J. Appl. Cryst. (1999). **32**, 1017–1020

MIMS: a program for measuring four-dimensional Fourier maps of incommensurate modulated structures

Yang Li, Zheng-Hua Wan and Hai-Fu Fan* *at Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China. E-mail: fan@aphy.iphy.ac.cn*

(*Received 20 October 1998; accepted 18 May 1999*)

Abstract

The program *MIMS* (measuring incommensurate modulated structures) has been written for the determination of structural parameters of incommensurate one-dimensionally modulated structures by an automatic search routine on four-dimensional Fourier maps. Test results show that the program works accurately and efficiently.

1. Introduction

It is well known that incommensurate modulated structures are more difficult to solve than ordinary structures. For the determination of an incommensurate modulated structure without using a pre-assumed model, there are three main problems to solve: (i) phasing the diffraction data, (ii) building a structure model according to the resultant Fourier map, and (iii) refining structure parameters. The first problem has been treated successfully by multidimensional direct methods (Hao *et al.*, 1987; Fan *et al.*, 1993; Fan, 1998). For the third problem, a number of program packages are available (Petricek *et al.*, 1991; Yamamoto, 1991; Cheng *et al.*, 1998). The goal of the present work is the automatic solution of the second problem. This is important, since manual interpretation of a four-dimensional Fourier map is time-consuming and prone to inaccuracies.

2. Description of incommensurate one-dimensionally modulated structures

For details of the superspace description of incommensurate structures the reader is referred to papers by de Wolff (1974, 1977), Janner *et al.* (1983), Yamamoto (1982) and van Smaalen (1995). In the following only a brief description is given.

Incommensurate one-dimensionally modulated structures can be regarded as the result of applying a one-dimensional periodic modulation to a three-dimensional basic structure, the periodicity of which does not match that of the modulation wave. The diffraction pattern of an incommensurate modulated structure is characterized by additional satellite reflections, which do not fit the three-dimensional reciprocal lattice constructed by main ordinary reflections. For one-dimensionally modulated structures, the modulation waves are of one type and have a common wavevector

$$\mathbf{q} = q_1\mathbf{a}^* + q_2\mathbf{b}^* + q_3\mathbf{c}^*, \tag{1}$$

where $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ are vectors defining the reciprocal lattice of the basic structure. Since the modulation is incommensurate, at least one of the components, q_1, q_2 and q_3, should be irrational. The position vector of a Bragg reflection is thus

$$\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}, \tag{2}$$

where h, k, l and m are all integers; $m = 0$ for main reflections, $m \neq 0$ for satellites. We can imagine that $\mathbf{q}$ is the projection of a four-dimensional vector onto the three-dimensional physical space. Therefore we can construct a four-dimensional reciprocal lattice having basic vectors

$$\begin{aligned} \mathbf{b}_1 &= (\mathbf{a}^*, 0), \\ \mathbf{b}_2 &= (\mathbf{b}^*, 0), \\ \mathbf{b}_3 &= (\mathbf{c}^*, 0), \\ \mathbf{b}_4 &= (\mathbf{q}, \mathbf{d}), \end{aligned} \tag{3}$$

where $\mathbf{d}$ is a unit vector perpendicular to the three-dimensional physical space. According to the reciprocal relationship

$$\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij} \quad (i, j = 1, 2, 3, 4), \tag{4}$$

the basic vectors of the corresponding four-dimensional direct lattice should be

$$\begin{aligned} \mathbf{a}_1 &= \mathbf{a} - q_1\mathbf{d}, \\ \mathbf{a}_2 &= \mathbf{b} - q_2\mathbf{d}, \\ \mathbf{a}_3 &= \mathbf{c} - q_3\mathbf{d}, \\ \mathbf{a}_4 &= (0, \mathbf{d}). \end{aligned} \tag{5}$$

From (3), the position vector of a reflection in the four-dimensional reciprocal space becomes

$$\mathbf{h}_s = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3 + h_4\mathbf{b}_4, \tag{6}$$

where $h_1 = h$, $h_2 = k$, $h_3 = l$ and $h_4 = m$. From (5), the position vector of a point in a four-dimensional unit cell in direct space is

$$\mathbf{x} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3 + x_4\mathbf{a}_4, \tag{7}$$

where x_1, x_2, x_3 and x_4 are fractional coordinates. The diffraction pattern of an incommensurate one-dimensionally modulated structure corresponds to the projection of a four-dimensional reciprocal lattice. The incommensurate structure itself can be obtained by cutting a four-dimensional periodic structure perpendicular to the vector $\mathbf{d}$. A hypersection in the four-dimensional direct space perpendicular to the vector $\mathbf{d}$ satisfies

$$\mathbf{d} \cdot (x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3 + x_4\mathbf{a}_4) = 0. \tag{8}$$

