in the asymmetric unit. The two independent Ba atoms have their sites close to (0,0,0) and (0,0,1/2), while the two Ce atoms are close to (0,0,1/4) and (0,0,3/4). Hence there is a pseudo-translation vector $\underline{t}=\underline{c}/4$ in the unit cell. Patterson or conventional direct methods failed to give the true structure, since they could not find the positional shifts of Ba and Ce atoms correctly. A Fourier map phased with the average positions of Ba and Ce atoms yields eight rather than two indepemdent F atoms and six instead of three O atoms for each CO_3 group. This makes the structure analysis much more difficult. However, a default run of SAPI automatically solved all these problems. The reflections were classified automatically into four index groups and normalized separately. The phase derivation procedure resulted in an E map, of which the largest four peaks correspond to the four heavy atoms with correct positional shifts. Among the 17 next largest peaks, ten correspond to the light atoms and others correspond to pseudo translation images of some light atoms or diffraction ripples of the heavy atoms. Among the above peaks, those corresponding to true atoms are obviously larger than peaks of the corresponding pseudo-images of atoms. Hence there will be no difficulty in assigning an atom to a proper peak and rejecting the others which correspond to the pseudo-images of atoms. The result so obtained is given in Table 2(a). in comparison with the result obtained by Qian Jin-zi et al. (1982) after least-squares refinement (Table 2b).

Table 2. Atomic positions of hwangheite. (a) Results by a default run of SAPI; (b) results from least-squares refinement by Qian *et al.* (1982).

(a)

Peak No	Peak Height	Atom	Position X	Position Y	Position Z	Shift dX	Shift dY	Shift dZ
1	4994	Ce1	0.000	0.000	0.258	0.000	0.000	+0.008
2	4946	Ce2	0.000	0.000	0.749	0.000	0.000	-0.001
3	4330	Ba1	0.000	0.000	0.000	0.000	0.000	0.000
4	4101	Ba2	0.000	0.000	0.506	0.000	0.000	+0.006
11	726	F1	0.000	0.000	0.318			
9	775	F2	0.000	0.000	0.688			
10	762	O1	0.275	0.146	0.132			
12	708	O2	0.275	0.147	0.388			
21	577	O3	0.150	0.292	0.617			
8	789	O4	0.148	0.291	0.873			
6	820	C1	0.000	0.000	0.130			
17	615	C2	0.000	0.000	0.388			
14	658	C3	0.000	0.000	0.618			
7	818	C4	0.000	0.000	0.886			

(b)

Atom	Position X	Position Y	Position Z	Shift dX	Shift dY	Shift dZ
Ce1	0.000	0.000	0.255	0.000	0.000	+0.005
Ce2	0.000	0.000	0.745	0.000	0.000	-0.005
Ba1	0.000	0.000	0.000	0.000	0.000	0.000
Ba2	0.000	0.000	0.501	0.000	0.000	+0.001
F1	0.000	0.000	0.317			
F2	0.000	0.000	0.685			
O1	0.294	0.150	0.127			
O2	0.298	0.149	0.395			
O3	0.139	0.286	0.608			
O4	0.148	0.290	0.872			
C1	0.000	0.000	0.127			
C2	0.000	0.000	0.394			
C3	0.000	0.000	0.609			
C4	0.000	0.000	0.874			

