

Direct Methods for Incommensurate Intergrowth Compounds. I. Determination of the Modulation

BY FAN HAI-FU*

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

SANDER VAN SMAALEN

*Laboratory of Chemical Physics, Materials Science Center, University of Groningen, Nijenborgh 4,
NL-9747 AG Groningen, The Netherlands*

AND ERWIN J. W. LAM AND PAUL T. BEURSKENS

*Laboratory for Crystallography, University of Nijmegen, Toernooiveld, NL-6525 ED Nijmegen,
The Netherlands*

(Received 28 December 1992; accepted 10 March 1993)

Abstract

A direct method is proposed for the determination of the modulation in incommensurate intergrowth compounds. The method is based on a new type of Sayre equation that relates the phase of a satellite reflection to the sum of structure-factor products of pairs of main reflections. Phases of satellite reflections are thus uniquely determined by the phases of main reflections. This reflects the fact that the modulation in intergrowth structures is the result of the interaction of all of the subsystems that form the basic structure. Test calculations were done with experimental data of two known composite structures of the inorganic misfit layer compounds $(\text{LaS})_{1.14}\text{NbS}_2$ and $(\text{PbS})_{1.18}\text{TiS}_2$. The results showed that the method is accurate and efficient and is fully independent of any preliminary assumption of the model of modulation.

Introduction

Incommensurate intergrowth compounds can be considered as coherent combinations of two or more modulated structures (Janner & Janssen, 1980; van Smaalen, 1992). Each of the structures (subsystems) is characterized by a unit cell and a set of modulation wave vectors. The diffraction pattern has main reflections at the nodes of each of the reciprocal lattices of the subsystems and has satellites at positions defined by the modulation wave vectors. Usually, two subsystems have a common reciprocal-lattice plane, thus providing only a single incommensurate direction. The coherent intergrowth means that the basic periodicities of one subsystem provide the modulation periods in the other subsystem. Composite struc-

tures or incommensurate intergrowth compounds differ from ordinary incommensurately modulated structures in that they do not have three-dimensional periodic basic structures. The basic structure of an incommensurate intergrowth compound is already a four- or higher-dimensional periodic structure.

Multidimensional direct methods (Hao, Liu & Fan, 1987; Xiang, Fan, Wu, Li & Pan, 1990; Mo, Cheng, Fan, Li, Sha, Zheng, Li & Zhao, 1992) have been proposed and successfully used for the determination of incommensurately modulated structures having three-dimensional basic structures. In this paper, the method is extended to incommensurately modulated structures having four- or higher-dimensional periodic basic structures. In this case, a new type of Sayre phase relation is found, which relates the phase of a satellite reflection to the sum of structure-factor products of pairs of main reflections. This makes it possible to compute the phases of the satellite reflections from the structure factors of the main reflections and, thus, to determine the modulation. The method is illustrated by its application to the known structures of the inorganic misfit layer compounds $(\text{LaS})_{1.14}\text{NbS}_2$ and $(\text{PbS})_{1.18}\text{TiS}_2$.

The method

According to the multidimensional Sayre equation (Hao, Liu & Fan, 1987), for an incommensurately modulated structure we have the following phase relation:

$$\varphi[F(\mathbf{H})] = \varphi \left[\sum_{\mathbf{H}'} F(\mathbf{H}') F(\mathbf{H} - \mathbf{H}') \right], \quad (1)$$

where $\varphi[F(\mathbf{H})]$ denotes the phase of $F(\mathbf{H})$ and $F(\mathbf{H})$ is the structure factor with multidimensional reciprocal-lattice vector \mathbf{H} . The summation on the

* Visiting the Laboratory for Crystallography, University of Nijmegen, Toernooiveld, NL-6525 ED Nijmegen, The Netherlands.