According to (5) we have

$$-q_1x_1 - q_2x_2 - q_3x_3 + x_4 = 0. \tag{9}$$

Defining

$$t = -q_1x_1 - q_2x_2 - q_3x_3 + x_4, \tag{10}$$

the four-dimensional periodic structure may also be described using $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $\mathbf{d}$ as the basic vectors. The position vector in a four-dimensional unit cell in direct space is thus

$$\mathbf{x} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} + t\mathbf{d}, \tag{11}$$

where x, y, z and t are fractional coordinates. Values of x, y and z with respect to the basic vectors **a**, **b** and **c** are respectively the same as x_1, x_2 and x_3 with respect to basic vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. A one-dimensionally incommensurate modulated structure in three-dimensional physical space is described by the corresponding four-dimensional periodic structure on the hypersection at $t = 0$. Parameters of a modulated atom on the hypersection at $t = 0$ can be expressed with respect to their average values (see Fig. 1). We write

$$\xi^\mu = \bar{\xi}^\mu + u^\mu(\bar{x}_4), \tag{12}$$

or according to equations (1) and (9) we have equivalently

$$\xi^\mu = \bar{\xi}^\mu + u^\mu(\mathbf{q} \cdot \bar{\mathbf{x}}^\mu), \tag{13}$$

where μ denotes the μth atom in a unit cell of the basic structure, $\bar{\xi}^\mu$ is the average parameter, which equals $\mathbf{L} + \bar{\xi}_0^\mu$ for positional parameters or equals $\bar{\xi}_0^\mu$ for occupational/substitutional and displacement parameters, **L** is a lattice vector of the basic structure, $\bar{\xi}_0^\mu$ is the average parameter in the unit cell with its origin at $\mathbf{L} = 0$, u is the modulation function with period equal to unity, $\bar{x}_4$ is the fourth coordinate of a point in four-dimensional space having its first three coordinates respectively equal to the average coordinates $\bar{x}_1$, $\bar{x}_2$ and $\bar{x}_3$, **q** is the modulation wavevector, $\bar{\mathbf{x}}^\mu = \mathbf{L} + \bar{\mathbf{x}}_0^\mu$ is the average position vector of the μth atom, $\bar{\mathbf{x}}_0^\mu$ is the average position vector in the unit cell at $\mathbf{L} = 0$. The modulation function u can be expanded into a Fourier series

$$u^\mu(\bar{x}_4) = \sum_{n=1}^{\infty}[A_n^\mu \cos(2\pi n\bar{x}_4) + B_n^\mu \sin(2\pi n\bar{x}_4)]. \tag{14}$$

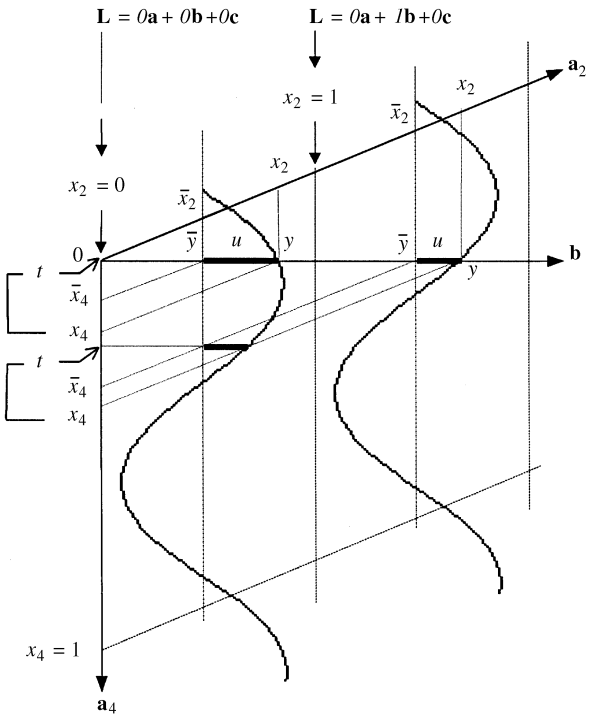

Fig. 1. The parameter y as a function of its average value $\bar{y}$ and the modulation function $u(\bar{x}_4)$.