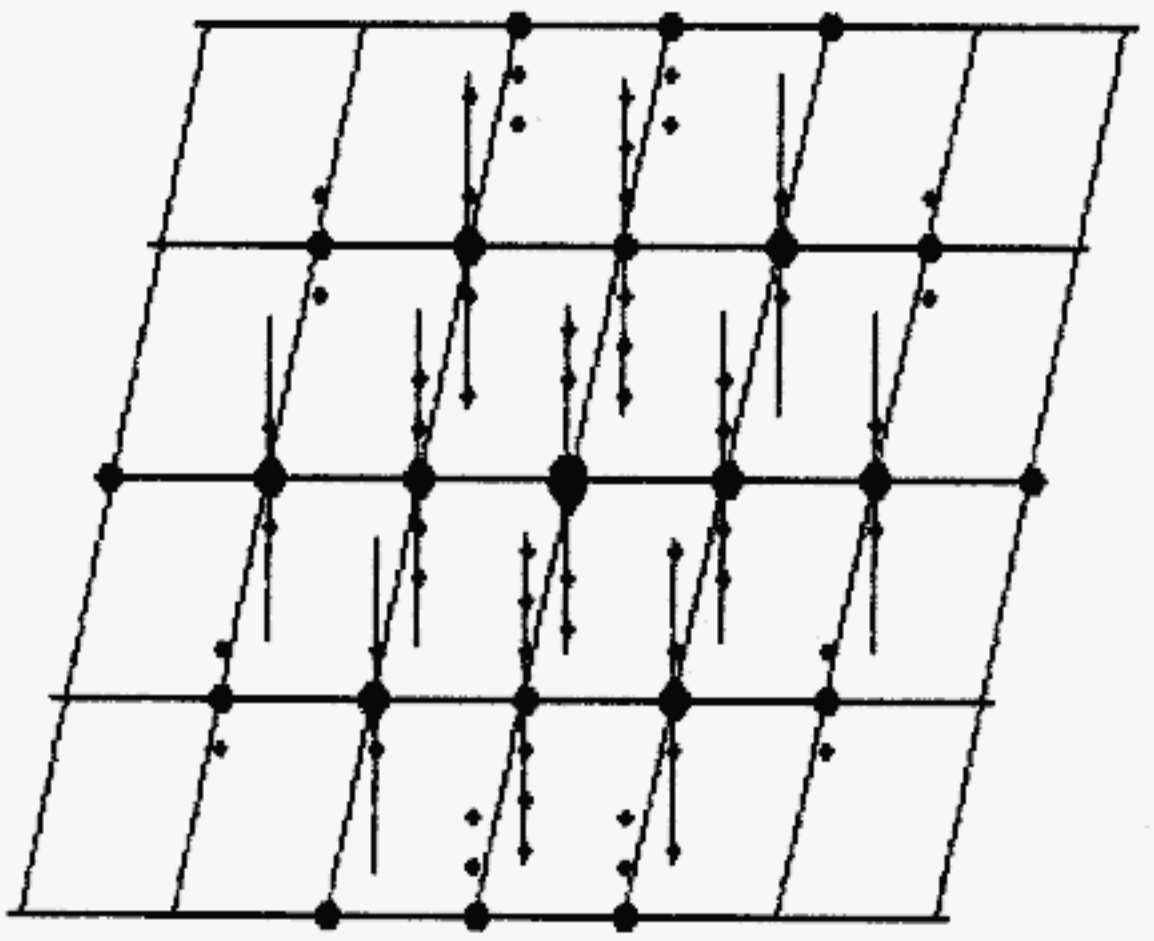

Fig. 2. Schematic diffraction photograph of an incommensurate modulated structure. The vertical line segments indicate the projection of lattice lines parallel to the fourth dimension.

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The fourth dimension in structure analysis

During the determination of the incommensurate modulated structure γ-Na_2CO_3 (Aalst, Hollander, Peterse & Wolff, 1976; Wolff, 1977), de Wolff introduced an extra-dimension into reciprocal space for indexing the satellite reflections. This extra dimension in fact specifies the direction and period of the modulation wave. An incommensurate modulated structure produces a three-dimensional diffraction pattern, which contains satellites round the main reflections. A section of the three-dimensional diffraction pattern is shown schematically in Fig. 2. The main reflections are consistent with a regular three-dimensional reciprocal lattice. However the satellites can not fit the same lattice, or some of the translation vectors will be very short, leading to an unreasonably large unit cell in real space. On the other hand as is seen in Fig. 2. although the satellites are not commensurate with the main reflections, they have their own periodicity. Hence, in this example, it can be imagined that the three-dimensional diffraction pattern is the projection of a four-dimensional reciprocal lattice, in which the main and the satellite reflections are all regularly situated at the lattice nodes. According to the convolution theorem, the incommensurate modulated structure here considered can be regarded as a three-dimensional 'section' of a four-dimensional periodic structure. This representation greatly simplified the structure analysis of γ-Na_2CO_3. The above example belongs to a one-dimensional modulation. For an n-dimensional (n=1,2,...) modulation, it needs a (3+n)-dimensional description.