right-hand side of (1) can be split into three parts, *i.e.*

$$\begin{aligned} \varphi[F(\mathbf{H})] = \varphi \left[\sum_{\mathbf{H}'} F_m(\mathbf{H}') F_m(\mathbf{H} - \mathbf{H}') \right. \\ \left. + \sum_{\mathbf{H}'} F_m(\mathbf{H}') F_s(\mathbf{H} - \mathbf{H}') \right. \\ \left. + \sum_{\mathbf{H}'} F_s(\mathbf{H}') F_s(\mathbf{H} - \mathbf{H}') \right]. \quad (2) \end{aligned}$$

Here, the subscript *m* is used for main reflections while the subscript *s* is used for satellites. Because the intensities of satellites are on average much weaker than those of main reflections, the last summation on the right-hand side of (2) is negligible in comparison with the second, while the last two summations on the right-hand side of (2) are negligible in comparison with the first. Now, if $F(\mathbf{H})$ on the left-hand side of (2) represents the structure factor of a main reflection, we have, to a first approximation,

$$\varphi[F_m(\mathbf{H})] \approx \varphi \left[\sum_{\mathbf{H}'} F_m(\mathbf{H}') F_m(\mathbf{H} - \mathbf{H}') \right]. \quad (3)$$

This implies that it is possible to solve the basic structure in multidimensional space using only main reflections. On the other hand, if $F(\mathbf{H})$ on the left-hand side of (2) represents the structure factor of a satellite, we have

$$\begin{aligned} \varphi[F_s(\mathbf{H})] \approx \varphi \left[\sum_{\mathbf{H}'} F_m(\mathbf{H}') F_m(\mathbf{H} - \mathbf{H}') \right. \\ \left. + \sum_{\mathbf{H}'} F_m(\mathbf{H}') F_s(\mathbf{H} - \mathbf{H}') \right]. \quad (4) \end{aligned}$$

For a conventional incommensurately modulated structure, the first summation on the right-hand side of (4) will be equal to zero because the sum of two lattice vectors, \mathbf{H}' and $\mathbf{H} - \mathbf{H}'$, belonging to the same three-dimensional reciprocal lattice can never produce a point outside that lattice (satellite). Therefore, (4) reduces to

$$\varphi[F_s(\mathbf{H})] = \varphi \left[\sum_{\mathbf{H}'} F_m(\mathbf{H}') F_s(\mathbf{H} - \mathbf{H}') \right]. \quad (5)$$

However, for an incommensurate intergrowth compound having a four- or higher-dimensional basic structure, the first summation on the right-hand side of (4) will not vanish. Hence, we have instead of (5) the following phase relation:

$$\varphi[F_s(\mathbf{H})] = \varphi \left[\sum_{\mathbf{H}'} F_m(\mathbf{H}') F_m(\mathbf{H} - \mathbf{H}') \right], \quad (6)$$

where \mathbf{H}' and $\mathbf{H} - \mathbf{H}'$ are main reflections of two different subsystems.

Equations (5) and (6) are two different types of phase relation. The former has already been used

successfully in solving conventional incommensurately modulated structures (Xiang *et al.*, 1990; Mo *et al.*, 1992), while the latter can be used for deriving phases of satellite reflections of a composite structure provided its basic structure is known. In terms of structure analysis, (6) includes more information than (5) does. Equation (5) just tells us how the phases of satellite reflections are related through the main reflections, while (6) can tell us how the phases of satellite reflections are uniquely determined by the main reflections. This is not surprising when we consider the fact that the incommensurate modulation in a composite structure is the result of the interaction of different subsystem structures, which together form the basic structure. Equations (3) and (6) provide the basis of a two-step procedure for solving composite structures:

(1) The basic structure is determined from the main reflections only;

(2) The incommensurate modulation is determined by the derivation of phases of satellite reflections from the known phases of main reflections.