Hence atomic coordinates can be expressed as a Fourier series with its zero-order coefficient equal to the corresponding average coordinate, *i.e.*

$$\xi^\mu = A_0^\mu + \sum_{n=1}^{\infty}[A_n^\mu \cos(2\pi n\bar{x}_4) + B_n^\mu \sin(2\pi n\bar{x}_4)], \tag{15}$$

where $A_0^\mu = \bar{\xi}^\mu$.

3. Searching strategy

A modulated atom in four-dimensional space will behave as a waving string extended in the direction of the fourth axis $\mathbf{a}_4$. Position modulation changes the deviation from average position along the string, occupation/substitution modulation causes variation on the integrated density along the string, while temperature-factor modulation affects mostly the width variation of the string. By tracing a modulated atom in the four-dimensional space, all three kinds of modulation can be determined. However, there are strong interactions between the effect of occupation/substitution modulation and that of temperature-factor modulation. Hence, parameters of these two kinds of modulation can only be obtained semi-quantitatively. To start an automatic search, a four-dimensional Fourier map phased by multidimensional direct methods is calculated with grid spacing approximately equal to 0.25 Å. A fast Fourier transform (FFT) algorithm is used for the calculation. The three-dimensional hypersection at a given t value (usually 0 or $\frac{1}{2}$) is obtained from the four-dimensional Fourier map. Then a search is performed to locate atoms on the hyperplane. The searching algorithm is similar to that used for ordinary structures. This results in rough positions of intersection between the hyperplane and atom strings. The positions are then used as starting points for tracing atom strings one by one. A small portion of the hypersection is recalculated around a starting point with a grid spacing of about 0.03 Å. A discrete Fourier transform algorithm is used instead of the FFT. The accurate intersecting position is obtained by locating the density maximum along each of the three crystallographic axes. This gives the first point of the string. Another partial hypersection is calculated with t displaced from that of the starting point by 0.02. Finding the density peak position along each crystallographic axis gives the second point of the string. The central curve of the string, the positional modulation function, can be located accurately by repeating the above step for a series of t values with intervals of 0.02. The density variation of the string is then measured accordingly. Finally all the atomic parameters are expressed as a Fourier series,

$$\xi^\mu = C_0^\mu + \sum_{n=1}^{\infty}[C_n^\mu \cos(2\pi nt) + S_n^\mu \sin(2\pi nt)], \tag{16}$$

where $C_0^\mu = \bar{\xi}^\mu$. This equation differs from equation (15) only in that the argument used is t rather than $\bar{x}_4$. By default, the maximum order of the Fourier coefficients is set to 4. In the case that equation (16) does not fit the modulation function very well, the trigonal-wave description (Lam *et al.*, 1995) or the sawtooth-wave description (Gao *et al.*, 1993) is available as an alternative.

The program is written in Fortran 77. A number of keywords are provided for changing some of the control parameters. The program accepts at most 3000 independent reflections, including mains and satellites, provided that there are no more than 16 000 reflections in the full reciprocal space. This

Table 1. *Fourier coefficients of the Na(3) atom in γ-Na_2CO_3*

x, y and z are positional parameters in fractional coordinates. p is the occupational parameter. w^{ii} are proportional to the displacement parameters B^{ii}. A_i and B_i are the ith-order Fourier coefficients in equation (15) with $\bar{x}_4$ as argument. Corresponding refined Fourier coefficients according to van Aalst *et al.* (1976) are shown in parentheses.

	x	y	z	p	w^{11}	w^{22}	w^{33}
A_0	0.1694 (0.1706)	0.5000 (0.5000)	0.7491 (0.7478)	0.9573	0.403	0.492	0.436
A_1	0.0000	0.0558 (0.0687)	0.0000	0.0000	0.000	0.000	0.000
B_1	0.0000	−0.0032 (−0.0057)	0.0000	0.0000	0.000	0.000	0.000
A_2	−0.0003	0.0000	−0.0009	0.0186	0.013	−0.028	−0.014
B_2	0.0005	0.0000	0.0003	0.0025	0.003	−0.002	0.007
A_3	0.0000	0.0039	0.0000	0.0000	0.000	0.000	0.000
B_3	0.0000	−0.0011	0.0000	0.0000	0.000	0.000	0.000
A_4	0.0000	0.0000	0.0000	0.0254	0.009	−0.066	0.016
B_4	0.0000	0.0000	−0.0004	−0.0080	−0.003	0.002	−0.004

restriction arises from the need to calculate the discrete Fourier transform with a small grid spacing of ∼0.03 Å, and depends on the computing power of a personal computer. This restriction can be relaxed if a more powerful computer is used. On the other hand, in order to construct an initial model to be used in the least-squares refinement, only the largest E or F_{obs} parameters are needed to calculate the Fourier maps. Hence 3000 independent reflections are adequate for this purpose. The program will be available on the World Wide Web in due course. Readers who wish to use the program without documentation may contact the corresponding author.