(3+n)-dimensional description and the modified Sayre equations

A (3+n)-dimensional reciprocal vector is expressed as

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

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

$$\mathbf{F}(\mathbf{H}) = \sum_{j=1}^{N} f_j(\mathbf{H}) \exp\left[i2\pi(h_1\bar{x}_{j1} + h_2\bar{x}_{j2} + h_3\bar{x}_{j3})\right] \quad , \qquad (6)$$

where

$$f_j(\mathbf{H}) = f_j(\mathbf{H}) \int_0^1 d\bar{x}_4 \ldots \int_0^1 d\bar{x}_{3+n} \; P_j(\bar{x}_4, \ldots, \bar{x}_{3+n})$$

$$exp\left\{i2\pi\left[(h_1U_{j1} + h_2U_{j2} + h_3U_{j3}) + (h_4x_{j4} + \ldots + h_{3+n}x_{j(3+n)})\right]\right\} \quad . \qquad (7)$$

$f_j(\underline{H})$ on the right hand side of (7) is the ordinary atomic scattering factor; P_j is the occupational modulation function; U_j describes the deviation of the j^{th} atom from its average position. For more details on (6) and (7) the reader is referred to the papers by de wolff (1977), Yamamoto (1982) and Hao Quan, Liu Yi-wei & Fan Hai-fu (1987). What should be emphasized here is that, according to (6) a modulated structure can be regarded as a set of 'modulated atoms' situated at their average positions in three-dimensional space. The 'modulated atom' is in turn defined by a 'modulted atomic scattering factor' expressed as (7). With