Test and results

(1) Test data

$(\text{LaS})_{1.14}\text{NbS}_2$ consists of two subsystems (Fig. 1). Both are orthorhombic, with superspace groups $Fm2m(\alpha, 0, 0)\bar{1}1s$ for NbS_2 and $Cm2a(\alpha^{-1}, 0,$

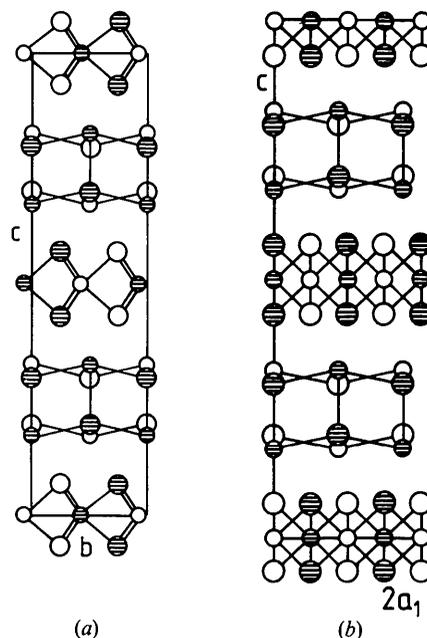


Fig. 1. The structure of the inorganic misfit layer compound $(\text{LaS})_{1.14}\text{NbS}_2$. Large circles denote sulfur atoms; small circles denote lanthanum and niobium in their respective subsystems. Hatched and open circles differ by one-half in the projected coordinate. (a) Projection along *a*. (b) Projection along *b*.

Table 1. *Test for the self-consistency of (3)*

(a) (LaS) _{1.14} NbS ₂		Reflections for which the phases are obtained from (3)		Average phase error (°)
Number of reflections	Index type of reflections	Number of reflections	Index type of reflections	
584	<i>hkl0</i> and <i>0klm</i>	584	<i>hkl0</i> and <i>0klm</i>	10.5
		70	<i>0kl0</i>	14.0
261	<i>hkl0</i>	261	<i>hkl0</i>	16.5
		70	<i>0kl0</i>	32.7
393	<i>0klm</i>	393	<i>0klm</i>	14.0
		70	<i>0kl0</i>	34.2
(b) (PbS) _{1.18} TiS ₂		Reflections for which the phases are obtained from (3)		Average phase error (°)
Number of reflections	Index type of reflections	Number of reflections	Index type of reflections	
1462	<i>hkl0</i> and <i>0klm</i>	1462	<i>hkl0</i> and <i>0klm</i>	12.3
		169	<i>0kl0</i>	23.7
500	<i>hkl0</i>	500	<i>hkl0</i>	11.2
		169	<i>0kl0</i>	15.1
1131	<i>0klm</i>	1131	<i>0klm</i>	13.9
		169	<i>0kl0</i>	28.5

$1/2\bar{1}\bar{1}1$ for LaS. The basic structure can be described as the alternate stacking of two types of layers (Wiegiers *et al.*, 1990). The first subsystem comprises the three-atom-thick NbS₂ layers. Their structure is equivalent to that of a single layer in pure NbS₂. The LaS layers form the second subsystem. They can be regarded as two-atom-thick (100) slices of rock-salt-type structure. Perpendicular to the layers, the two subsystems have the same periodicity \mathbf{c}^* . Within the layers, the reciprocal axis \mathbf{b}^* is common to the two subsystems (Fig. 1a), while the two \mathbf{a}^* axes are different, thus providing the incommensurateness (Fig. 1b). The modulation was shown to be relatively small, with displacement amplitudes of the order of 0.1 Å (van Smaalen, 1991). The reciprocal lattices of the two subsystems, $\nu = 1$ and 2, respectively, are denoted by $\Lambda_\nu = \{\mathbf{a}_{\nu 1}^*, \mathbf{a}_{\nu 2}^*, \mathbf{a}_{\nu 3}^*\}$. Each subsystem has a one-dimensional modulation with wave vector $\mathbf{q}^{\nu'} = \mathbf{a}_{\nu 1}^*$ ($\nu' \neq \nu$).