4. Tests and results

4.1. *A hypothetical structure*

In order to test the measuring accuracy of the program, a hypothetical incommensurate one-dimensionally modulated structure was constructed, containing only one atom in the unit cell with sinusoidal positional modulation. The magnitude of the modulation was 0.3 Å. A set of structure factors were calculated at 0.7 Å resolution, including up to second-order satellites. A default run of *MIMS* with the resultant four-dimensional Fourier map yielded a measured structure model. The structure-factor magnitudes calculated from this model led to an R factor of 0.063 against those from the original structure model. The maximum deviation between the measured and the original modulation curves was 0.03 Å. If structure factors at 0.3 Å resolution with up to sixth-order satellites were used in the calculation of the four-dimensional Fourier map, then the resultant R factor dropped to 0.01, while the maximum deviation between the measured and the original modulation curves decreased to 0.0015 Å. This test showed that the program *MIMS* works perfectly well with theoretical data, provided that the data are at high enough resolution.

4.2. *γ-Na_2CO_3*

This is a one-dimensionally modulated structure with a = 8.904, b = 5.239, c = 6.042 Å, $\alpha = \gamma = 90$, $\beta = 101.35°$, and the modulation wavevector $\mathbf{q} = 0.182\mathbf{a}^* + 0.318\mathbf{c}^*$. The superspace group is $C2/m\ (q_1\ 0\ q_3)\ 0\ s$. The modulated structure was originally solved by van Aalst *et al.* (1976) using X-ray diffraction data with a trial-and-error method. The X-ray diffraction data used in our test were obtained from the archives of the IUCr as supplementary material for the paper by van Aalst *et al*. (1976). Only a subset of observed structure-factor magnitudes was used in the calculation, which included 300 main reflections, 250 first-order satellites and 150 second-order satellites. The program *SAPI* (Fan *et al.*, 1991) was used to derive the phases of the main reflections while the program *DIMS* (Fu & Fan, 1994) was used for phasing the satellites. A four-dimensional Fourier map was then calculated. The interpretation of this Fourier map using the program *MIMS* led to a complete structure model. Table 1 shows measured Fourier coefficients of the sodium atom Na(3) in comparison with the corresponding refined Fourier coefficients according to van Aalst *et al.* (1976) (shown in parentheses).

In practice, a variation is considered to be negligible if it is less than 0.01 Å for positional parameters, or less than 0.1 for occupational and displacement parameters. Hence, it is evident from Table 1 that the modulation actually exists only in the y coordinate. The measured model gives an R factor of 0.189 for all reflections. R factors after least-squares refinement are listed in Table 2 in comparison with those from van Aalst *et al.* (1976).

It is apparent that the R factors resulting from our refinement are smaller than those of van Aalst *et al.* (1976). The reason may be that only 700 strong reflections were involved in our refinement, while 2668 reflections were used by Aalst *et al.*. This test shows that *MIMS* works very well with X-ray diffraction data.

4.3. *Pb-doped Bi-2223 ($Bi_2Sr_2Ca_2Cu_3O_{10}$) superconductor*

The symmetry of this sample belongs to the superspace group $B\ bmb\ (0\ q_2\ 0)$, with the three-dimensional unit cell a = 5.49, b = 5.41, c = 37.1 Å, $\alpha = \beta = \gamma = 90°$ and the modulation vector $\mathbf{q} = 0.117\mathbf{b}^*$. The modulated structure has been studied by Mo *et al.* (1992) with two-dimensional electron diffraction data using the multi-dimensional direct method. The present test started with a set of direct-method phased ($0klm$) electron diffraction data. A Fourier map was calculated, which is the four-dimensional potential distribution projected down the **a** axis. The interpretation of this map using the program *MIMS* led to a projected structure model containing all the metal atoms and some of the non-overlapping oxygen atoms. Least-squares refinement led easily from this model to the final result of Mo *et al.* (1992). Table 3 shows Fourier coefficients of the Bi

Table 2. *R factors for the diffraction data of γ-Na_2CO_3 after least-squares refinement*

	All reflections	Main reflections	First-order satellites	Second-order satellites
Result of least-squares refinement based on the model derived by *MIMS*	0.05	0.048	0.045	0.080
Result of Aalst *et al.* (1976)	0.075	0.061	0.064	0.197

Table 3. *Fourier coefficients of the Bi atom in the Pb-doped Bi-2223 superconductor*

C_i and S_i are the ith-order Fourier coefficients in equation (16) with t as argument. Other symbols have the same meaning as in Table 1.