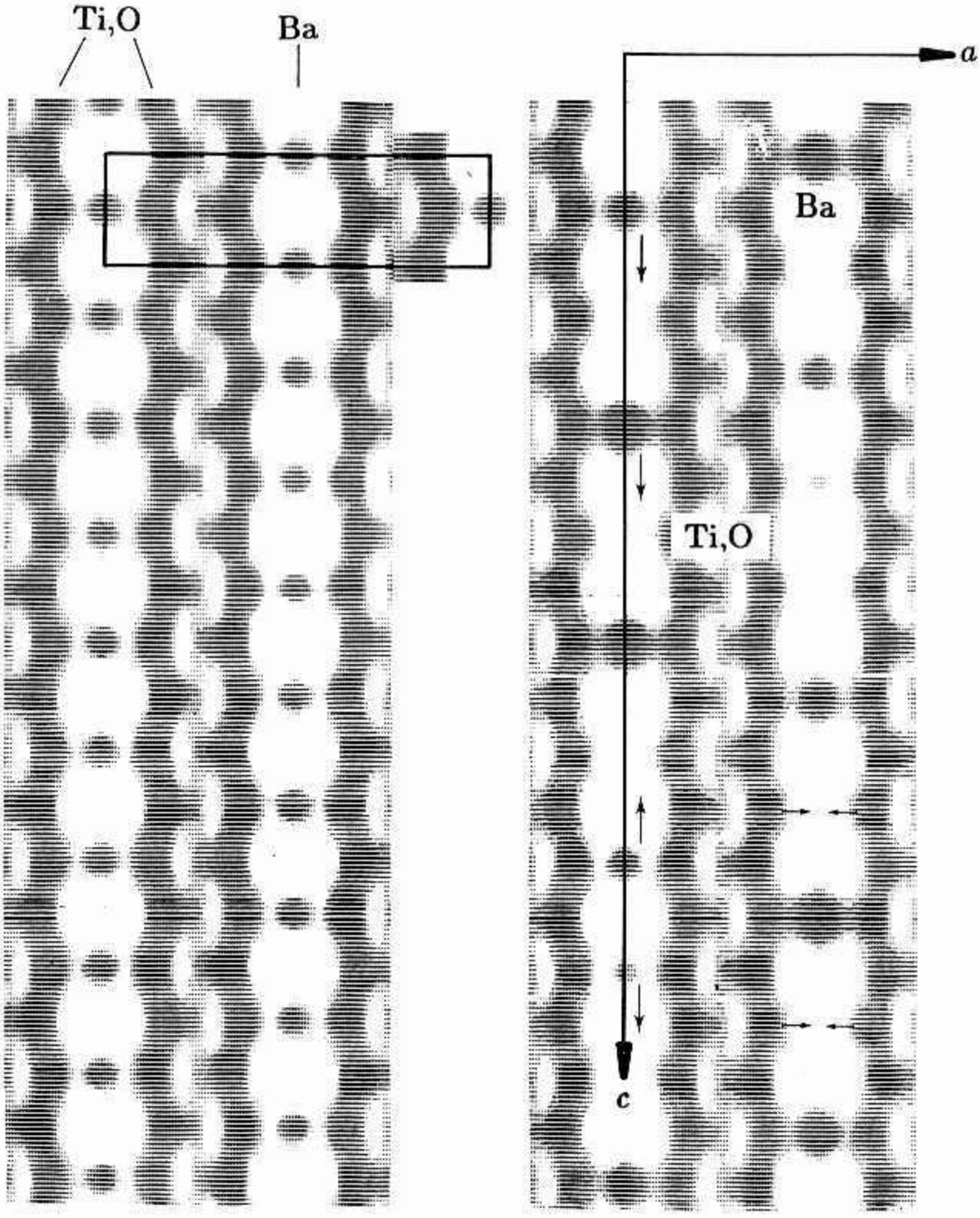

Fig. 3. Electron potential distibution of ankangite projected along the b axis. (a) The average structue calculated using 24 main reflections of the type $(h_1,0,h_3,0)$, a unit cell of which is indicated by the rectangle; (b) the incommensurate modulated structure calculated using 24 main reflections of the type $(h_1,0,h_3,0)$ and 36 satellite reflections of the type $(h_1,0,h_3,1)$ and $(h_1,0,h_3,2)$. The occupational modulation of Ba atoms is clearly seen, it appears as the ordered vacancies along the c direction and disordered vacancies perpendicular to the c direction. In addition positional modulations of Ba as well as Ti,O atoms are also observed as indicated by the short arrows.

this description, two kinds of modified Sayre equations were obtained (Hao Quan, Liu Yi-wei & Fan Hai-fu, 1987):

$$\mathbf{F}_m(\hat{\mathbf{H}}) = \frac{\Theta}{V} \sum_{\hat{\mathbf{H}}'} \mathbf{F}_m(\hat{\mathbf{H}}')\ \mathbf{F}_m(\hat{\mathbf{H}} - \hat{\mathbf{H}}') \quad , \tag{8}$$

$$\mathbf{F}_s(\hat{\mathbf{H}}) = 2\frac{\Theta}{V} \sum_{\hat{\mathbf{H}}'} \mathbf{F}_m(\hat{\mathbf{H}}')\ \mathbf{F}_s(\hat{\mathbf{H}} - \hat{\mathbf{H}}') \quad . \tag{9}$$

Where $F_m(\underline{H})$ denotes structure factors of the main reflections; $F_s(\underline{H})$ denotes those of the satellites. (8) indicates that the phases of main reflections can be derived by a conventional direct method neglecting the satellites. While (9) can be used for phase extension from the main reflections to the satellites. The latter provides a way to determine directly the modulation function, without preliminary assumptions.

Example on solving an unknown incommensurate modulated structure

Ankangite, $Ba_{0.8}(Ti,V,Cr)_8O_{16}$, is a newly found mineral. The average structure belongs to space group I4/m with unit cell a=b=10.12 A, and c=2.96 A. The modulation wave is parallel to the c axis with a period 2.27 times longer than c. An electron diffraction pattern containing reflections of the type $(h_1,0,h_3,h_4)$ was used to determine the modulation of Ba atoms (Xiang Shi-bin, Fan Hai-fu, Wu Xiao-jing, Li Fang-hua & Pan Qing, 1990). Starting from the known phases of the main reflections $(h_1,0,h_3,0)$, phases of the satellites were derived by making used of (9). The resulted Fourier map is shown in Fig. 3b revealing clearly the occupational modulation of Ba atoms. Positional modulations are also observed.

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