All Bragg reflections can be indexed with four integer indices, *hklm*, based on the set of reciprocal vectors $M = \{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*, \mathbf{a}_4^*\}$. These vectors are defined as $\mathbf{a}_1^* = \mathbf{a}_{11}^* = \mathbf{q}^2$, $\mathbf{a}_2^* = \mathbf{a}_{12}^* = \mathbf{a}_{22}^*$, $\mathbf{a}_3^* = \mathbf{a}_{13}^* = \mathbf{a}_{23}^*$ and $\mathbf{a}_4^* = \mathbf{a}_{21}^* = \mathbf{q}^1$. It is then easily seen that *hkl0* reflections comprise main reflections of the first subsystem, that *0klm* are main reflections of the second subsystem and that *hklm* reflections ($h \neq 0$ and $m \neq 0$) are satellites. X-ray diffraction intensities were measured by Meerschaut, Rabu & Rouxel, (1989). 860 unique reflections were obtained with intensities greater than 2.5 times their standard deviations. There are 584 main reflections and 276 satellites. The main reflections divide into 261 *hkl0* reflections for the subsystem NbS₂ and 393 *0klm* reflections for the subsystem

LaS. Both subsets include 70 *0kl0* main reflections common to the subsystems.

The method was also tested for (PbS)_{1.18}TiS₂, a compound similar to (LaS)_{1.14}NbS₂ but with monoclinic symmetry $C2_1/m(\alpha, 0, 0)1\bar{1}$ (van Smaalen, Meetsma, Wiegiers & de Boer, 1991). For this compound, 500 *hkl0* main reflections of subsystem TiS₂, 1131 *0klm* main reflections of subsystem PbS and 190 satellite reflections are available. Both main-reflection subsets now include 169 common *0kl0* reflections. The modulation is weaker than that in (LaS)_{1.14}NbS₂.

(2) *Test for self-consistency among phases of main reflections.*

Known phases of main reflections were substituted into the right-hand side of (3) to obtain new phases for the same set of main reflections on the left. The new phases were then compared with the original ones to check the self-consistency. This procedure corresponds to a single-step phase refinement. The results are listed in Table 1 for (LaS)_{1.14}NbS₂ and (PbS)_{1.18}TiS₂. For both structures, the phases of three different subsets of reflections were used as input. First, all the main reflections, *hkl0* and *0klm*, were input into (3) to derive new phases for the same set. For the structure (LaS)_{1.14}NbS₂, this resulted in an average phase error of 10.5° for all main reflections and an error of 14.0° for only the *0kl0* main reflections, which are common to both subsystems. Second, only the main reflections of subsystem 1, *hkl0*, were input into (3). For the structure (LaS)_{1.14}NbS₂, this resulted in an average error of 16.5° for all *hkl0* reflections and an error of 32.7° for only the *0kl0* reflections.

Table 2. Test of *ab initio* phasing of satellite reflections

Test structure	Number of main reflections input in (6)	Number of satellite reflections obtained from (6)	Average phase error (°)
(LaS) _{1.14} NbS ₂	584	276	17.6
(PbS) _{1.18} TiS ₂	1462	190	5.6

Finally, only the main reflections of subsystem 2, $0klm$, were input into (3). The resulting phase error is 14.0° for all the $0klm$ reflections and 34.2° for only the $0kl0$ reflections. Similar results were obtained for the structure (PbS)_{1.18}TiS₂.

From the above test, it is seen that the self-consistency for phases of the complete set of four-dimensional main reflections is extremely good. One can expect that a four-dimensional direct-methods procedure could be used for *ab initio* determination of the four-dimensional basic structure. Besides, the self-consistency for phases of main reflections from either of the two subsystems is also reasonable, though it is not as good as that for the set of all main reflections. In particular, the agreement of the phases of the $0kl0$ reflections then becomes worse because the $0kl0$ reflections depend on both subsystems.

(3) Test of *ab initio* phasing of satellite reflections

Phases of satellite reflections were derived from the phases of the main reflections using (6). The main reflection phases were obtained from the refinement of the basic structure. The resulting phases of satellites were compared with the corresponding phases obtained from the refined modulated structure (van Smaalen, 1991; van Smaalen *et al.*, 1991). It is seen that the phases from (6) are sufficiently accurate for the modulation to be revealed (Table 2). The best illustration for this statement is provided by the four-dimensional Fourier syntheses.