Fourier coefficients from the direct-method phased Fourier map measured using *MIMS*

	y	z	p	w^{22}	w^{33}
C_0	−0.0001	0.0445	0.517	0.732	1.050
C_1	−0.0001	0.0081	−0.470	0.069	0.139
S_1	0.0049	0.0007	−0.001	−0.009	−0.068
C_2	0.0000	0.0071	0.023	−0.096	−0.258
S_2	0.0024	0.0010	−0.002	−0.013	−0.093

Fourier coefficients from the final results of Mo *et al.* (1992)

	y	z	p	B_{iso}
C_0	0	0.0528	0.648	1.0
C_1	0	0.0076	−0.534	0.0
S_1	0	0.0000	0.000	0.0
C_2	0	0.0012	0.118	0.0
S_2	0	0.0000	0.000	0.0

atom obtained by the program *MIMS* in comparison with those from the final result of Mo *et al.*

This test shows that even with inaccurate electron diffraction data, *MIMS* still gives reliable results, which are good enough to serve as a starting point for least-squares refinement.

This project is supported by the National Natural Science Foundation of China. The authors would like to thank the referees whose comments improved this paper. The authors would like to thank also Dr Jiang Hua for helpful discussions.

References

Aalst, W. van, den Hollander, J., Peterse, W. J. A. M. & de Wolff, P. M. (1976). *Acta Cryst.* B**32**, 47–58.

Cheng, T.-Z., Wan, Z.-H., Sha, B.-D., Fu, Z.-Q., Li, Y. & Fan, H.-F. (1998). *A Least-Squares Refinement Program for One-Dimensionally Incommensurate Modulated Structures.* University of Science and Technology of China, Hefei, People's Republic of China, and Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China.

Fan, H.-F. (1998). In *Electron Crystallography*, edited by D. L. Dorset, S. Hovmöller & X. Zou, pp. 193–202. Dordrecht: Kluwer Academic Publishers.

Fan, H.-F., van Smaalen, S., Lam, E. J. W. & Beurskens, P. T. (1993). *Acta Cryst.* A**49**, 704–708.

Fan, H.-F., Yao, J.-X., Zheng, C.-D., Gu, Y.-X. & Qian, J.-Z. (1991). *SAPI*91. *A Computer Program for Automatic Solution of Crystal Structures form X-ray Diffraction Data*. Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China.

Fu, Z.-Q. & Fan, H.-F. (1994). *J. Appl. Cryst.* **27**, 124–127.

Gao, Y., Coppens, P., Cox, D. E. & Moodenbaugh, A. R. (1993) *Acta Cryst.* A**49**, 141–148.

Hao, Q., Liu, Y.-W. & Fan, H.-F. (1987). *Acta Cryst.* A**43**, 820–824.

Janner, A., Janssen, T. & de Wolff, P. M. (1983). *Acta Cryst.* A**39**, 658–666.

Lam, E. J. W., Beurskens, P. T., Smits, J. M., van Smaalen, S., de Boer, J. L. & Fan, H.-F. (1995). *Acta Cryst.* B**51**, 779–789.

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.

Petricek, V., Maly, K. & Cisarova, I. (1991). In *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. Peres-Mato. F. J. Zúñiga & G. Madariaga, pp. 262–267. Singapore: World Scientific.

Smaalen, S. van (1995). *Crystallogr. Rev.* **4**, 79–202.

Wolff, P. M. de (1974). *Acta Cryst.* A**30**, 777–785.

Wolff, P. M. de (1977). *Acta Cryst.* A**33**, 493–497.

Yamamoto, Y. (1982). *Acta Cryst.* A**38**, 87–92.

Yamamoto, Y. (1991) In *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. Péres-Mato, F. J. Zúñiga & G. Madariaga, pp. 249–261. Singapore: World Scientific.