The principal part of the modulation in (LaS)_{1.14}NbS₂ is on lanthanum, with a first harmonic wave describing displacement along a_{22} and a second harmonic wave displacement along a_{23} . In (PbS)_{1.18}TiS₂, the modulation mainly resides on lead, with only a first harmonic defining displacements along a_{22} . The La atom and the Pb atom are thus the best candidates for studying the effect of the modulation on the Fourier synthesis. Here, we only discuss the results for lanthanum. Completely equivalent results have been obtained for lead.

The main reflections $hkl0$ contain the contribution from the h th-order satellites of the second subsystem and *vice versa* for the $0klm$ reflections. This provides sufficient satellite information to refine the modulation, as was shown by Kato (1990). However, with only the main reflections, it is impossible to reveal the modulation directly in a Fourier synthesis. This

can be seen in the Fourier syntheses made for the main reflections with phases obtained from the basic structure refinement and from the modulated structure refinement, respectively (Fig. 2), which show bands almost perfectly straight along \bar{x}_4 . The reason is that the Fourier syntheses in Fig. 2 can be expressed as

$$\int [F(hkl0) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) + F(0klm) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r})] d\mathbf{H} \\ = \mathcal{F}^{-1}[F(hkl0)] + \mathcal{F}^{-1}[F(0klm)],$$

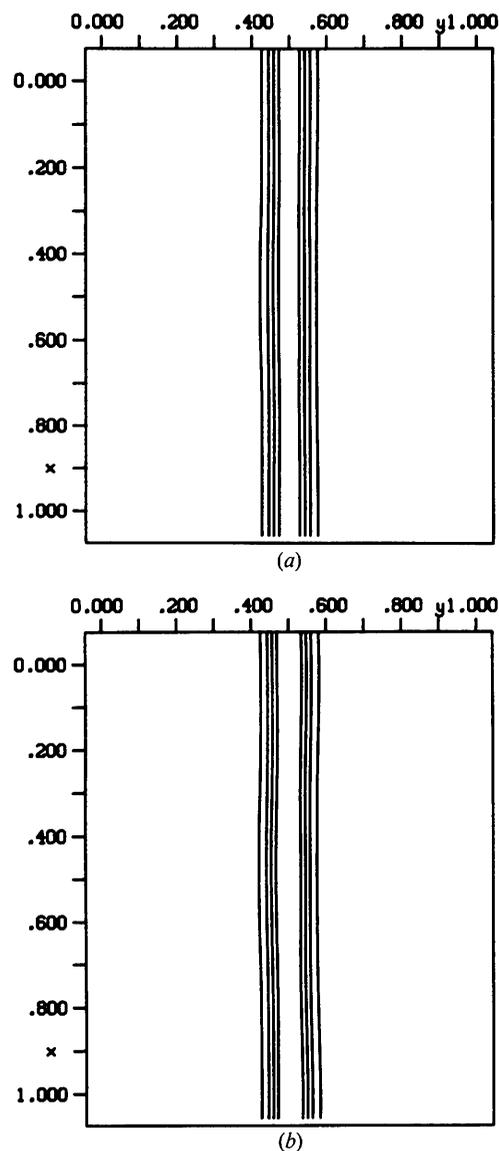
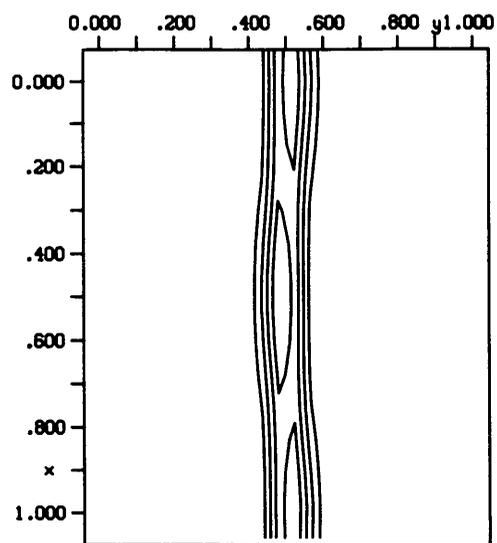
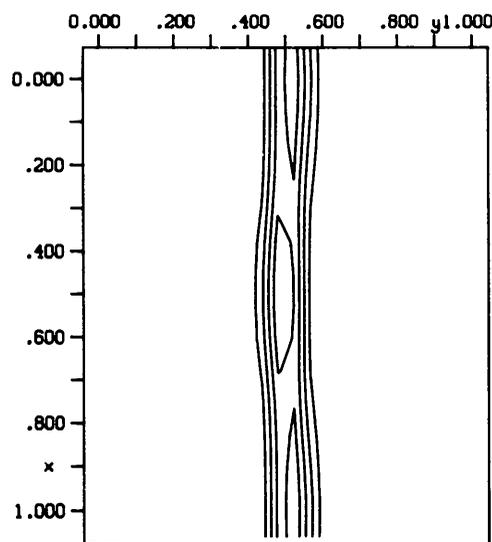


Fig. 2. Section of the four-dimensional Fourier synthesis of (LaS)_{1.14}NbS₂ at the position of the La atom ($x=0$ and $z=0.174$). Contours are plotted at intervals of $1/5$ of the maximum density. (a) Main reflections with phases from the basic structure refinement. (b) Main reflections with phases from the modulated structure refinement.

where \mathcal{F}^{-1} stands for the inverse Fourier transform. The first term on the right-hand side is the projection



(a)



(b)

Fig. 3. The same section of the four-dimensional Fourier synthesis as in Fig. 2, now with both main reflections and satellites included (a) with phases from the refinement of the modulated structure, (b) with phases from the direct-methods procedure.

of the four-dimensional electron-density function of the first subsystem along its modulation direction \bar{x}_4 , while the second term is the projection of the second subsystem along its modulation direction \bar{x}_1 . Consequently, all modulation effects were averaged during the Fourier summation. This means that the modulation waves cannot be revealed directly by Fourier syntheses without involving satellite reflections. Fig. 3 shows the Fourier syntheses of all reflections with the satellite reflections phased by the modulation refinement and by the direct method. It can be seen that the two Fourier syntheses are nearly the same and clearly show the modulation wave. This proves that the direct method can be successfully used to determine the modulation function for atoms of an incommensurate intergrowth compound.

Concluding remarks

For the first time, direct methods have successfully been used to determine the modulation in incommensurate intergrowth compounds. The procedure is straightforward and fully independent of any preliminary assumption of the modulation form. This provides a new more convenient and reliable approach to the study of modulation in intergrowth compounds. A new field has been opened for the application of direct methods.

References

- HAO, Q., LIU, Y. W. & FAN, H. F. (1987). *Acta Cryst.* **A43**, 820-824.
 JANNER, A. & JANSSEN, T. (1980). *Acta Cryst.* **A36**, 408-415.
 KATO, K. (1990). *Acta Cryst.* **B46**, 39-44.
 MEERSCHAUT, A., RABU, P. & ROUXEL, J. (1989). *J. Solid State Chem.* **78**, 35-45.
 MO, Y. D., CHENG, T. Z., FAN, H. F., LI, J. Q., SHA, B. D., ZHENG, C. D., LI, F. H. & ZHAO, Z. X. (1992). *Supercond. Sci. Technol.* **5**, 69-72.
 SMAALEN, S. VAN (1991). *J. Phys. Condens. Matter*, **3**, 1247-1263.
 SMAALEN, S. VAN (1992). *Mater. Sci. Forum*, **100&101**, 173-222.
 SMAALEN, S. VAN, MEETSMA, A., WIEGERS, G. A. & DE BOER, J. L. (1991). *Acta Cryst.* **B47**, 314-325.
 WIEGERS, G. A., MEETSMA, A., HAANGE, R. J., VAN SMAALEN, S., DE BOER, J. L., MEERSCHAUT, A., RABU, P. & ROUXEL, J. (1990). *Acta Cryst.* **B46**, 324-332.
 XIANG, S. B., FAN, H. F., WU, X. J., LI, F. H. & PAN, Q. (1990). *Acta Cryst.* **A46**, 929-934.